









# THE

# AMERICAN JOURNAL OF SCIENCE.

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# CONTENTS TO VOLUME XXXIX.

# Number 229.

	Page
ART. I.—The Ternary System CaO-Al <sub>2</sub> O <sub>2</sub> -SiO <sub>2</sub> ; by G. A. RANKIN. With Optical Study by FRED E. WRIGHT	1
II.—New Meteoric Iron from Sams Valley, Oregon; by W. M. FOOTE	80
III.—New Longirostral Mastodon, Tetrabelodon lulli. Pre- liminary Notice ; by E. H. BARBOUR	87
IV.—Repulsion of Two Metallic Disks, nearly in Contact; by C. BARUS	93
V.—Lawsonite from the Central Coast Ranges of California ; by A. F. ROGERS	105
VI.—Preparation and Hydrolysis of Ethyl Hydracrylate; by W. A. DRUSHEL	113

### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Coal Tar Chemical Industry, B. C. HESSE, 121.— Freezing-Point of Milk, HENDERSON and MESTON: Chemical Technology and Analysis of Oils, Fats and Waxes, J. LEWKOWITSCH, 122.—Laboratory Manual of Qualitative Chemical Analysis, A. R. BLISS, JR.: Absorption and Resonance of Helium, F. PASCHEN, 123.—Intermittent Vision, S. P. THOMPSON: Bausteine zur Flugbahn- und Kreisel-Theorie, A. DÄHNE, 125.—Text Book on Wireless Telegraphy, R. STANLEY, 126.—Principles of Electrical Measurements, A. W. SMITH: Geometry of Four Dimensions, H. P. MANNING, 127.—Experiments, P. E. EDELMAN, 128.
- Geology and Mineralogy Transportation of Debris by running Water, G. K. GILBERT, 128. Mississippian Brachiopoda of the Mississippi Valley Basin, S. WELLER, 129. Anticosti Island faunas, W. H. TWENHOFEL: British Carboniferous Producti, I. Genera Postula and Overtonia, I. THOMAS, 130. Palaeontologische Zeitschrift: Topographic and Geologic Survey Commission of Pennsylvania, 131. Geological Survey of New Jersey: Iowa Geological Survey: Wisconsin Geological and Natural History Survey: College Physiography, R. S. TARR and L. MARTIN, 132. Deposits of the Useful Minerals and Rocks, 133. Practical Instruction in the Search for and Determination of the Useful Minerals, A. MCLEOD: Origin of Thaumasite, F. I. ALLEN, 134.
- Miscellaneous Scientific Intelligence—National Academy of Sciences, 135.— Study of Foods, R A. WARDALL and E. N. WHITE : Source, Chemistry and Use of Food Products, E. H. S. BAILEY : Food Industries, H. T. VULTÉ and S. B. VANDERBILT, 136.

# Number 230.

	rage
ART. VII.—Physiography and Glacial Geology of the North ern Catskill Mountains; by J. L. RICH	137
VIII.—Outbreak of Mauna Loa, Hawaii, 1914; by T. A. JAGGAR, JR.	167
IXCarboniferous Plant Tissue; by E. H. BARBOUR	173
X.—Crystallization—Differentiation in Silicate Liquids; by N. L. Bowen	175
XIBottom Currents in Lake Ontario ; by E. M. KINDLE _	192
XII.—Separation and Estimation of Aluminium associated with Iron, by the Action of Acetyl Chloride in Acetone;	
by H. D. MINNIG.	197
XIIISolar Constant; by F. W. VERY.	201
XIVAn Eocene Ancestor of the Zapodilla; by E. W.	
BERRY. (With Plate I)	208

### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Molecular Weight of Sodium Carbonate and the Atomic Weight of Carbon referred to Silver and Bromine, RICHARDS and HOOVER, 213.—Molecular Weight of Sodium Sulphate and Atomic Weight of Sulphur, RICHARDS and HOOVER : Separation of Tungsten and Molydenum, E. E. MARBAKER, 214.—Standardization of Acidimetric Solutions, E. D. DODGE : Chemical Technology and Analysis of Oils, Fats and Waxes (J. Lewkowitsch), G. H. WARBURTON : High Frequency Spectra of the Elements, 215.—Biflar Property of Twisted Strips, J. C. BUCKLEY, 216.—Volatility of Thorium D, A. B. WOOD : Lecture Experiment on Dispersion, S. P. THOMPSON, 218.—Experimental Studies in Electricity and Magnetism, F. E. NIPHER: Smithsonian Physical Tables, F. E. FOWLE, 219.
- Geology and Mineralogy—"Ferns Ledges" Carboniferous Flora of St. John, N. B., M. C. STOPES, 219.—Pre-Cambrian Algonkian Algal Flora, C. D. WALCOTT: Petrology of the Orijärvi Region in Southwestern Finland, P. ESKOLA, 221.—The Crowsnest Volcanics, J. D. MACKENZIE, 222.— Mineral Empressite, W. M. BRADLEY, 223.—Report of Director of Bureau of Mines, J. A. HOLMES, 224.
- Miscellaneous Scientific Intelligence—Annual Report of the Secretary of Commerce, W. C. REDFIELD: Work and Needs of the United States Coast and Geodetic Survey, 225.—Report of Secretary of Smithsonian Institution, C. D. WALCOTT, 227.—Annual Report of Board of Regents of Smithsonian Institution: Proceedings of the National Academy of Sciences, 238.—Memoirs of the National Academy of Sciences: Samuel Franklin Emmons Memorial Fellowship: Feeblemindedness: Its Causes and Consequences, H. H. GODDARD, 229.—Awards by the Franklin Institute, 230.
- Obitnary-C. S. Minot: A. C. PEALE: J. MUIR: J. W. HITTORF: N. CRIST-OFFER DUNÉR: M.C. COOKE: J. BORGMANN, 230.

# Number 231.

	1 480
ART. XV.—The Salton Sea; by D. T. MACDOUGAL	231
XVI.—Illustrations of the Stem Structure of Tietea Singu- laris; by O. A. DERBY	251
XVII.—Petrographic Evidence on the Origin of the Cata- houla Sandstone of Texas; by M. I. GOLDMAN	261
XVIII.—Age of the Igneous Rocks of the Adirondack Region; by H. P. CUSHING	288
XIX.—Unstable Chromium Sesquioxide, and Corrections of Previous Work on the Heat Effect of Chromium and Aluminum Sesquioxides in Fusions with Sodium Per- oxide; by W. G. MIXTER	295
XX Note on the Shape of Pebbles; by H. E. GREGORY	300
XXIRelation of the Late Tertiary Faunas of the York-	

town and Duplin Formations; by JULIA A. GARDNER. 305

### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Determination of Cuprous and Cupric Sulphides in Mixtures of the Two, E. POSNJAK: Feldspar as a Possible Source of Potash, A. S. CUSHMAN and G. W. COGGESHALL, 311.—Qualitative Test for Water, E. R. WEAVER: The Rare Earths, S. I. LEVY, 312.—Ampère Molecular Currents, H. K. ONNES, 313.—Elements of Electricity and Magnetism, W. S. FRANKLIN and B. MACNUTT: Molecular Physics, J. A. CROWTHER, 314.—General Physics; Electricity, Electromagnetic Waves and Sound, J. A. CULLER, 315.
- Geology—Thirty-fifth Annual Report of the Director of the U. S. Geological Survey, G. O. SMITH: Publications of the United States Geological Survey, 316.—Sixth Biennial Report of the Commissioners of the State Geological and Natural History Survey of Connecticut for 1913-14: Topographic and Geologic Survey of Pennsylvania, R. R. HICE: The Problem of Volcanism, J. P. IDDINGS, 318.—Pleistocene Mammals of Iowa, O. P. HAY, 320.—Notes on Agelacrinidæ and Lepadocystinæ, with descriptions of Thresherodiscus and Brockocystis, A. F. FOERSTE: Introduction to the Study of Fossils (Plants and Animals), H. W. SHIMER: Paleontology of Preston County; Fossil fauna of the Conemaugh rocks, W. A. PRICE, 322. A Beatricea-like organism from the Middle Ordovician, P. E. RAYMOND: Middle Triassic marine invertebrate faunas of North America, J. P. SMITH: New Miocene Coleoptera from Florissant, H. F. WICKHAM, 323.
- Miscellaneous Scientific Intelligence-Insects Injurious to the Household,
  G. W. HERRICK, 323.—Germ-cell Cycle in Animals, R. W. HEGNER:
  Dynamic Evolution; A Study of the Causes of Evolution and Degeneracy,
  C. L. REDFIELD: Physikalische Chemie der Zelle und der Gewebe, R.
  HÖBER, 324 —Infection and Resistance, H. ZINSSER: British Museum Publications, 325.
- Obituary-A. W. PHILLIPS: C. F. BRACKETT: B. SHARP: SIR G. NARES: J. S. HARDING: F. W. RUDLER, 326.

Dago

## Number 232.

<ul> <li>ART. XXII.—Pleistocene Ground Sloth, Mylodon harlani, from Rock Creek, Texas; by R. S. LULL</li></ul>	1	age
<ul> <li>XXIII.—Simple and Inexpensive Apparatus for Tidal Analysis; by E. W. BROWN, F.R.S.</li> <li>386</li> <li>XXIV.—Radio-active Content of Certain Minnesota Soils; by J. C. SANDERSON</li> <li>391</li> <li>XXV.—Use of Hydrochloric Acid in the Estimation of Cer- tain Forms of Organic Nitrogen; by W. A. DRUSHEL and M. M. BRANDEGEE</li> <li>398</li> <li>XXVI.—Supposed Vanadic Acid from Lake Superior is Cop- per Oxide; by W. T. SCHALLER</li> <li>404</li> <li>XXVII.—The System Anorthite-Forsterite-Silica; by O. ANDERSEN</li> <li>407</li> <li>XXVIII.—Studies on the Etched Figures of Japanese Quartz; by S. ICHIKAWA. (Plates II to VII)</li> <li>455</li> <li>XXIX.—Datolite from North Plainfield, Somerset County, New Jersey; by A. C. HAWKINS</li> </ul>	ART. XXII.—Pleistocene Ground Sloth, Mylodon harlani, from Rock Creek, Texas; by R. S. LULL	327
<ul> <li>XXIV.—Radio-active Content of Certain Minnesota Soils; by J. C. SANDERSON</li></ul>	XXIII.—Simple and Inexpensive Apparatus for Tidal Analysis; by E. W. Brown, F.R.S.	386
<ul> <li>XXV.—Use of Hydrochloric Acid in the Estimation of Certain Forms of Organic Nitrogen; by W. A. DRUSHEL and M. M. BRANDEGEE</li></ul>	XXIV.—Radio-active Content of Certain Minnesota Soils; by J. C. SANDERSON	391
<ul> <li>XXVI.—Supposed Vanadic Acid from Lake Superior is Copper Oxide; by W. T. SCHALLER 404</li> <li>XXVII.—The System Anorthite-Forsterite-Silica; by O. ANDERSEN 407</li> <li>XXVIII.—Studies on the Etched Figures of Japanese Quartz; by S. ICHIKAWA. (Plates II to VII) 455</li> <li>XXIX.—Datolite from North Plainfield, Somerset County, New Jersey; by A. C. HAWKINS 473</li> </ul>	XXV.—Use of Hydrochloric Acid in the Estimation of Cer- tain Forms of Organic Nitrogen; by W. A. DRUSHEL and M. M. BRANDEGEE	398
<ul> <li>XXVII.—The System Anorthite-Forsterite-Silica; by O. ANDERSEN</li></ul>	XXVI.—Supposed Vanadic Acid from Lake Superior is Cop- per Oxide ; by W. T. SCHALLER	404
<ul> <li>XXVIII.—Studies on the Etched Figures of Japanese Quartz; by S. ICHIKAWA. (Plates II to VII)</li></ul>	XXVII.—The System Anorthite-Forsterite-Silica; by O. ANDERSEN	407
XXIX.—Datolite from North Plainfield, Somerset County, New Jersey; by A. C. HAWKINS	XXVIII.—Studies on the Etched Figures of Japanese Quartz; by S. ICHIKAWA. (Plates II to VII)	455
	XXIX.—Datolite from North Plainfield, Somerset County, New Jergey; by A. C. HAWKINS	473

### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Production of Chloropicrin from Organic Compounds, R. L. DATTA and N. R. CHATTERJEE: Determination of Gasolene Vapor in Air, G. A. BURRELL and A. W. ROBERTSON, 475.—Transmutation of the Chemical Elements, W. P. JORISSEN and J. A. VOLLGRAFF: Chemistry of Cyanogen Compounds, H. E. WILLIAMS: Chemie der hydraulischen Bindmittel, H. KÜHL and W. KNOTHE, 476.—Diffusion of Gases through Mercury Vapor, W. GAEDE, 477.—Elektrische Spektralanalyse chemischer Atome, J. STARK: Advanced Electricity and Magnetism, W. S. FRANKLIN and B. MACNUTT, 489.
- Geology and Mineralogy-Canada, Department of Mines, Geological Survey Branch, R. W. BROCK, 481.—State Geological Survey of Illinois: Further Notes on Meteor Crater, Arizona, D. M. BARRINGER, 482.—New Meteorites, O. C. FARRINGTON: Neues Jahrbuch für Mineralogie, etc.; Festschrift Max Bauer zum seibzigsten Geburtstage gewidmet: Amethysts in Egypt, 483.
- Miscellaneous Scientific Intelligence.-Carnegie Institution of Washington, Year Book No. 13, 1914: Report of the Librarian of Congress, H. W. PUTNAM, etc.-Text-book of Embryology, W. HEAPE, 485.-Neue Grundlagen der Logik, Arithmetik und Mengenlehre, J. KÖNIG: United States Coast and Geodetic Survey: The Smithsonian Institution, W. H. DALL, 486.
- Obituary-J. GEIKIE: G. F. J. A. AUWERS: C. E. BESSEY: L. L. DYCHE, 486.

# Number 233.

	rage
ART. XXXFormation and Distribution of Fluviatile and	
Marine Gravels; by H. E. GREGORY	487
XXXI.—Coal Measures Amphibian with an Osseous Tarsus;	
by R. L. Moodie	509
XXXIIContributions to Sardinian Petrography: I. The	P* 2
Rocks of Monte Ferru; by H. S. WASHINGTON	513
XXXIIIEstimation of Pentavalent Vanadium by Means	
of Sodium Thiosulphate; by G. O. OBERHELMAN	530
XXXIVDevelopment of the Mesenteries in the Zooids	
of Anthozoa and its Bearing upon the Systematic Posi-	
tion of the Rugosa; by T. C. BROWN	535
XXXVUse of the Roentgen Ray in Paleontology: Ski-	
agraphy of Fossils; by R. M. FIELD. (With Plate VIII)	543
XXXVINew Ordovician Eurypterid; by E. W. SHULER	551
XXXVIINew Mosasaur from the Ft. Pierre; by F. B.	
LOOMIS	555
XXXVIIIGrowing Crystals for Measurement; by J. M.	
BLAKE	567
XXXIXPrimary Analcite of the Crowsnest Volcanics; by	
J. D. MACKENZIE	571
XLNew Genera of Permian Reptiles; by S. W. WILLISTON	575
XLI Radium Content of Water from the Gulf of Mexico;	
by S. J. LLOYD	580
XLIL-Mobilities of Ions in Air: by E. M. WELLISCH	583

### SCIENTIFIC INTELLIGENCE.

C	<i>hemistry and Physics</i> —Production and Uses of Hydrogen, A. F. SEEKER,
	600Density of Lead from Ceylon Thorite, F. SODDY, 601Analysis of
	Alloys containing Tin, Antimony and Arsenic, F. A. STIEF: Density and
	Dispersion of Liquid Hydrogen and Nitrogen, H. AUGUSTIN, 602 Absorp-
	tion Spectrum of Chlorophyll, D. VAN GULIK: New Type of Band Series,
	A. FOWLER, 604.

- Geology—Problems of American Geology, W. N. RICE, etc., 605.—West
   Virginia Geological Survey: Illinois Geological Survey, 607.—South
   Dakota Geological Survey: Report of State Geologist on Mineral Industries
   and Geology of Vermont, 1913-1914: Les Variations Périodiques des Glaciers, XIX<sup>me</sup> Rapport, 1913, A. HAMBERG et P. L. MERCANTON, 608.—
   Additional Facts in Regard to the Discovery of the Meteorites of Brenham, Kiowa County, Kansas, J. W. DAVIS, 609.
- Miscellaneous Scientific Intelligence-National Academy of Sciences, 610.-The Common Law and the Case Method in American University Law Schools: Publications of the Allegheny Observatory of the University of Pittsburgh, 611.-Laboratory Manual for the Detection of Poisons and Powerful Drugs (W. Autenrieth), W. H. WARREN: What is Adaptation? R. E. LLOYD, 612.

Obituary-R. Lydekker: A. A. W. Hubrecht: A. S. Lea, 612.

# Number 234.

ART. XLIII.—Vertebrate Fossils of Rock Creek, Texas; by	
E. L. TROXELL. (With Plate IX)	613
XLIV.—Volumetric Determination of Polythionic Acids by	
Potassium Iodate; by G. S. JAMIESON	639
XLVDatolite from Great Notch, New Jersey; by C. W.	
Cook and E. H. KRAUS	642
XLVI.—Fully Exposed Reef of Calcareous Algæ (?) in the	
Middle Cambrian of the Teton Mountains; by E.	
BLACKWELDER	646
XLVII.—Limestone Solution on the Bottom of Lake Ontario;	
by E. M. KINDLE	651
XLVIII.—Certain Points in Petrographic Classification; by	
W. CRoss	657
XLIX.—Separation of Magnesium from Lithium by Means	
of Ammonium Carbonate in Alcoholic Solution; by J.	
G. DINWIDDIE	662
LExtrusive Basalt of Cambrian Age in the Blue Ridge of	
Virginia; by T. L. WATSON and J. H. CLINE	665
LI.—Identity of Footeite with Connellite together with the	
Description of two new Occurrences of the Mineral; by	
W. E. FORD and W. M. BRADLEY	670

### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Fixation of Atmospheric Nitrogen, W. S. LANDIS, 676.—Electroplating with Cobalt, H. T. KALMUS, C. H. HARFER, and W. L. SAVELL: Use of Mercuric Oxide for Standardizing Volumetric Solutions, M. A. ABELMANN: Manual of Practical Physical Chemistry, F. W. GRAY, 677.—Practical Physical Chemistry, A. FINDLAY: Molecular Association, W. E. S. TURNER: X-Rays and Crystal Structure, W. H. and W. L. BRAGG, 678.—Elementary Chemical Microscopy, E. M. CHAMOT, 679.— Hancock's Applied Mechanics for Engineers, N. C. RIGGS: Electricity for the Farm, F. I. ANDERSON, 680.
- Geology—Geology of the North American Cordillera at the Forty-ninth Parallel, R. A. DALY: Florida State Geological Survey, E. H. SELLARDS, 681.—Biennial Report of Topographic and Geologic Survey of Pennsylvania for the two years ending June 1, 1914: Geological Survey of Illinois, J. A. UDDEN: Publikationer fra det Danske Meteorologiske Institut, C. RYDER, 682.—Dew-Ponds; History, Observation and Experiment, E. A. MARTIN; Union of South Africa, Department of Mines and Industries: Fossil Birds in the Marsh Collection, C. W. SHUFELDT, 683.
- Miscellaneous Scientific Intelligence—Report on the Starfishes of the West Indies, Florida, and Brazil, etc., A. E. VERRILL, 684.—American Hydroids, Part III; The Campanularidæ and the Bonneviellidæ, C. C. NUTTING: Nahrungsmittelehemie in Vorträgen, W. KERP, 684.—Leavening Agents, N. HART: Mining World Index, Vol. VI: Museum of the Brooklyn Institute of Arts and Sciences: Report of Board of Scientific Advice for India, 1913– 1914, 685.
- Obituary-S. Smith, 685.-W. G. Adams: E. FRAAS: E.-H. AMAGAT, 686. INDEX, 687.

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# AMERICAN JOURNAL OF SCIENCE

# FOURTH SERIES.

ART. I. - The Ternary System CaO-Al, O, -SiO, ; by G. A. With Optical Study by FRED. E. WRIGHT. RANKIN.

#### CONTENTS.

INTRODUCTION. REVIEW OF THE BINARY SYSTEMS. Lime-Silica System. Alumina-Silica System. Lime-Alumina System.

PHASE RULE AND ITS APPLICATION TO TERNARY SYSTEMS. Application to the System Lime-Alumina-Silica. Typical Three-Component Systems.

EXPERIMENTAL METHODS. EXPERIMENTAL INVESTIGATION.

General Relations of Binary Compounds in Ternary Mixtures. The Ternary Compounds. The Stability Fields. The Boundary Curves. The Quintuple Points. Eutectics.

Quintuple points not eutectics.

RECAPITULATION ; THE CONCENTRATION-TEMPERATURE MODEL. SOME GENERAL CONSIDERATIONS.

The Various Binary Systems within the Ternary System. Crystallization in Ternary Systems.

APPLICATION OF THE EQUILIBRIUM DIAGRAM TO PROBLEMS INVOLVING THE THREE OXIDES:

To Portland Cement Clinker.

To Certain Geological Inquiries.

SUMMARY.

### INTRODUCTION.

It is a matter of interest to ascertain the stability relations in the ternary system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, not only from a purely scientific point of view, but also from the bearing of the facts

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thus discovered upon a number of geological inquiries and upon the problem of the nature of portland cement clinker. Many papers on this general topic have, of course, already been published, but the work recorded is, in the main, fragmentary and of little avail in settling the large general questions involved. The present investigation aims to treat the system rather completely, to ascertain the equilibrium relations in the system. To this end we have determined all the possible compounds which are found in dry melts of the three oxides CaO,  $Al_{2}O_{3}$ ,  $SiO_{3}$ , studying especially those which are stable at the liquidus; this involves measurements of the respective melting points or dissociation temperatures, and the determination of the invariant points, boundary curves (monovariant systems) and fields of stability (divariant systems) of the various compounds.

In the following pages we present a summary record of the work performed; it is the first thoroughgoing attempt, we believe, to determine all the compounds, both binary and ternary, made up only of CaO,  $Al_2O_3$ ,  $SiO_2$ , and the mutual relations of these compounds, many of which have, of course, previously been made synthetically by others. The data obtained are made use of in a discussion of the nature and constitution of portland cement clinker and of the formation of certain natural minerals from the magma.

Three papers dealing with this system have already been published from this laboratory. The first two dealt with the binary systems,\* while in the third† provisional locations were assigned to ternary quintuple points and boundary curves and the relations discovered applied in a discussion of the constitution of portland cement clinker. In the present paper we are able to give more exactly the location of eutectics, quintuple points and boundary curves, together with the corresponding temperatures. Owing to the large number of data it will not be possible to give in a paper of this nature more than the mean values obtained from a large number of determinations of the various points.

### THE COMPONENTS AND THE BINARY SYSTEMS.

It is well to begin by reviewing briefly the results obtained in the study of binary systems, partly in order that we may

<sup>\*</sup> The Lime Silica Series of Minerals. A. L. Day, E. S. Shepherd, F. E. Wright, this Journal (4), xxii, 265, 1906. The Binary Systems of Alumina, with Silica, Lime and Magnesia, E. S. Shepherd, G. A. Rankin, F. E. Wright, ibid. (4), xxviii, 293, 1909.

 $<sup>\</sup>uparrow$  Preliminary Report on the Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. A Study of the Constitution of Portland Cement Clinker. E. S. Shepherd, G. A. Rankin, F. E. Wright, J. Ind. Eng. Chem., iii, 211–227, 1911.

have clearly before us the conclusions upon which the present work is based and partly because improved methods of melting point determinations have resulted in the establishment of new temperature values for some of the points.

# THE THREE COMPONENTS : LIME, ALUMINA, SILICA.

Lime, CaO. The melting point of pure CaO has recently been determined by Kanolt\* as 2570°; Kanolt used a graphite furnace and took extreme precautions to prevent contamination of the charge. It is difficult to state just how accurate this point may be considered to be, but it is the best available at the present time. No indications of a second form have so far been observed.

Well-developed crystals of lime were obtained only from relatively large melts of pure CaO. The crystals are colorless or pale yellow, transparent, and were observed only in unmodified cubes of the isometric system. Cleavage perfect after the cube (100). The crystals are isotropic; occasionally the larger individuals show optical anomalies, due probably to internal strain. In the preparations the free lime appears usually in fine isotropic grains, usually rounded in outline and of very high refractive index (about 1.83). The grains are easily recognizable, even when only a few thousandths of a millimeter in diameter.

Alumina,<sup>†</sup> Al<sub>2</sub>O<sub>3</sub>. Artificial Corundum.—The melting point of Al<sub>2</sub>O<sub>3</sub> as determined by Kanolt<sup>‡</sup> is 2050°.

Optically, the properties of artificial corundum agree well with those of the natural mineral. Grains crystallized from a melt of pure Al<sub>2</sub>O<sub>3</sub> rarely show crystal outline; they are rounded in outline and less than  $0.05^{mm}$  in diameter. Minute air cavities in the grains are abundant and characteristic. Hardness 9. Refractive indices :  $\omega_{Na} = 1.768 \pm 0.003$ ;  $\epsilon_{Na} =$  $1.760 \pm 0.003$ ; birefringence fairly weak, about 0.009. Uni-axial, optically negative. From mixtures it usually crystallizes in thin, sharply defined hexagonal plates.

Silica, SiO<sub>2</sub>. An extensive investigation of the stability relations of the different crystal modifications of SiO<sub>2</sub> has been carried out in this laboratory by C. N. Fenner.§ Briefly summarized, the results of this investigation are :

\*J. Wash. Acad. Sci., iii, 315, 1913. †A second form of Al<sub>2</sub>O<sub>3</sub> has recently been observed during work on the ternary system CaO-Al<sub>2</sub>O<sub>3</sub>-MgO. A complete description of this new form will be given when that system is published. ‡J. Wash. Acad. Sci., iii, 315, 1913. 5 This Lournel (4) arrest 221 1019

§ This Journal (4), xxxvi, 331, 1913.

3

Inversion Temperature Remarks	
aquartz $575^{\circ}$ Rapid, reversible. $\beta$ quartz $575^{\circ}$ Sq0° ± 10° $\beta_{2}$ tridymite $870^{\circ} \pm 10^{\circ}$ Very sluggish, reversible. $\alpha$ tridymite $1470^{\circ} \pm 10^{\circ}$ Very sluggish, reversible. $\alpha$ tridymite $117^{\circ}$ Rapid, reversible. $\beta_{1}$ tridymite $163^{\circ}$ Rapid, reversible. $\alpha$ cristobalite $220^{\circ}-275^{\circ}$ Rapid, reversible. $\alpha$ tridymite $163^{\circ}$ Rapid, reversible. $\alpha$ cristobalite $220^{\circ}-275^{\circ}$ Rapid, reversible. $\alpha$ tridymite $163^{\circ}$ Rapid, reversible. $\alpha$ cristobalite $220^{\circ}-275^{\circ}$ Rapid, reversible. $\alpha$ tridymite $163^{\circ}$ Rapid, reversible. $\alpha$ cristobalite $220^{\circ}-275^{\circ}$ Rapid, reversible. $\alpha$ cristobalite $10^{\circ}$ reversible. $\alpha$ cristobalitecristobalite $\alpha$ cristobalite	era- ous bly ow- nite

a flux at relatively low tem-

peratures.

The melting point of cristobalite is about 1625°, that of metastable quartz 1470°. Recent investigations by N. L. Bowen\* of this laboratory have shown that the melting temperature of cristobalite under certain conditions is considerably above 1625° and that probably the melting temperature, like the inversion temperature, is variable, the cristobalite behaving in these respects as a solid solution of two components.

The forms which exist at low temperature are: a quartz, a tridymite, a cristobalite and chalcedony.

a quartz crystals obtained in sodium tungstate melts rarely exceed 0.1<sup>mm</sup> in length; they are doubly terminated with the unit prism and rhombohedrons as bounding faces. The crystals are hexagonal and resemble in every respect natural quartz crystals. Refractive indices for sodium light:  $\omega_{Na} = 1.544$ ;  $\epsilon_{Na} = 1.553$ ; birefringence about 0.01. Uniaxial, optically positive.

a Tridymite crystals occur in cryptocrystalline aggregates of hexagonal habit. Refractive indices approximately  $a_{Na}=1.469$ ,  $\gamma_{Na}=1.473$ . Birefringence extremely weak. Optic axial angle, large. The *a* form is probably orthorhombic, while the  $\beta$  forms, stable above 117°, are hexagonal.

a cristobalite appears also in cryptocrystalline aggregates. Refractive indices:  $a_{Na} = 1,484$ ,  $\gamma_{Na} = 1.487$ ; birefringence weak. Crystal system probably tetragonal or orthorhombic. The  $\beta$ -form crystallizes in the isometric system.

*Chalcedony* was not produced artificially; the optical characters of the natural mineral are given in the standard text books on microscopical petrography.

### THE LIME-SILICA SYSTEM.

Lime and silica when heated together can unite to form four distinct compounds: (1) the metasilicate  $CaO.SiO_{2}$ ; (2) the compound  $3CaO.2SiO_{2}$ ; (3) the orthosilicate  $2CaO.SiO_{2}$ ; (4)

\* This Journal (4), xxxviii, 218, 1914.

the compound 3CaO.SiO. Several of these compounds appear in more than one crystal modification. The temperature concentration diagram of this binary system is given in fig. 1.

Calcium metasilicate CaO.SiO, (CaO 48.2, SiO, 51.8).\* This compound appears in two distinct forms: (1) the mineral wollastonite ( $\beta$ CaO.SiO<sub>2</sub>), which is found especially in limestone



Concentration-Temperature Diagram for the System Lime-Silica. FIG. 1.

contact metamorphic aureoles and is stable up to 1200°, the reversible inversion point; (2) pseudowollastonite (aCaO.SiO<sub>2</sub>), which has never been observed in nature but only in artificial melts and slags; it is the stable form between 1200° and its melting temperature,  $1540^{\circ} \pm 2^{\circ}$ . Pseudowollastonite takes up about 2 per cent of either lime or silica in solid solutions; these additions affect the inversion point, the lime lowering it to

\* All compositions are in weight percentages unless it is expressly stated otherwise.

5

1190° while the silica raises it to 1210°. The eutectic between aCaO.SiO<sub>2</sub> and tridymite (the stable form of silica at the eutectic temperature) has the weight percentage composition, CaO 37, SiO<sub>2</sub> 63; its melting temperature is 1436° ± 2°. The other general relations are obvious from the diagram.

 $a CaO.SiO_{2}$  crystallizes in equant grains without decisive crystal outline; polysynthetic twinning is not uncommon and, together with the optical evidence, indicates that the crystal system is probably monoclinic. Refractive indices:  $\gamma_{\text{Na}} =$  $1.654 \pm 0.002$ ;  $a_{\text{Na}} = 1.610 \pm 0.002$ ; birefringence, strong,  $\gamma$ -a about 0.041; optical axial angle, small, nearly uniaxial; optical character positive.

 $\beta CaO.SiO_{2}$  occurs in lath-shaped individuals similar in every respect to the natural mineral wollastonite. Cleavage parallel to the elongation of the laths and fibers is well marked. Crystal system monoclinic; refractive indices:  $\gamma_{Na} = 1.631 \pm$ 0.002,  $\beta_{Na} = 1.629 \pm 0.002$ ,  $\alpha_{Na} = 1.616 \pm 0.002$ ; birefringence medium,  $\gamma - \alpha$  about 0.015; extinction parallel to elongation; optic axial angle 2E, about 70°; optical character negative; plane of optic axes normal to cleavage lines.

(2) The compound  $3CaO.2SiO_2$  (CaO 58.2, SiO<sub>2</sub> 41.8) dissociates into  $2CaO.SiO_2$  and liquid at  $1475^\circ \pm 5^\circ$ , and consequently shows no true melting point. In the binary series it occurs as primary phase on the liquidus only with mixtures of composition ranging from 54.5 to 55.5 per cent lime. It is best formed by holding glass of the composition  $3CaO.2SiO_2$  at a temperature slightly below  $1475^\circ$  until crystallization occurs.

This compound crystallizes in rounded irregular grains, without definite crystal outline and without distinct cleavage. Crystal system, probably orthorhombic. Refractive indices:  $\gamma_{\text{Na}} = 1.650 \pm 0.002$ ,  $a_{\text{Na}} = 1.641 \pm 0.002$ ; birefringence fairly weak,  $\gamma - a$  being about 0.01; optic axial angle large; optical character positive.

It was at first thought that this substance might be pure åkermanite, whose formula, according to Vogt, is  $4\text{CaO.3SiO}_{27}$ , but åkermanite is tetragonal and uniaxial with refractive indices:  $\gamma_{\text{Na}}$  about 1.640,  $\alpha_{\text{Na}}$  about 1.635. The presence of magnesia in Vogt's åkermanite may account for the observed differences in optical behavior of the two substances; and if so, the formula for pure åkermanite should be 3CaO.2SiO, rather than 4CaO.3SiO<sub>2</sub>.

The compound 3CaO.2SiO<sub>2</sub> forms with aCaO.SiO<sub>2</sub> a eutectic mixture of the weight percentage composition CaO 54.5, SiO<sub>2</sub> 45.5, which melts at 1455°  $\pm$  2°. It does not form a eutectic with 2CaO.SiO<sub>2</sub>; the quadruple (invariant) point at which these two compounds are stable in coexistence with liquid and vapor is at the composition CaO 55.5, SiO<sub>2</sub> 44.5, the corresponding temperature being 1475°  $\pm$  5°.

# Rankin and Wright—Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.

(3) Calcium orthosilicate,  $2CaO.SiO_2$  (CaO 65.0, SiO<sub>2</sub> 35.0). —This compound occurs in three forms,  $a, \beta, \gamma$ , and possibly a fourth,  $\beta'$ , which is monotropic. The high temperature a form melts at 2130° ± 20°; at 1420° ± 2° it undergoes a reversible change to the  $\beta$  form, which in turn passes reversibly to the  $\gamma$  form at 675°. The inversion  $\beta$  to  $\gamma$  is accompanied by an increase in volume of about 10 per cent which shatters the charge into fine dust; the phenomenon, frequently observed in the burning of portland cement, is well known as dusting.

a 2CaO.SiO, occurs in irregular grains so intricately interwoven and twinned that a satisfactory measurement of their optical properties is exceedingly difficult. They show occasionally prismatic development with good cleavage parallel with the prism axis. Twinning is a characteristic feature and is often extremely complicated; different sets of twinning lamellæ occur intersecting at various angles and, together, form an interpenetrating mass not unlike microcline or leucite. Occasionally in a thin particle only one set of polysynthetic twinning lamellæ is present, and resembles then a plagioclase section twinned after the albite law. The crystal system is either monoclinic or triclinic. Refractive indices:  $a_{Na} = 1.715$  $\pm 0.002$ ,  $\beta_{Na} = 1.720 \pm 0.003$ ,  $\gamma_{Na} = 1.737 \pm 0.002$ . Bire-fringence fairly strong, about 0.023; optic axial angle large; plane of optic axes nearly parallel with the elongation of the crystals; optical character positive. Extinction angles in twinned flakes were observed as high as  $c: a' = 18^{\circ}$  though smaller angles are more common. Hardness between 5 and 6.

 $\beta$  2 CaO.SiO, appears in irregular rounded grains, often prismatic in shape with cleavage parallel to the prism axis. The crystal system is apparently orthorhombic, though the presence of twinning lamellæ with low extinction angles up to  $c: a' = 10^{\circ}$  in certain of the grains which may be of the a form would indicate a still lower symmetry. Refractive indices:  $a_{Na} = 1.717 \pm 0.002$ ;  $\gamma_{Na} = 1.735 \pm 0.002$ ; birefringence medium, the interference colors in the finely-powdered grains rarely exceeding blue of the second order; optic axial angle large; optical character positive. Plane of optic axes parallel with the elongation. The optical properties of the  $\alpha$  and  $\beta$ forms are unfortunately so similar that it is often exceedingly difficult to distinguish between them. The intricate twinning of the  $\alpha$  form does not appear in the  $\beta$  form, and is apparently the best criterion to use. The birefringence of the  $\beta$  form appears also to be slightly weaker than that of the a form.

 $\gamma 2 CaO.SiO$ , is obtainable from the inversion of the  $\beta$  form on cooling only as a fine powder, by reason of the "dusting" noted above. It is colorless, prismatic in habit, with perfect cleavage along the prism axis. Occasionally indications of

7

twinning lamellæ parallel with the cleavage were observed; showing small extinction angles not exceeding  $c: \gamma' = 3^{\circ}$ ; usually the extinction is parallel. Crystal system, probably monoclinic. Refractive indices:  $a_{\text{Na}} = 1.642 \pm 0.002$ ,  $\beta_{\text{Na}} = 1.645 \pm 0.003$ ,  $\gamma_{\text{Na}} = 1.654 \pm 0.002$ ; birefringence medium about 0.015; optic axial angle 2E approximately 52°; plane of optic axes normal to cleavage direction; optical character negative. This form of the orthosilicate is readily distinguished from the a and  $\beta$  forms by its lower refractivity, the position of its plane of optic axes, and its optical character.

 $\beta'2CaO.SiO_2$  is an unstable form which was obtained only by quenching an old hydrated sample from a temperature of about 1425°; it could not be obtained from fresh preparations, indeed we have obtained it only from one particular sample, and then in fine equant grains without apparent cleavage. The average refractive index is about 1.715 and the birefringence very weak. Interference figures are difficult to obtain because of the fine granularity and the weak birefringence, but the optic axial angle appears to be small or zero and the optical character positive. The form appears to be monotropic, but the evidence thus far obtained can hardly be considered to have established beyond question the existence of this form.

4. Tricalcic silicate  $3CaO.SiO_2$  (CaO 73.6, SiO<sub>2</sub> 26.4) is unstable at its melting point, but unlike the compound 3CaO. 2SiO<sub>2</sub> it does not occur as a primary phase at any point on the liquidus curve of the binary system lime-silica. Although a definite binary compound, it is found as a primary phase only within the ternary system. It dissociates at 1900° ± 20° into CaO and 2CaO.SiO<sub>2</sub>; the fact that this temperature is below that of the eutectic between CaO and 2CaO.SiO<sub>2</sub> (2065°, composition CaO 67.5, SiO<sub>2</sub> 32.5) explains why 3CaO.SiO<sub>2</sub> does not occur in contact with the melt in the binary system.

This compound occurs in small equant grains not over  $0.03^{\text{mm}}$ in diameter, colorless and apparently without cleavage. Average refractive index approximately 1.715; birefringence very weak, not over 0.005. The grains appear uniaxial or biaxial with small optic axial angle; optical character negative. In certain of the preparations of ternary mixtures, fine twinning lamellæ with low extinction angles were observed on some of the grains, indicating that the crystal system is possibly monoelinic.

It is an interesting fact that in the formation of this compound from the mixed oxides at 1400° or 1500°, orthosilicate is first formed and unites on longer heating with free lime to form the tricalcic silicate.

### THE BINARY SYSTEM: ALUMINA-SILICA.

The general behavior of the system alumina-silica is obvious from the diagram, fig. 2. In this binary series only one compound,  $Al_2O_3$ .SiO<sub>2</sub>, sillimanite, appears; it melts at  $1816^{\circ} \pm 10^{\circ}$ and forms eutectic mixtures both with alumina and with silica. The eutectic between sillimanite  $Al_2O_3$ .SiO<sub>2</sub> and  $Al_2O_3$ , has the composition  $Al_2O_3$  64, SiO<sub>2</sub> 36 and melts at  $1810^{\circ} \pm 10^{\circ}$ ; that



FIG. 2. Concentration-Temperature Diagram for the System Alumina-Silica.

between sillimanite and cristobalite (the only form of SiO<sub>2</sub> occurring on the liquidus curve in this system) consists of  $Al_2O_3$  13, SiO<sub>2</sub> 87, and melts at 1610°. Two other forms of  $Al_2O_3$ .SiO<sub>2</sub>, namely, andalusite and cyanite or disthene, occur in nature, but they have not been observed with certainty in the laboratory nor has anything bearing on their relation to sillimanite been established beyond the fact that on heating they pass into sillimanite. The laboratory and field evidence, so far as it goes, indicates that they are monotropic with respect to sillimanite.

Artificial sillimanite crystallizes from the melt as finegrained, fibrous to lath-shaped individuals, which, like the natural mineral, are often in close parallel groups. Terminal sections of the fibers are square in outline, weakly birefracting. and extinguish parallel with the diagonals of the rectangles. In the center of nearly every section a minute inclusion is present, often in the shape of a cross, the arms of which are parallel with the sides. Refractive indices :  $a_{Na} = 1.638 \pm 0.003$ , ably lower than those of the natural mineral; birefringence medium,  $\gamma - \alpha$  about 0.014. The optic axial angle is not large : optical character positive; the acute bisectrix lies in the direction of the elongation of the fibers, along which the cleavage is Minute inclusions of a lower refracting isotropic distinct. substance (n about 1.530) are almost invariably present in the artificial sillimanite preparations and are apparently glass. No satisfactory explanation has been found for their occurrence unless sillimanite is unstable at its melting point and dissociates into Al<sub>2</sub>O<sub>3</sub> and glass. This might also explain the fine cross-shaped inclusions noted above. The temperature of possible dissociation is, however, so high (above 1800°) that no satisfactory methods are available to test this hypothesis.

### THE BINARY SYSTEM : LIME-ALUMINA.

In this system four distinct compounds occur, namely (1) tricalcic aluminate  $(3\text{CaO.Al}_{2}\text{O}_{3})$ ; (2) the compound 5CaO.  $3\text{Al}_{2}\text{O}_{3}$ ; (3) calcium aluminate  $(\text{CaO.Al}_{2}\text{O}_{3})$  and (4) the compound  $3\text{CaO.5Al}_{2}\text{O}_{3}$ . Several of these compounds are dimorphous. The concentration-temperature diagram is given in fig. 3.

(1) Tricalcic-aluminate,  $3CaO.Al_2O_3$  (CaO 62.2, Al\_2O\_3 37.8) is unstable at its melting point, but occurs as primary phase on the liquidus curve of mixtures of composition ranging from CaO 50 to 59, Al\_2O\_3 50 to 41. It dissociates at  $1535^{\circ}\pm5^{\circ}$  into CaO and liquid; it is, for this reason, best obtained by crystallization from glass of its own composition at a temperature below  $1535^{\circ}$ . It forms with the compound  $5CaO.3Al_2O_3$  a entectic mixture of the composition CaO 50, Al\_{2}O\_3 50, which melts at  $1395^{\circ}\pm5^{\circ}$ . It does not form a eutectic with CaO; but the composition CaO 59, Al\_2O\_41 is the quadruple (invariant) point at which these two compounds are stable in contact with liquid and vapor, the equilibrium temperature being  $1535^{\circ}$ .

This compound occurs in equant colorless grains  $0.1^{\text{mm}}$  and less in diameter, often hexagonal or rectangular in outline with indications of imperfect cleavage after the octahedron or rhombicdodecahedron. Crystal system, isometric. Refractive index,  $n_{\text{Na}} = 1.710 \pm 0.001$ . Hardness, 6. Fracture, conchoidal. Luster, vitreous. Occasionally faint gray interference colors were observed and were evidently due to strain.

# Rankin and Wright-Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 11

(2) The compound 5CaO.3Al<sub>2</sub>O<sub>3</sub> (CaO 47.8, Al<sub>2</sub>O<sub>3</sub> 52.2) occurs in two forms: I, a stable form; II, an unstable mono-tropic form.

I. The stable form melts at  $1455^{\circ} \pm 5^{\circ}$ . It forms with the compound 3CaO.Al<sub>2</sub>O<sub>3</sub> the eutectic mixture noted above; and





with calcium aluminate a eutectic mixture which has the composition CaO 47, Al<sub>2</sub>O<sub>3</sub> 53, and melts at  $1400^{\circ} \pm 5^{\circ}$ . The stable form crystallizes in rounded grains without

The stable form crystallizes in rounded grains without definite crystal outline or distinct cleavage. Luster, vitreous; fracture, conchoidal and often interrupted; hardness, 5. Crystal system, isometric; refractive index,  $n_{\rm Na} = 1.608 \pm 0.001$ .

The refractive index of glass of the same composition is approximately 1.662.

II. The unstable form has neither a definite melting point nor any temperature range of real stability. It is obtained only under special conditions of cooling and is usually not well developed in single crystallites, but occurs as radial spherulites or aggregates of overlapping, and often approximately parallel, fibers. Crystal habit, fibrous and prismatic; luster, vitreous; color usually pale green; hardness about 5; crystal system, probably orthorhombic. Refractive indices:  $a_{\rm Na} = 1.687 \pm$ 0.002,  $\gamma_{\rm Na} = 1.692 \pm 0.002$ ; birefringence weak. Optic axial angle apparently large; plane of optic axes and extinction are parallel with the fiber direction; optical character apparently negative but difficult to determine because of overlapping fibers. The more deeply colored grains are pleochroic; a = blue-green,  $\gamma =$  olive-green; absorption  $a < \gamma$ .

(3) Calcium aluminate, CaO.Al<sub>2</sub>O<sub>3</sub> (CaO 35.4, Al<sub>2</sub>O<sub>3</sub> 64.6) melts at  $1600^{\circ} \pm 5^{\circ}$ . It forms with the compound  $5CaO.3Al_2O_3$ the eutectic mixture noted above; and with the compound  $3CaO.5Al_2O_3$  a eutectic mixture of the composition CaO 33.5, Al<sub>2</sub>O, 66.5, which melts at  $1590^{\circ} \pm 5^{\circ}$ .

It crystallizes readily in irregular grains and often in prismatic to fibrous aggregates. Twinning is a characteristic feature and is especially prominent on sections nearly normal to the acute bisectrix. Such sections are intricately divided into a hexagonal meshwork of interlocking sextants which extinguish in different positions. Cleavage parallel with the fiber direction is occasionally indicated. Hardness about 6.5; luster vitreous. Crystal system, monoclinic or triclinic, probably monoclinic. Refractive indices:  $a_{\text{Na}} = 1.643 \pm 0.002$ ,  $\beta_{\text{Na}} = 1.655 \pm 0.002$ ;  $\gamma_{\text{Na}} = 1.663 \pm 0.003$ ; birefringence fairly strong, about 0.02. Optic axial angle  $2V = 36^{\circ} \pm 4^{\circ}$ . Optical character, negative.

(4) The compound  $3CaO.5Al_2O_s$  (CaO 24.8, Al<sub>2</sub>O<sub>3</sub> 75.2) crystallizes in two forms, (I) stable, (II) unstable and apparently monotropic with respect to (I).

(I) This form melts at  $1720^{\circ} \pm 10^{\circ}$ . It forms with calcium aluminate the eutectic mixture noted above and with alumina a eutectic of weight percentage composition CaO 24, Al<sub>2</sub>O<sub>3</sub> 76, which melts at  $1700^{\circ} \pm 10^{\circ}$ .

It crystallizes readily in rounded colorless grains, often with indications of rectangular outline. Cleavage poor if present. Hardness about 6.5; luster vitreous. Crystal system, possibly tetragonal. Refractive indices,  $\omega_{Na} = 1.617 \pm 0.002$  $\epsilon_{Na} = 1.652 \pm 0.002$ . Birefringence strong, approximately 0.035; uniaxial, optically positive. Indications of biaxial character with small 2E were noted occasionally. The interference figures are easy to obtain even on grains measuring only  $01^{mm}$ in diameter. The grains often contain fine threadlike inclusions of a higher refracting, weakly birefracting isotropic substance which are too fine for satisfactory determination. Their total amount is very slight.

(II) The unstable form crystallizes occasionally from the rapidly cooled liquid. It occurs rarely in the ternary mixtures; has no definite melting point and apparently no definite region of real stability; it inverts so rapidly at high temperatures to the stable form that perfectly homogeneous preparations could not be obtained. Crystal habit, prismatic to fibrous with fair prismatic cleavage. Luster, vitreous. Hardness 5.5 to 6. Crystal system orthorhombic, or monoclinic, probably orthorhombic, though in one preparation twinning phenomena were observed which might indicate monoclinic symmetry. Refractive indices:  $\gamma_{Na} = 1.674 \pm 0.002$ ,  $\beta_{Na} = 1.671 \pm 0.002$ ,  $a_{Na} = 1.662 \pm 0.003$ ; birefringence medium,  $\gamma$ -a approximately 0.013. Optic axial angle  $2V_{Na} = 35^{\circ} \pm 5^{\circ}$ . Optical character negative. Axial dispersion strong,  $2V_r > 2V_v$ . Plane of optic axes and extinction parallel to the prismatic, positive elongation.

### THE PHASE RULE AND ITS APPLICATION TO TERNARY SYSTEMS.

It may be well to review briefly the general principles upon which is based the experimental investigation of a ternary system, before the actual methods of experiment and the results obtained are given. The main and essential guiding principle is the phase rule, which is, of course, just as applicable to mixtures of mineral oxides which are liquid only at high temperatures as it is to ordinary solutions. In either case it is necessary that the phase rule be applied properly; indeed this constitutes the only method of attack in problems so complicated as the investigation of the system  $CaO-Al_2O_s-SiO_s$ ; for in this system we have found no fewer than 14 distinct compounds, each with a stable region of existence correlated with a definite range of conditions.

### THE PHASE RULE.

"Gibbs showed how in a perfectly general manner, free from all hypothetical assumptions as to the molecular condition of the participating substances, all cases of equilibrium could be surveyed and grouped into classes and how similarities in the behavior of apparently different kinds of systems and differences in apparently similar systems could be explained."

"In deducing the law of equilibrium, Gibbs' regarded a system as possessing only three independently variable factors—

temperature, pressure, and the concentration of the components of the system—and enunciated the general theorem now usually known as the Phase Rule, by which he defined the conditions of equilibrium as a relationship between the number of what are called the phases and the components of the system." \*

*Phases.*<sup>+</sup>—<sup>*i*</sup> A heterogeneous system is made up of different portions, each in itself homogeneous, but marked off in space and separated from the other portions by bounding surfaces. These homogeneous, physically distinct and mechanically separable portions are called *phases.*"

*Components.*<sup>‡</sup>—" As the components of a system there are to be chosen the *smallest number* of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation."

"Variable factors or degrees of freedom."§—" The number of degrees of freedom of a system is the number of the variable factors, temperature, pressure and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined."

"The Phase Rule of Gibbs, now, which defines the condition of equilibrium by relation between the number of coexisting phases and the components, may be conveniently summarized in the form of an equation as follows:

P + F = C + 2 or F = C + 2 - P

where P denotes the number of phases, F the degrees of freedom and C the number of components. From the second form of the equation it can be readily seen that the greater the number of phases the fewer are the degrees of freedom. With increase in the number of phases, therefore, the condition of the system becomes more and more defined, or less and less variable."

"In accordance with the phase rule, therefore, we may classify the different systems which may be found into invariant, univariant, bivariant, multivariant, according to the relation which obtains between the number of components and the number of coexisting phases; and we shall expect that in each case the members of any particular group will exhibit a uniform behavior. By this means we are enabled to obtain an insight into the general behavior of any system, so soon as we have determined the number of the components and the number of coexisting phases.

> \* Findlay, "Phase Rule," p. 8. † Findlay, ibid., p. 9. ‡ Findlay, ibid., p. 12. § Findlay, ibid. || Findlay, ibid., p. 16.

"The adoption of the phase rule for the purposes of classification has been of great importance in studying changes in the equilibrium between different substances: for not only does it render possible the grouping together of a large number of isolated phenomena but the guidance it affords has led to the discovery of new substances, has given the clue to the conditions under which these substances can exist and has led to recognition of otherwise unobserved resemblance between different systems." \*

"The phase rule informs us only as to the general conditions of equilibrium and leaves the determination of the definite experimental data to experiment."<sup>+</sup>

Before taking up, then, the experimental study of any system, it is important to consider the general conditions of equilibrium for that system, as deduced from the phase rule.

THE APPLICATION OF THE PHASE RULE TO THE STUDY OF EQUILIBRIA IN THE SYSTEM CAO-AL<sub>2</sub>O<sub>2</sub>-SIO<sub>2</sub>.

For systems, such as those involving CaO,  $Al_2O_3$  and  $SiO_2$ , certain restrictions can be imposed, which will not appreciably affect the definitions of conditions of equilibrium and which will reduce to a considerable extent the number of possibilities which we have to consider.

Since the change in vapor pressure of these three oxides is unimportant over the range of temperatures at which we wish to study them, we may assume that under constant pressure (atmospheric) any system may be defined by the degrees of freedom, temperature and concentration. The vapor phase must, however, always be considered to be present. As liquids these three oxides are miscible in all proportions, so that for any system there can be but one liquid phase. From the experimental study we know that as solids the various oxides and their compounds are practically immiscible, so that in discussing theoretical possibilities we will not take up solid solution.

The systems, then, which we will have to consider are those in which (1) the vapor pressure of the solid and liquid is substantially constant during temperature change, (2) there is but one liquid phase, and (3) there are no solid solutions formed.

According to the Phase Rule, P + F = C + 2; hence since in this case C = 3, the number of the phases and degrees of freedom (P+F) = 5, so that F may be 0, 1 or 2.

In order that a three component system be nonvariant five phases are necessary, of which there are two possible such systems, S-S-S-V and S-S-S-L-V. (S=Solid; L=Liquid; V = Vapor.) In order that the system be univariant four

> \* Findlay, "Phase Rule," pp. 17-18. † Findlay, ibid., p. 53.

phases are necessary. There are two possible such systems, S-S-S-V and S-S-L-V. In order that the system be bivariant three phases are necessary. There are two possible such systems, S-S-V and S-L-V. The solid phases may be components, binary or ternary compounds.

From the general conditions of equilibrium as deduced from the phase rule for three component systems under the conditions we have mentioned it is now possible to ascertain something of the nature of such systems.

The equilibrium relations in a three component system are most easily grasped if the compositions are plotted on an equilateral triangle; the same scale is taken for the binary systems on the sides of the triangle as for the ternary system in the interior. On such a diagram\* the pure components are given by the apices of the triangle, the invariant systems by points (quintuple points), the univariant systems by lines (boundary curves) and divariant systems by fields included within the triangle. All compositions will be given here in percentage weights of the components.

The effects of the change of the variable-temperatureare more obvious if a solid model is made by erecting, at each point in the plane of the triangular diagram, lines perpendicular to that plane, the length of each being proportional to the equilibrium temperature at that composition.<sup>+</sup> For our present purpose, however, projection of ternary curves on the plane of the triangle will be used.

\*Roozeboom, Zs. physik. Chem., xv, 13, 1894; Bancroft, J. phys. Chem., i, 403, 1897.

+ An ingenious method for the construction of a solid concentrationtemperature model has been devised by Mr. England of this laboratory. This model represents accurately concentrations and the corresponding temperatures for a three component system.—On a flat piece of well-seasoned wood is securely fastened a piece of sheet tin, which serves as a base for the solid model. On the surface of the sheet tin is drawn an equilateral triangle, on which are represented the compositions of the compounds (binary and ternary), the quadruple and quintuple points, and the boundary curves, which define the limits of the various ternary fields, as lines. The concentration-temperature diagram for each binary system (not only the binary systems of which the sides of the triangle give the compositions but also the binary systems included within the ternary system) and each boundary curve is cut from a piece of sheet tin. The lowest temperature for each concentration-temperature diagram must necessarily be a common temperature, which is that represented by the plane of the base of the model. Each of the concentration-temperature diagrams is placed along its particular concentration line on the triangular base, perpendicular to the plane of this base, and is then soldered in place. The resulting figure is a skeleton, form which represents the compositions and corresponding temperatures of the compounds, quadruple points, quintuple points and boundary curves. If now we fill in each space in the skeleton with plaster of Paris, which is surfaced to conform to the slopes of the curves surrounding each space, we have produced a solid model, points on the surface of which represent compositions and the corresponding melting temperatures of ternary mixtures. Changes which take place in solid ternary crystalline mixtures, of course can not be represented in this solid model.

"A theorem by Van Rijn van Alkemade serves as a very effective guide in regard to temperature changes in the interior of the triangle. If the two points in the triangle which correspond to the composition of two solid phases be connected by a line, the temperature at which these same two phases can be in equilibrium with solution and vapor rises as the boundary curve approaches this line, becoming a maximum at the intersection, though the boundary curve often ceases to be stable before this point is reached. When the two solid phases are two of the components, the line connecting their compositions is one of the sides of the triangle. It is, therefore, clear that the temperature must always rise in passing along a boundary curve to the side of the triangle if the theorem of van Alkemade be right."\*

The usefulness of the theorem of van Alkemade will be more apparent when applied in the study of the different types of three component systems.

### TYPICAL THREE-COMPONENT SYSTEMS.

Six simple representative types of three-component systems, in which no solid solutions occur, are given to illustrate some of the general principles; they are represented by diagrams in fig. 4.

The simplest type (1) is that in which the three components are the only solid phases. A, B and C are the three components, whose respective melting points are represented by the apices of the triangle, the sides of which represent the melting temperatures for the binary mixtures, A-B, B-C and C-A. The arrows on the sides of the triangle indicate the direction of falling temperature and the points 1, 2 and 3 are the quadruple points at which each pair of components, C-A, B-C and A-B respectively, are in equilibrium with solution and vapor. If, as in the present case, the quadruple points are the lowest melting temperatures for each two-component system, they are known as eutectic points.

Inside of the triangle there is for each component a definite area (field) in which it is in equilibrium with solution and vapor; in other words, there is a definite field which represents the melting temperatures of one component in mixtures containing the other two components. The lines 1-4, 2-4, 3-4separating these fields are known as boundary curves, each of which represents a condition of 4-phase equilibrium between two components, liquid and vapor; that is, a boundary curve represents the melting temperatures of mixtures of two components containing varying proportions of the third component.

\* Bancroft, "The Phase Rule," p. 149.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 229.—January, 1915. 2

### 18 Rankin and Wright—Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.

The starting point of a boundary curve 1-4 is a quadruple point (1) in a binary system A-C; as we proceed along the boundary curve into the ternary system the corresponding equilibrium temperature will fall, as postulated by the theorem of Alkemade. The two phases in this case are the two components A and C; according to the theorem, temperatures along 4-1 must rise as it approaches A-C (temperatures along 1-4 must fall as 1-4 leaves A-C and enters the ternary system). The point 4, at which the three boundary curves meet,



FIG. 4. Six Typical cases of Three-Component System.

is a quintuple point at which A, B, and C are in equilibrium with solution and vapor. Since 4 is the lowest melting temperature for any mixture of A, B, C, it is known as a eutectic point.

The next simplest cases of three-component systems are those in which there is one binary compound; these are illustrated by II, III, IV and V.

In II A and B unite to form the compound  $\overline{AB}$  which is stable at its melting point. The binary system A-B will possess then a maximum (the melting point of  $\overline{AB}$ ) and two eutectics (3 and 4). Within the triangle there will be four fields; one for each of the components A, B, C and one for the compound  $\overline{AB}$ ; and five boundary curves of which 5-6 is the only one which we need to consider especially, since the

others are altogether analogous to those already discussed. The boundary curve 5-6, which lies wholly within the triangle, delimits the fields for component C and the compound AB. Now if the line C-AB crosses 5-6, it follows from the theorem of Alkemade that the point of intersection will be the maximum temperature on the boundary 5-6. The points 5 and 6 will, therefore, be eutectic points, as indicated by the arrows which give the direction of falling temperature on the boundary curves. If, however, (as is the case in III) the line C-ABdoes not cross boundary 5-6, then boundary 5-6 does not possess a maximum and temperatures along 5-6 will fall continuously from 5 to 6, the latter being a eutectic point. This is a case where the boundary approaches a maximum, but the compound ceases to be stable before the maximum is attained. Point 5 is a quintuple point but not a entectic; that is, 5 is not the lowest melting temperature on the three boundary curves of which it is a common point.

In IV  $\overline{AB}$  is a compound, unstable at its melting point, which dissociates at the temperature of point 4 into solid Aand liquid, so that the composition of  $\overline{AB}$  (point X) lies outside of the field 4-5-6-3 in which  $\overline{AB}$  occurs as primary phase. Point 4 is a quadruple point at which A and  $\overline{AB}$  are in equilibrium with liquid and vapor, but 4 is not a eutectic. In the ternary system point 6 is a eutectic and 5 a quintuple point not a eutectic.

In V  $\overline{AB}$  is an unstable binary compound which dissociates into solid A and solid B, so that in binary mixtures  $\overline{AB}$  does not occur at the liquidus. In ternary mixtures, however,  $\overline{AB}$ is stable in contact with solution, because the melting temperatures of certain ternary mixtures are below the dissociation temperature of  $\overline{AB}$ . The field for  $\overline{AB}$  is bounded by curves which are wholly within the triangle, and the temperature along two of these curves will rise to a common vertex which will point toward the binary system in which  $\overline{AB}$  occurs.

Case VI (fig. 4) represents a system in which there is one binary and one ternary compound ( $\overline{AB}$  and  $\overline{ABU}$ ), each of which has a definite melting point. The field for the ternary compound is surrounded by boundary curves which lie entirely within the triangle; the composition and corresponding melting point of the ternary compound are represented by the maximum within the field.

If a ternary compound is unstable at its melting point it may dissociate either into two solid phases and liquid, in which case its composition will lie outside of its field; or it may dissociate into three solids and then there is no field in which it occurs in equilibrium with solution.

Of course, in a ternary system there may be any number of compounds, binary and ternary, stable or unstable, but the generalizations which hold for the simple cases are also applicable to the complex systems. For this reason we have not taken up all possible cases but merely a few typical examples. A more complete discussion of the possibilities in three-component systems may be found in "The Phase Rule," by W. D. Bancroft, or "Die Heterogenen Gleichgewichte," Dritte Heft, Erster Teil, by Roozeboom.

Thus the phase rule together with the theorem of Alkemade enables us to predict how many solid phases we may expect to find at equilibrium under definite conditions, and informs us not only as to the position of maxima on the boundary curves but also as to the direction of rising or falling temperature on those boundaries; all of which is of assistance in the location of new compounds and in the determination of the conditions under which these compounds exist. The actual location of compounds, the conditions for their existence and their relation to each other (involving the location of quintuple points and boundary curves), however, can only be determined by experiment.

### EXPERIMENTAL METHODS.

In work of this kind there are three general experimental methods of attack, all of which have been largely made use of in the present investigation, though the third one serves our purpose best.

1. The first method is to ascertain the energy changes occurring in the system as registered by the thermoelement, and in this way to endeavor to unravel the phase relations. This method is invaluable, but like all methods employed in the exploration of new fields, it gains strength when employed in conjunction with other methods even though the latter be inferior in the scope of their practical application. With silicates as with alloys, it is much easier to interpret the thermal data if one knows the nature of the reacting phases.

2. The second method is to bake the different preparations for long periods of time at appropriate temperatures in order to allow time for the reactions to become complete and for the growth of crystals of measurable size, thus rendering microscopic examination much easier.

3. The third method has for its object the determination of the boundaries of the various fields in which particular phases have their stable existence, i.e., of the location of the bound-
ary curves. In the case of ternary systems at ordinary temperatures, this is usually done either by adding the phase under investigation and finding out whether or not it dissolves in the saturated solution or by allowing the saturated solution to crystallize slightly so that the first crystals to form may be identified.\* To apply this method at high temperatures a small amount of the material of the desired composition is placed in a furnace and held at constant temperature until on quenching (sudden cooling by dropping into a bath of mercury or water), only one kind of crystal is present, and the rest of the solution is cooled to a glass before it has time to crystallize. The exact temperature for any given mixture must be determined by a series of trials with sufficient variation of the conditions of experiment to rule out effects due to slowness of reaction or of crystallization. Temperatures will thus be found where the charge is wholly glass, and also where the product obtained by quenching is wholly crystalline. The method also allows the crystals time to grow to measurable size, thus assisting the microscopic examination. In other words, the method develops the primary phase (Bodenkörper) embedded in the glass (solution) and allows a rapid and very satisfactory mapping of the fields of stability for each phase. The method is impracticable when the temperature rises too high for the platinum furnace (1600°); the iridium furnace (1600°-2100°) does not serve well for it. Naturally the method does not work so well where two kinds of crystals are present. To get the most satisfactory results, i. e., fair-sized crystals of the primary phase, the charge should be held at a temperature just below that of complete fusion for the composition in question.

The material to be investigated by each of the three methods is prepared as follows: The finely powdered oxides + CaO (as CaCO<sub>3</sub>), Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> are mixed in the desired proportions, placed in a platinum crucible, and fused in a Fletcher gas furnace. The charge is then removed from the crucible; broken up in a steel mortar; ground to a fine powder in a mechanical agate mortar and fused again. The process of fusion, with fine grinding between fusions, is repeated at least three times to obtain a product chemically homogeneous. In this process there are two operations, during which there is danger of losing a portion of the charge and also of introducing foreign material, (1) during the breaking up of the charge in the steel mortar, and (2) the subsequent grinding in the agate mortar. If, however, great care is exercised charges can be prepared in this way, without the addition of over 0.2 per cent foreign material or a change of over 0.2 per cent from the original percentage of the oxides. We have found that charges of twenty

\* Cf. Roozeboom, loc. cit.

<sup>+</sup> Careful tests of the purity of the materials used showed that they contained no appreciable amount of impurity. grams are easy to manipulate and are usually sufficient for both the optical and thermal study.

The amount of a charge required for each of the three methods is as follows: (1) For the determination of energy changes, we have found that in order to obtain the sharpest break (which is the record, on a heating curve, of an energy change) a charge of 2 5 to 5 grams should be used. (2) For baking in order to grow crystals, the charge varies from 1 to 100 grams. (3) For quenching, a charge of 0.1 to 0.5 gram is sufficient for the microscopical examination, and such a charge is easily maintained at constant temperature.

All experiments were performed in an oxidizing atmosphere (air); the furnaces used were of platinum or iridium. The platinum furnace consists of a coil of platinum wire (wire 1.2<sup>mm</sup> diameter; coil 2½ inches diameter, 9 inches long, six turns to the inch) wound on the inside of a cylinder of impure magnesite which is insulated with MgO powder and a fire clay cylinder. Temperatures within the platinum furnace are measured with a platinum-rhodium thermoelement, in connection with a potentiometer and galvanometer.\* It is heated by the current from a storage battery (voltage 110, capacity 300 amp. hrs.), and the temperature within the furnace can be maintained constant  $(\pm 2^{\circ})^{1}$  at 1550° for a period of 12 hours; for lower temperatures the temperature can be maintained constant for much longer periods of time.

The iridium furnace consists of a straight iridium tube about  $18^{\rm cm}$  long and  $4^{\rm cm}$  in diameter and is heated by a low voltage alternating current. Temperatures within this furnace are measured with an optical pyrometer.<sup>+</sup> This furnace is used only for the determination of melting-points of substances which melt completely at a definite temperature within the range  $1600^{\circ}-2100^{\circ}$ .

### EXPERIMENTAL INVESTIGATION.

## GENERAL RELATIONS OF THE BINARY COMPOUNDS IN THE TERNARY SYSTEM.

The investigation of the three binary systems showed that in the ternary system, in addition to the components themselves, the following binary compounds would occur, viz :— CaO.SiO<sub>2</sub>; 3CaO.2SiO<sub>2</sub>; 2CaO.SiO<sub>2</sub>; 3CaO.Al<sub>2</sub>O<sub>3</sub>; 5CaO. 3Al<sub>2</sub>O<sub>3</sub>; CaO.Al<sub>2</sub>O<sub>3</sub>; 3CaO.5Al<sub>2</sub>O<sub>3</sub>; Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>; 3CaO.SiO<sub>2</sub>.

In fig. 5 the compositions of the binary compounds and quadruple points are given as points on the sides of the tern-

\* Walter P. White: Potentiometer Installation, especially for high temperature and thermo-electric work, Phys. Rev. xxv, 334-352 (1907).

† Day, Shepherd and Wright: Lime-Silica Series of Minerals, this Journal, (4), xxii, 286, 1906.

Rankin and Wright-Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 23

ary diagram. These quadruple points are the starting points of the boundary curves which enter the triangle from the sides, but nothing definite as to the course of these boundary curves can be predicted from the binary systems, except that the direction of falling temperature will be from the sides of the triangle toward the interior.

However, it is of great assistance in locating these boundary curves to know their starting points; to know that they limit



FIG. 5. Composition of binary compounds and quadruple points projected on the ternary diagram.

in certain directions the fields of stability for those compounds which occur as primary phase both in the binary and ternary systems and that for each of these fields there will be two such boundary curves. If these two boundary curves start, one from either side of the composition of a compound, then that compound is stable at its melting point and its composition lies inside the field within which it is the primary phase. Such stable binary compounds are the following: CaO. SiO<sub>2</sub>; 2CaO. SiO<sub>2</sub>; 5CaO.  $3Al_2O_3$ ; CaO.  $Al_2O_3$ ;  $3CaO.5Al_2O_3$ ;  $Al_2O_3$ . SiO<sub>2</sub>; the three components behave likewise. If, on the other hand, the starting points of both boundary curves are on the same side of the composition of a compound, then that compound is unstable at its melting point and its composition lies outside of the ternary field in which it occurs as primary phase. Such unstable binary compounds are the following:  $3CaO.Al_2O_2$ and  $3CaO.2SiO_2$ .

As for the unstable binary compound 3CaO.SiO<sub>2</sub> which does not occur as primary phase in the binary system, it is not possible to say from the binary investigation whether or not it will have a field of stability in the ternary system or what the nature of such a field might be; except that if the field is three-sided, the temperature along two of the boundaries would rise to a common vertex which would point in the direction of the binary system in which the compound 3CaO.SiO<sub>2</sub> occurs.

In taking up, then, the experimental investigation of the system  $CaO-Al_2O_3-SiO_2$ , we know at the start that there are at least 12 compounds, some of which occur in more than one crystalline form, whose stability relations in the ternary system must be established. Beside these 12 there may be any number of ternary compounds, all of which must have their conditions of stability in the ternary system determined.

The first step in this investigation consisted in the preparation of charges whose compositions represented intervals of 5 per cent over the entire range of ternary mixtures. The primary crystalline phase was then determined for each of these charges which could be quenched at some temperature below 1600° in such a way that a single crystalline phase imbedded in glass could be obtained. From this preliminary reconnaissance a general idea is obtained of the number and character of the different crystalline phases which are stable in contact with the liquid, and of their relations to each other in ternary mixtures. In other words, we located approximately the fields with their limiting boundary curves and quintuple points. With these general data as a basis, other intermediate charges were prepared and their primary phases determined; this secured a more exact location of the boundary curves and quintuple points, the compositions along boundary curves (lines) being accurate to within  $\pm 1.0$  per cent and quintuple point compositions being accurate within a radius of 0.5 per cent.

The limits of the fields of stability of the various crystalline phases, determined in this way, are represented on the triangular diagram (fig. 6). The dots given in the diagram represent the compositions examined; for the sake of clearness they have been made different in adjoining fields; these dots, however, do not indicate all the concentrations examined or the many heat treatments and examinations required to determine the relations of any one concentration. The entire ternary system has necessitated the preparation of about 1000 different concentrations and fully 7000 heat treatments and micro-scopical examinations.

When the compositions within each field, along each boundary curve, and at each quintuple point are known, it is still necessary to determine the composition of each unknown



FIG. 6. Projection of concentration-temperature diagram for the ternary system  $CaO-Al_2O_3-SiO_2$ , giving compositions whose primary phases determined the location of boundary curves and quintuple points.

crystalline phase, and the equilibrium temperature within the fields, along the boundary curves and at each quintuple point. Examination of fig. 6 shows: that there are three new crystalline phases, not found in the binary series, which are ternary compounds; that there are 14 fields, 30 boundary curves and 21 quintuple points.

### THE TERNARY COMPOUNDS.

Of the three ternary compounds, two were found to be stable in contact with liquid, and as the field for each of these two compounds exhibits a maximum, the composition of the compound is represented by the position of the maximum. The molecular compositions of these two compounds are  $CaO.Al_2O_3.2SiO_2$  and  $2CaO.Al_2O_3.SiO_2$ . The third ternary compound was found to be unstable in contact with liquid, so that in order to determine its composition it was found necessary to crystallize glass of various compositions until a composition was obtained in which the compound was the only phase present. The molecular composition of this compound was thus found to be  $3CaO.Al_2O_3.SiO_2$ .

Artificial anorthite,  $CaO.Al_2O_3.2SiO_2$  (CaO 20.1, Al\_2O\_3 36.6, SiO<sub>2</sub> 43.3). Pure artificial anorthite melts at  $1550^{\circ} \pm 2^{\circ}$ ; its ternary field is bounded by the ternary fields for tridymite,  $aCaO.SiO_2, 2CaO.Al_2O_3.SiO_2, Al_2O_3.SiO_2, Al_2O_3$ ; it forms quintuple point mixtures with tridymite and  $aCaO.SiO_2$ , with tridymite and Al\_2O\_3.SiO\_2, with Al\_2O\_3.SiO\_2 and Al\_2O\_3, with Al\_2O\_3 and 2CaO.Al\_2O\_3.SiO\_2, and with 2CaO.Al\_2O\_3.SiO\_2 and  $aCaO.SiO_2$ .

It appears in the preparations either in lath-shaped individuals elongated after the edge (001)(010) or as tabular crystals after the side pinacoid M(010). Polysynthetic twinning after the albite law is common and characteristic. Crystal system triclinic. Refractive indices:  $\gamma_{\rm Na} = 1.589 \pm 0.001$ ;  $\beta_{\rm Na} = 1.585 \pm 0.001$ ,  $a_{\rm Na} = 1.576 \pm 0.001$ . (These values are identical, within the limits of error, with those of the natural anorthite.) Birefringence not strong,  $\gamma$ -a about 0.013. Extinction angle on basal pinacoid approximately 35°; optic axial angle large, optical character negative.

The compound  $2CaO.Al_2O_3.SiO_2$  (CaO 40.8, Al\_2O<sub>3</sub> 37.2, SiO<sub>2</sub> 22) melts at  $1590^{\circ} \pm 2^{\circ}$ ; its ternary field is bounded by the ternary fields for CaO.Al\_2O\_3.2SiO\_3, Al\_2O\_3.3CaO.5Al\_2O\_3, CaO.Al\_2O\_3, a2CaO.SiO\_2,  $\beta$ 2CaO.SiO\_3, 3CaO.2SiO\_2, aCaO.SiO\_2; it forms quintuple point mixtures with CaO.Al\_2O\_32SiO\_2 and Al\_2O\_3, with Al\_2O\_3 and 3CaO.5Al\_2O\_3, with 3CaO.5Al\_2O\_3 and CaO.Al\_2O\_3, with CaO.Al\_2O\_3 and  $\beta$ 2CaO.SiO\_2, with a2CaO.SiO\_2 and  $\beta$ 2CaO.SiO\_2, with  $\beta$ 2CaO.SiO\_2 and 3CaO.2SiO\_3, with 3CaO.2SiO\_2 and aCaO.SiO\_2, with aCaO.Al\_2O\_3. 2SiO\_2.

It crystallizes in clear, glassy, colorless grains which show distinct but not perfect basal cleavage. Fracture, conchoidal. Hardness about 6. Specific gravity about 3.038. Crystal system, tetragonal. Refractive indices:  $\omega_{\text{Na}} = 1.669 \pm 0.001$ ,  $\epsilon_{\text{Na}} = 1.658 \pm 0.001$ ; birefringence not strong, interference

colors are confined usually to the first order, a pronounced yellow hue being noticeably common. Uniaxial, optically negative.

The compound  $3CaO.Al_2O_3.SiO_2$  (CaO 50.9, Al<sub>2</sub>O, 30.9, SiO<sub>2</sub> 18.2) is unstable at its melting point and in the ternary system there is no field. Its position in the ternary system is shown in fig. 6. It dissociates at  $1335^{\circ} \pm 5^{\circ}$  into 2CaO.SiO<sub>2</sub> and CaO.Al<sub>2</sub>O<sub>3</sub>, and hence is best formed by crystallization from glass of its own composition at a temperature below  $1335^{\circ}$ . Even then the preparation appears under the microscope dusty and so unsatisfactory that it is not possible to state definitely that it is homogeneous. The crystalline mass is usually crypto- to microcrystalline and consists of overlapping fibers and grains. The larger grains show under high powers the ribbed structure common to crystal skeletons. Crystal system possibly orthorhombic. Refractive indices,  $a_{Na} = 1.675$  $\pm 0.005$ ,  $\gamma_{Na} = 1.685 \pm 0.005$ . Birefringence medium,  $\gamma$ -*a* about 0.01. Optic axial angle medium to fairly large. Optical character positive. Plane of optic axes is apparently parallel with positive elongation of fibers.

### THE STABILITY FIELDS.

In the complete CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> diagram there proved to be 14 separate fields of stability; that is there are 14 separate regions—one for each separate chemical compound (including the original components) which occurs in the system —within which a single particular compound is in equilibrium with liquid and vapor. Each field may be regarded as the solubility region of a single compound in solutions of two other definite compounds or the melting region of a single compound in solutions of three definite compounds.

The melting temperatures within each field are obtained either from heating curves, which serve to record the temperature at which the energy change accompanying melting occurs (a melting temperature within a field is the last absorption of heat recorded on a heating curve) or by quenching to determine the temperature above which a substance is obtained as a glass (liquid) and below which a single crystalline phase is obtained imbedded in glass, as determined by optical examination with the microscope. Both methods are used, but if the energy change is not evident, owing to sluggishness of the change or to confusion with other energy changes, then the quenching method is generally the more reliable. If, however, the quenching method can not be applied, because of difficulty of distinguishing the solid phases, then the heating curve method is preferable. For some points both methods could be used; in such cases the results obtained by both methods checked within the limit of error  $(\pm 5^{\circ})$ . For certain compositions it was not possible to determine the melting temperature by either method.

We shall now consider the fields separately, the numbers and letters used to designate them being those given in fig. 6. In the tables only mean values obtained from a large number of determinations are given.

I. The field of silica  $(SiO_2)$ —K-A-2-1-J.—Within the region where SiO<sub>2</sub> is the stable primary phase it exists in two forms, tridymite and cristobalite; K-10 is the boundary curve above which cristobalite is the stable form and below which tridymite is the stable form. Owing to the extreme viscosity of the melts within this field, satisfactory melting temperatures could not be obtained either by heating curves or quenchings; but an idea of the general slope of the melting surface of this field was obtained from the slope of the curves bounding it, which are the equilibrium curves—A-2; 2-1; 1-J;  $J-SiO_2$ ;  $SiO_2-A$ .

II. The field of  $CaSiO_3$ —(A-B-6-5-2).—Though there are two forms of CaSiO<sub>3</sub> yet only one of these appears in the ternary system as a primary phase, for the reason that the temperature at the eutectics 2 and 5 is higher than the inversion temperature of  $\beta$  to  $aCaSiO_3$ . This inversion temperature varies somewhat with the gross composition of the ternary mixture, because CaSiO<sub>3</sub> takes up in solid solution to a small extent—not over 2 per cent—each of the compounds with which it is associated at the boundary curves; this variation is illustrated by the following table:

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To show th	ie change	of the	inversion	temperature	$a \longleftrightarrow$	$\beta\mathrm{CaSiO_3}$	caused
	by	the pre	sence of a	ditional solid	l phases.		

			Composition	Inversion
Weig	ht per	centage	* TT * 1 / /	tempera-
CaO	$A1_2O_3$	SiO2	weight percentage	ture
48.2		51.8	100% CaSiO <sub>s</sub> .	$1200^{\circ} \pm 2^{\circ}$
45		55	90% CaSiO, 10% SiO,	$1210^{\circ} \pm 5^{\circ}$
50		50	83% CaSiO, 13% Ca Si O,	$1190^{\circ}\pm5^{\circ}$
51.2	0.9	47.9	97% CaSiO, 3% CaÅl Si O.	$1195^{\circ}\pm5^{\circ}$
46.3	0.9	52.8	94% CaSiO, 3% SiO, 3% CaAl Si O.	$1165^{\circ}\pm5^{\circ}$
35	10	55	60% CaSiO, 15% SiO, 25% CaAl Si O.	$1165^{\circ}\pm5^{\circ}$
48	2	50	94% CaSiO. 6% Ca Al SiO.	$1175^{\circ}\pm 5^{\circ}$
45	5	50	86% CaSiO <sub>3</sub> . 10% CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> . 4% Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	$1155^{\circ}\pm5^{\circ}$

It is possible to determine the melting temperatures within the field for  $\alpha$ CaSiO<sub>a</sub> either by heating curves or quenchings; the mean values of a number of experiments with each composition are given in Table II.

## TABLE II.

Melting temperature of various compositions within field A-B-6-5-2. Primary phase is aCaSiO<sub>3</sub> (M. P. 1540°±2°).

Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	35 5 60	30 10 ≆60	$\begin{array}{c} 40 \\ 5 \\ 55 \end{array}$	$35 \\ 10 \\ 55$	45 5 50	40 10 50	$\begin{vmatrix} 35 \\ 15 \\ 50 \end{vmatrix}$	$\begin{array}{c} 45\\10\\45\end{array}$	$\begin{vmatrix} 40\\15\\45 \end{vmatrix}$
Temperature of melting		1408	1322	1449	1374	1481	1416	1330	1402	1345

III. The field of  $CaO.Al_2O_3.2SiO_2$ —(1-2-5-7-9).—The region in which CaO.Al\_ $Q_3.2SiO_2$  is the stable primary phase possesses a maximum temperature  $1550^\circ \pm 2^\circ$  (the melting point of CaO.Al\_ $Q_3.2SiO_2$ ). The melting temperatures of various compositions within this field are given in Table III.

#### TABLE III.

Melting temperature of various compositions within field 1-2-4-7-9. Primary phase is CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> (M. P. 1550° $\pm$ 2°).

Composition Wt. per cent	CaO Al <sub>2</sub> O, SiO <sub>2</sub>	$\begin{array}{c c}15\\20\\65\end{array}$	$     \begin{array}{r}       18 \\       21 \\       61     \end{array} $	15 25 60	20 25 55	25 25 50	20 30 50	$\begin{array}{c} 30\\25\\45\end{array}$	$\begin{array}{c} 25\\ 30\\ 45 \end{array}$	$20 \\ 35 \\ 45$	$\begin{array}{c} 30\\ 30\\ 40 \end{array}$	$\begin{array}{c} 25\\ 35\\ 40 \end{array}$	30 35 35
Temperature of melting		1384	1358	1447	1468	1466	1522	1433	1514	1545	1445	1523	1415

IV. The field of  $Al_2SiO_s$  (J-1-7-I).—Within this field it proved impracticable to determine melting temperatures on account of the extreme viscosity of the melts in portions of the field and of the high melting temperatures in the remainder. But, in spite of this, fairly accurate conclusions can be drawn as to the slope of the melting surface of this field, because the field is rather narrow and the melting temperatures for all sides of the field have been ascertained.

V. The field of  $3CaO.2SiO_2$  (B'-B-6-4).—This field differs somewhat in type from those preceding. In this case the compound is unstable and hence its composition lies outside of the field in which it occurs as primary phase. The slope of this narrow field is ascertained from the melting temperatures of its boundaries, which were determined.

## 30 Rankin and Wright—Ternary System CaO-Al, O,-SiO,.

VI. The field of  $2CaO.Al_2O_3.SiO_2$  (6-5-7-11-12-13-4).— This field, whose boundaries lie wholly within the triangle, possesses a maximum which is the melting point for the composition of the primary phase  $2CaO.Al_2O_3.SiO_2$  1590°  $\pm$  2°. The melting temperatures of various compositions within this field are given in Table IV.

TABLE IV.	
Melting temperature of various compositions within	field 6-5-7-11-12 13-4.
Primary phase is 2CaO.Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> (M. P.	$1590^{\circ} \pm 2^{\circ}$ ).

	CaO	40	35	45	40	35	30	31	45	35
Wt per cent	Al <sub>2</sub> O <sub>3</sub>	25	-30	25	30	35	40	41.5	30	40
we per cent	SiÔ <sub>2</sub> °	35	35	30	30	30	30	27.5	25	25
Temperature of melting		1475	1430	1554	1558	1503	1394	1450	1575	1537
			TABLE	: IV—(	Contin	ued.				
		46.3	45	36	48.8	45	40	47.6	47.	40
		33.7	35	46	35.6	40	45	38'	39.4	50
		20.	20	18	15.6	15	15	14.4	13.6	10
		1548	1569	1571	1490	1529	1564	1495	1490	1537

VII. The field of alumina  $(Al_2O_3)$  (7–I– $Al_2O_3$ –H–11).—In the preliminary report, a field was given between this field and that for  $Al_2SiO_5$  for a compound of unknown composition and properties. More careful study has shown this supposed new compound to be alumina. Most of the melting temperatures within this field are too high for determination; those of certain compositions are given in Table V.

### TABLE V.

Melting temperature of various compositions within field 7-I-Al<sub>2</sub>O<sub>3</sub>-H-11. Primary phase is Al<sub>2</sub>O<sub>3</sub> (M. P. 2050°).\*

Composition Wt. per cent	$\begin{array}{c} \text{CaO} \\ \text{Al}_2\text{O}_3 \\ \text{SiO}_2 \end{array}$	$14 \\ 38.5 \\ 47.5$	18.5 39. 42.5	20 40 40	23.5 41.5 35.	28.5 39.5 32.	$29 \\ 40 \\ 31$	30· 42·5 27·5	29 50•5 20•5
Temperature of melting		1575	1550	1560	1530	1395	1430	1475	1550

VIII. The field of calcium orthosilicate  $(Ca_2SiO_4)$   $(B'-4-1)_{\mu-15-16-C}$ .—Ca<sub>2</sub>SiO<sub>4</sub> occurs in 3 forms, two stable (a and  $\beta$ ) and one unstable  $(\beta')$ ; all 3 are found within the field. The

\* According to Kanolt, J. Wash. Acad. Sci., iii, 315, 1913.

 $\beta$  modification is the stable form within the regions 19-20-14-15 and 3-4-8, while in or near the latter region the  $\beta'$ form occurs with considerable frequency. Within the remainder of the field the *a* form is the stable phase.

Although Ca<sub>2</sub>SiO<sub>4</sub> shows practically no variation in optical properties over the entire range of this field, yet the inversion  $\beta \rightleftharpoons^a a$  takes place at different temperatures depending on the composition of the charge under investigation, as it is evident from Table VI.

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To show the change of the inversion temperature  $\beta \longrightarrow a \operatorname{Ca_2SiO_4}$  caused by the presence of additional solid phases.

Composition weight per cent	$\begin{array}{c} CaO\\ Al_2O_3\\ SiO_2 \end{array}$	65 0·0 35	$\begin{array}{c} 60\\5\\35\end{array}$	60 30 10	$55\\35\\10$	52 38 10	58 33 9
Inversion temperature		1420	1415	1395	1395	1415	1395

 $Ca_sSiO_4$  does not take up in solid solution an appreciable amount of any of the compounds with which it is associated in this system. Over the larger part of this field the melting temperatures are too high for accurate determination. Those we have determined are given in Table VII.

TABLE VII.

Melting temperature of various compositions within field  $\beta'$ -4-14-15-16-C; primary phase is Ca<sub>2</sub>SiO<sub>4</sub> (M. P. 2130°±20°).

~ ···	CaO	55	50	50	50.	50.7	513	50.9
Composition Wt por cont	Al <sub>2</sub> O <sub>3</sub>	5	10	15	17.5	$22 \cdot$	29.7	30.9
wt. per cent	SiŌ,	40	40	35	32.5	27.3	$19 \cdot$	18.2
Temperature of melting		1625	1400	1500	1550	1625	1590	1570
		TAB	LE VII	(Contin	ued).			
		50	57	<u>д0</u>	52	50	49	50
		32.8	30	27.5	38	40	42	42
		17.2	13	12.5	10	10	9	8
		1535	1580	1600	1460	1420	1390	1375

IX. The field of  $3CaO.5Al_2O_3$ . (11-12-G-H).  $-3CaO.5Al_2O_3$  occurs in two forms, a stable form and an unstable form which is occasionally found in melts. Melting temperatures of the stable form are given in Table VIII.

#### TABLE VIII.

Melting	temperature	of	various	compositio	ns v	vithin	field	11 - 12 -	G-H;
	primary	pha	ise is 3Ca	$0.5Al_2O_3$ . (	(M. F	P. 1720	$^{\circ}\pm10^{\circ}$	).	

	CaO	49	29	34.3	35	37
Composition	Al <sub>o</sub> O	30	$52^{-20}$	52.7	55	54
Weight per cent	SiÓ <sub>2</sub> <sup>°</sup>	21	19	13.	10	9
Temperature of melting		1540	1590	1570	1590	1509

X. The field of  $CaO.Al_2O_3$ . (F-G-12-13-14).—Table IX gives the melting temperatures of various compositions within this field.

### TABLE IX.

Melting temperature of various compositions within field F-G-12-13-14; primary phase is CaO.Al<sub>2</sub>O<sub>3</sub> (M. P. 1600° ± 5°).

Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	45 47 8	$48.5 \\ 45. \\ 6.5$	36.7 58.1 5.2	45 50 5	40 55 5	47 49 4	$47.5 \\ 49.5 \\ 3.0$
Temperature of melting		1456	1361	1549	1468	1535	1432	1421

XI. The field of  $5 \, CaO.3 \, Al_2O_3$  (*E*-*F*-14-15).—5CaO.3Al<sub>2</sub>O<sub>3</sub> occurs in two forms, a stable form and an unstable form which occurs in melts with considerable frequency. The melting slope of the narrow field for the stable form follows from the melting temperatures of the boundaries which have been ascertained.

XII. The field of  $3CaO.Al_2O_3$  (E-15-16-17-D.)-3CaO. Al\_QO\_3 is a compound unstable at its melting point, wherefore its composition lies outside of its field of stability. Table X gives the melting temperatures of various compositions within this field.

TABLE X.
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Melting temperature of various compositions within field E-15-16-17-D; primary phase is 3CaO.Al<sub>2</sub>O<sub>3</sub>.

Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>2</sub> SiO <sub>2</sub>	58.5 33.5 8.	$57.5 \\ 35. \\ 7.5$	$52.5 \\ 41.65 \\ 6.5$	60 35 5	$55\\40\\5$	$52.5 \\ 42.5 \\ 5.$
Temperature of melting		1448	1435	1370	1490	1437	1390

## Rankin and Wright—Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 33

XIII. The field of tricalcic silicate,  $3CaO.SiO_2$  (16-17-18). 3CaO.SiO<sub>2</sub> like 3CaO.Al<sub>2</sub>O<sub>3</sub> is unstable at its melting point, but unlike 3CaO.Al<sub>2</sub>O<sub>3</sub> the field of stability for 3CaO.SiO<sub>2</sub> lies wholly within the ternary system. This field is so narrow that the slope of the melting surface was deduced from the temperatures along the lines which bound it.

XIV. The field of lime, CaO(D-CaO-C).—Practically all the melting temperatures within this field are too high for determination, and hence the slope of its melting surface was deduced from the melting temperatures of the boundaries.

### THE BOUNDARY CURVES.

A boundary curve is the line which separates two fields and represents the temperatures and concentrations at which the solid phase of one field is in equilibrium with the solid phase of the other field in coexistence with solution and vapor.

The boundary lines in fig. 6 represent the projection upon the horizontal plane of the lines on the concentration-temperature solid model. In order to make clear the way in which the temperature varies along these lines, we have made projections on to a vertical plane, obtaining in this way the series of boundary curves reproduced in fig. 7, in which the numbers and letters used correspond to those in fig. 6. The ordinates represent temperatures, which were determined experimentally.

The direction of rising temperature along the boundary curves (fig. 7) can be predicted by the application of the theorem of Alkemade to the projections of these curves (fig. 6). For example, consider the boundary (5-2) in fig. 6, between CaSiO, and CaO.Al,O. 2SiO. It is quite evident that a straight line connecting the compositions of these two compounds would intersect the boundary (5-2), and from the theorem of Alkemade it follows that the point of intersection is a maximum temperature on this boundary. The concentration-temperature diagram for boundary (5-2) in fig. 7 shows this There are in fig. 6 nine boundary lines which one maximum. would expect to possess maximum temperatures, and the concentration-temperature diagram (fig. 7) for each of these boundary curves is found experimentally to show such a maximum. If now we consider boundary (1-9) between Al<sub>2</sub>SiO<sub>5</sub> and CaO. Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>4</sub>, it is evident that a straight line connecting the compositions of these two compounds would intersect boundary 1-9 only if this curve were produced beyond point 9. Hence from the theorem of Alkemade it follows that temperature along 1-9 should rise continuously from point 1 to point 9. The concentration-temperature diagram for boundary 1–9 in

Am. Jour. Sci. – Fourth Series, Vol. XXXIX, No. 229. – January, 1915.



FIG. 7. Temperature-concentration diagram of the 29 boundary curves which fix the limits of the fields within the ternary system  $CaO-Al_2O_3-SiO_2$ .

fig. 7 shows that such is the case. There are 19 of these boundary curves along which the temperature rises continuously; that is, there are 19 boundary curves which do not show a maximum.

Approximate temperatures along boundary curves may be deduced by extrapolation from the melting temperatures determined for points within the fields but for more exact temperatures heating curves and quenchings are required. For the experimental determination of the temperature of any point on a boundary curve it is not necessary to use the composition for that point; any composition may be used which is on a straight line passing through this point on the boundary curve and the composition of either solid phase which occurs on this boundary curve. The reason for this is obvious if we consider the successive changes which take place when a ternary mixture is heated.

In heating curves of ternary mixtures the first break (heat absorption) observed corresponds usually to the temperature of a quintuple point. If the heating is continued, melting proceeds and equilibrium follows along a boundary curve until one of the two solid phases in equilibrium with liquid and vapor has completely melted; at which point we find the second break, which is the melting temperature corresponding to that point on the boundary curve. Each point on the boundary curves represents the composition of the liquid which is in equilibrium at that point with the still solid portion of the charge, but when we have progressed along the boundary curve until it intersects the straight line drawn through the composition of the ternary mixure under investigation and the composition of the primary phase of that mixture, then the locus of the points representing the composition of the liquid phase leaves the boundary curve and passes into the appropriate field along the straight line.

A more complete discussion of the changes which take place during the heating of a ternary mixture will be given when we come to consider ternary crystallization curves. For the present it seemed to be sufficient to show: that the temperature for any point on a boundary curve may be determined from a number of different compositions; that for any ternary composition the point at which its heating curve will leave the boundary curve is known; that the second break in a heating curve is usually the temperature of a point on the boundary curve. For those ternary mixtures in which the second break in the heating curve is not a boundary curve temperature, it is necessary to determine by *quenching* the temperature at which on heating the composition leaves the boundary curve. This is done by determining the temperature above which one solid crystalline phase is obtained imbedded in glass and below which two crystalline phases are obtained imbedded in glass (liquid), as observed with the microscope.

The data obtained for temperatures along the boundary curves will not be presented, as the essential temperatures for these curves are given later as quintuple and quadruple point temperatures.

### THE QUINTUPLE POINTS.

A quintuple point, a common point for three boundary curves, is the point at which three solid phases are in equilibrium with solution and vapor. A quintuple point is known as a eutectic if its temperature is the lowest temperature on the three boundary curves of which it is a common point.

The temperature of a quintuple point may be determined in any mixture of the solid phases present at that quintuple point (for all ternary mixtures contain more or less of the quintuple point composition) either from heating curves, or from quenches by which it is possible to determine the temperature above which two crystalline phases are obtained imbedded in glass (liquid) and below which three solid crystalline phases are obtained; that is, the temperature at which glass first appears in a ternary mixture is the temperature of the quintuple point for that mixture. In presenting the data for quintuple points we will first consider the eutectics, of which there are 8, and then the 13 quintuple points not eutectics.

*Eutectics.*—In dealing with alloys, which contain more or less of a eutectic mixture, there is often developed what is known as a "eutectic structure" which is easily recognized by use of the microscope. So far as we have worked with silicate melts phenomena of that sort are rarely observed; in other words, a eutectic mixture of silicates has in general no special structure different from any other mixture. On the other hand, eutectic mixtures of silicates are extremely fine-grained and it is extremely difficult to develop or grow crystals in a charge containing a large amount of a eutectic.

Following is a list of the eutectics, giving compositions in weight percentages of CaO,  $Al_2O_3$ ,  $SiO_2$ , and the corresponding temperatures. All of the data on which is based the temperature of one single eutectic are given, but for lack of space it will be possible to give only one value (the mean of a large number of determinations) for each of the other eutectics. The number assigned to each eutectic corresponds to the number in fig. 6

Point 2 is the eutectic for SiO<sub>2</sub>,  $\alpha$ CaSiO<sub>3</sub> and CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>, (CaO 23.25, Al<sub>2</sub>O<sub>3</sub> 14.75, SiO<sub>2</sub> 62). Its melting temperature (1170° ± 5°) is based on the values obtained from various compositions as given in Table XI.

TABLE XI.

Melting point of eutectic 2 for  $aCaSiO_3 + CaO_1Al_2O_3.2SiO_2 + SiO_3$  as determined from various compositions.

~	CaO	25	20	15	30	25	20	15	35	30
Composition Wt non cont	Al <sub>2</sub> O <sub>2</sub>	5	10	15	5	10	15	20	5	10
wt. per cent	$\mathrm{Si}\check{\mathrm{O}}_{2}$	70	70	70	65	65	65	65	60	60
Temperature		1171	1183	1174	1165	1175	1173	1173	1170	1175
		1172	1174	1175	1165	1175	1177	1175	1171	1169
		1169	1183	1175	1165	1174		1173	1170	1173
				1174	1165			1169		1172
				1174						1171
				1173						
Mean		1171	1180	1174	1165	1175	1175	1172	1170	1172
			TABLE	XI (0	Continu	ied).				
	25	20	15	40	35	25	20	23.5	30	35
	15	20	25	5	10	20	25	14.5	10	10
	60	60	60	55	55	55	55	62	60	65
	1172	1167	1168	1165	1171	1176	1173	1165	1165	1170
	1173	1171	1163		1174	1173	1178	Quench	Quench	Quench
	1171	1172	1167		1174		1178			
		1173	1167							
			1166							
	1172	1171	1166	1165	1173	1175	1176	1165	1165	1170

Point 1 is the entectic for Al,SiO,, CaO.Al,O, 2SiO, and SiO,.

(CaO 9.8, Al<sub>2</sub>O<sub>3</sub> 19.8, SiO<sub>2</sub> 70.4);  $1345^{\circ} \pm 5^{\circ}$ . Point 5 is the eutectic for CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>, CaSiO<sub>3</sub>, and 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>. (CaO 38, Al<sub>2</sub>O<sub>3</sub> 20, SiO<sub>4</sub> 42);  $1265^{\circ} \pm 5^{\circ}$ .

Point 6 is the eutectic for  $2CaO.Al_2O_3SiO_2$ ,  $CaSiO_3$  and 3CaO.2SiO<sub>2</sub>. (CaO 47.2, Al\_2O\_311.8, SiO\_41); 1310° ± 5°.

Point 7 is the eutectic for  $Al_{2O_3}$  (CaO  $49\cdot 2$ ,  $Al_{2O_3}$  (CaO  $29\cdot 2$ ,  $Al_{2O_3}$ ,  $2CaO.Al_{2O_3}$ .SiO<sub>2</sub> and CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>. (CaO  $29\cdot 2$ ,  $Al_{2O_3}$ , 39, SiO<sub>3</sub>,  $31\cdot 8$ );  $1380^\circ \pm 5^\circ$ . Point 12 is the eutectic for  $2CaO.Al_{2O_3}$ .SiO<sub>4</sub>,  $3CaO.5Al_{2O_3}$ , and CaO.Al<sub>2</sub>O<sub>3</sub>. (CaO  $37\cdot 5$ ,  $Al_{2O_3}$ ,  $53\cdot 25$ , SiO<sub>4</sub>,  $9\cdot 25$ );  $1505^\circ \pm 5^\circ$ . Point 14 is the eutectic for Ca<sub>2</sub>SiO<sub>4</sub>,  $5CaO.3Al_{2O_3}$  and CaO. Al<sub>2</sub>O<sub>3</sub>. (CaO  $49\cdot 5$ ,  $Al_{2}O_3$ ,  $43\cdot 7$ , SiO<sub>4</sub>,  $6\cdot 8$ );  $1335^\circ \pm 5^\circ$ . Point 15 is the eutectic for Ca<sub>2</sub>SiO<sub>4</sub>,  $5CaO.3Al_{2O_3}$  and CaO.

Point 15 is the entrectic for Ca  $\dot{SiO}_4$ , 5CaO.3Al<sub>2</sub>O<sub>3</sub> and 3CaO. Al<sub>2</sub>O<sub>3</sub>. (CaO 52, Al<sub>2</sub>O<sub>3</sub> 41·2, SiO<sub>2</sub> 6·8); 1335° ± 5°.

The only satisfactory method for determining the melting points of eutectics 14 and 15 is by quenching. Heating curves to determine the temperatures of these two eutectics are unsatisfactory for the following reasons: (1) 5CaO.3Al,O<sub>s</sub>, either pure or in ternary mixtures, when finely powdered and heated to a temperature at which melting begins, will boil up and con-

3

tinue to boil more vigorously as the temperature rises. Most of a twenty gram charge will boil out of a  $100^{cc}$  platinum crucible. If large lumps of this compound or ternary mixtures of which this compound is a considerable part are melted, this phenomenon does not occur. The reason for this boiling we have not fully investigated, but it is probably due to absorbed gas which is liberated only at melting. What we do know is that this boiling is distressing when it occurs in a charge on which we wish to take a heating curve. (2) The unstable form of 5CaO.3Al<sub>2</sub>O<sub>3</sub> appears and disappears in melts in the ternary, as in the binary system. This causes uncertain and irregular breaks on heating which may occur at almost any temperature. For these reasons satisfactory heating curve breaks for these two eutectics are impossible except for those compositions containing but a small amount of 5CaO.3Al<sub>2</sub>O<sub>3</sub>, in which case so small an amount of the eutectic is present that the break is not very sharp.

Quintuple Points not Eutectics. The data for quintuple points not eutectics are presented in the same way as those for eutectics; that is, the complete series of observations on which is based the temperature of a single point is given but only one value (the mean of a large number of determinations) for each of the other points. The number assigned to each quintuple point corresponds to the number in fig. 6.

Point 4 is the quintuple point for 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>4</sub>,  $\beta$ Ca<sub>2</sub>SiO<sub>4</sub> and 3CaO.2SiO<sub>2</sub> (CaO 48.2, Al<sub>2</sub>O<sub>3</sub> 11.9, SiO<sub>2</sub> 39.9). Its melting temperature,  $1335^{\circ} \pm 5^{\circ}$ , is based on the values obtained from various compositions as given in Table XII.

TABLE	XII.
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Melting temperature: quintuple point 4 for  $\beta$ 2CaO.SiO<sub>2</sub>+2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>+ 3CaO.2SiO<sub>2</sub> as determined from various compositions.

Composition Wt. per cent	$\begin{array}{c} CaO\\ Al_2O_3\\ SiO_2 \end{array}$	60 5 35	$55\\10\\35$	$\begin{array}{r} 45\\30\\25\end{array}$	$55\\5\\40$	48•5 12• 39•5
Temperature		1333	1337	1334	1333	1337
		1334	1337	1337	1336	Quench
		1334	1338	1337	1333	
		1332	1339	1336		
			1340	1336		
			1341			
Mean		1333	1338	1336	1333	1337

Point 3 is the quintuple point for  $a2CaO.SiO_2$ ,  $\beta 2CaO.SiO_2$  and  $3CaO.2SiO_2$ . (CaO 53.0, Al<sub>2</sub>O<sub>3</sub> 4.2, SiO<sub>2</sub> 42.8); 1415  $\pm$  5°.

Point 8 is the quintuple point for a2CaO.SiO<sub>2</sub>,  $\beta$ 2CaO.SiO<sub>2</sub> and 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>. (CaO 49, Al<sub>2</sub>O<sub>3</sub> 14·4, SiO<sub>2</sub> 36·6); 1415° ± 5°.

8

Point 9 is the quintuple point for Al<sub>2</sub>O<sub>3</sub>, CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>. (CaO 15.6, Al<sub>2</sub>O<sub>3</sub> 36.5, SiO<sub>2</sub> 47.9);  $1512^{\circ} \pm 5^{\circ}$ . Point 10 is the quintuple point for SiO<sub>2</sub> (tridymite), SiO<sub>2</sub>

Point 10 is the quintuple point for SiO<sub>2</sub> (tridymite), SiO<sub>2</sub> (cristobalite) and Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (sillimanite). (CaO 6.6, Al<sub>2</sub>O<sub>3</sub> 17.6, SiO<sub>2</sub> 75.8); 1470°.

SiO<sub>2</sub> 75.8); 1470°. Point 11 is the quintuple point for 3CaO 5Al<sub>2</sub>O<sub>3</sub>, 2CaO.Al<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. (CaO 31.2, Al<sub>4</sub>O<sub>3</sub> 44.5, SiO<sub>2</sub> 24.3); 1475°  $\pm$  5°. Point 13 is the quintuple point for 2CaO.Al<sub>2</sub>O<sub>3</sub>. SiO<sub>3</sub>, 2CaO.SiO<sub>2</sub> and CaO.Al<sub>2</sub>O<sub>3</sub>. (CaO 48.3, Al<sub>2</sub>O<sub>3</sub> 42, SiO<sub>2</sub> 9.7); 1380°  $\pm$  5°.

and CaO.Al<sub>2</sub>O<sub>3</sub>. (CaO 48'3, Al<sub>2</sub>O<sub>3</sub> 42, SiO<sub>2</sub> 9'7); 1380  $\pm$  5°. Point 16 is the quintuple point for 3CaO.Al<sub>2</sub>O<sub>3</sub>, 3CaO.SiO<sub>2</sub> and 2CaO.SiO<sub>2</sub>. (CaO 58.3, Al<sub>2</sub>O<sub>3</sub> 33, SiO<sub>2</sub> 8'7); 1455°  $\pm$  5°.

Point 17 is the quintuple point for CaO,  $3CaO.Al_{.O}$ , and  $3CaO.SiO_{2}$ . (CaO 59.7,  $Al_{.O}$ , 32.8,  $SiO_{.}$ , 7.5);  $1470^{\circ} \pm 5^{\circ}$ .

Point 18 is the quintuple point for CaO, 2CaO.SiO, and 3CaO. SiO<sub>2</sub>. (CaO 68.4, Al<sub>2</sub>O<sub>2</sub> 9.2, SiO<sub>2</sub> 22.4); 1900°  $\pm$  20.

Point (18) was located by extrapolation of the boundary curves 16-18 and 17-18. The direction of the lower parts of these curves—temperature up to  $1600^{\circ}$ —was determined by quenchings; the temperature of the upper parts of these is beyond the range of our temperature measurements, so that neither the location or temperature of point 18 is very accurate. Point 18 is the dissociation temperature of  $3CaO.SiO_{2}$ .

Point 19 is the quintuple point for  $a2CaO.SiO_2$ ,  $\beta 2CaO.SiO_2$ and  $3CaO.Al_2O_1$  (CaO 54.5,  $Al_2O_3$  38,  $SiO_2$  7.5); 1390°.

Point 20 is the quintuple point for a2CaO.SiO<sub>2</sub>, β2CaO.SiO<sub>4</sub> and 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>4</sub> (CaO 48.7, Al<sub>2</sub>O<sub>3</sub> 39.3, SiO<sub>2</sub> 12); 1430°.

## RECAPITULATION; THE CONCENTRATION-TEMPERATURE MODEL.

In the preceding pages we have recorded equilibrium temperatures as determined within the limits of our apparatus for the three binary systems and for the ternary system; in other words, we have presented the temperatures corresponding to quintuple points, boundary curves and fields. By interpolation from the determined melting temperatures we may draw constant temperature lines or isotherms; this has been done for every 100° from 1200° to 1700° and the resulting diagram is given in fig. 8, which shows, moreover, the melting temperatures and compositions of each compound, component, quadruple point and quintuple point.

By erecting the concentration-temperature diagram (fig. 7) for each boundary curve (fig. 6) perpendicular to the plane of the corresponding projection of each boundary curve (fig. 6), one constructs a concentration-temperature solid model whose surface represents the melting temperature of all ternary compositions of  $CaO-Al_2O_3$ -SiO<sub>2</sub>. A detailed description of the method used in the construction of a solid model is given in a

footnote, page 16. Photographs of a solid model constructed in this way are given in figs. 9–11. Fig. 9 is taken from the SiO<sub>2</sub> end and shows the binary systems CaO-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>6</sub> and also the slopes of the ternary fields which have their



FIG. 8. Projection of concentration-temperature diagram of ternary system  $CaO-Al_2O_3-SiO_2$  with isotherms and melting temperatures of compounds and invariant points.

origin in the two binary systems. In the same way fig. 10 shows the binary systems of CaO-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>3</sub> and their relation to the ternary system. Fig. 11 is a photograph taken from directly above the solid model and shows the relative positions and slopes of the various fields.

# Rankin and Wright-Ternary System CaO-Al2O3-SiO2. 41

As can be seen from the three photographs, the concentration-temperature model of the ternary system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> has the general appearance of a mountain range; the mountain

FIG. 9.

CAO AL203 S102

FIG. 9. Photograph of solid model of concentration-temperature diagram of ternary system; showing relation of binary systems  $CaO-SiO_2$  and  $Al_2O_3-SiO_2$  to the ternary system.

peaks are melting points of components or of compounds stable at the melting point; the continuous slopes on the sides of each mountain represent the melting temperatures of a stable com-

# 42 Rankin and Wright-Ternary System CaO-Al, O,-SiO,.

pound or component in ternary solutions; if there is a break in the continuous slope of a mountain side, then the slope from the break down to the foot of the mountain represents

## FIG. 10.



FIG. 10. Photograph of solid model showing relation of binary systems  $CaO-Al_2O_3$  and  $Al_2O_3-SiO_2$  to the ternary system.

melting temperatures of an unstable compound in ternary solutions; the valleys between mountains represent boundary curves; the points where the rivers in three valleys meet to form a lake is a eutectic point, but if two rivers meet at a point where they unite to form a single river, then that point is a quintuple point but not a eutectic.

## Some General Considerations on the System CaO-Al<sub>2</sub>O<sub>3</sub>-SIO<sub>2</sub>.

In what precedes we have taken up the various points, curves and regions separately; we shall now proceed to discuss

FIG. 11.



FIG. 11. Photograph of solid model taken from directly above, showing relation of various fields.

some of the more general relationships. For convenience in these discussions each component will be designated by its first letter, thus—C = CaO;  $A = \text{Al}_2\text{O}_3$ ;  $S = \text{SiO}_2$ . This simplifies the designation of compounds thus— $CS = \text{CaO.SiO}_3$ ;  $CAS_2 = \text{CaO.Al}_2\text{O}_3.2\text{SiO}_2$ ;  $C_3A_5 = 3\text{CaO.5Al}_2\text{O}_3$ ; etc.

## THE VARIOUS BINARY SYSTEMS WITHIN THE TERNARY SYSTEM.

These relationships may be ascertained from a study of the diagram fig. 12. In this diagram are drawn, besides the boundary curves, straight lines connecting the compositions of each pair of compounds whose fields have a common boundary



FIG. 12. Diagram of the ternary system showing the various binary systems within ternary system.

curve; each of these straight lines, which represents all possible mixtures of the two compounds whose compositions it connects, is a horizontal projection of the melting curve of these mixtures in solutions of themselves. From a glance at the diagram it will be seen that while (a) certain of the straight lines, drawn as full lines, lie entirely within the fields of the two

compounds whose compositions they connect, (b) others drawn as dotted lines lie partially within these two fields, (c) still others lie partially within only one of these two fields and (d)one lies entirely without these two fields.

(a) The straight line lies entirely within the fields of the two compounds whose compositions it connects. As an example of this, consider the line joining the compositions of the two compounds CS (CaO.SiO<sub>2</sub>) and  $CAS_2$  (CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>). This line intersects the ternary boundary 5-2 for CS and  $CAS_{2}$  at point M. That portion of the line connecting CS and M is then the melting curve of CS in solutions with  $CAS_{a}$  and the portion of the line connecting CAS, and M is the melting curve of CAS, in solutions with CS. Point M is the point at which CS and CAS, melt together and is a eutectic point. The system  $CS-CAS_2$  is, therefore, a simple binary eutectic system if one considers the compounds CS and  $CAS_2$  as components. There are eight of these binary systems represented by full lines in fig. 12. Two of these systems,  $C > -C_{*}AS$  and  $C_{*}AS - CA$ , occur on the same straight line and will be treated as a single binary system in which there is one stable compound formed  $C_{s}AS$ . The data for the important points of these systems are given in Tables XIII-XX, and the corresponding temperature-concentration diagrams are given in figs. 13-16. The abscissa or concentration line for each of these systems is taken directly from fig. 12 and ordinates were erected to represent temperatures.

		Component SiO <sub>2</sub>	Eutectic		Component CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>
Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	0.0 0.0 100.0	10.5 19.5 70.	$19^{\circ}$ $34^{\circ}9$ $46^{\circ}1$	20.09 36.63 43.28
Melting temperature		1625	1359	1542	1550

TABLE XIII. Melting temperatures of the binary system SiO<sub>2</sub>-CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.

TABLE XIV.

$\alpha_{10101112}$ remperatories of the binary system $\alpha_{100102} = \alpha_{1000} \alpha_{1203} \alpha_{1000}$	Melting	temperatures of	of the binary	system CaOSiO	-CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>
--	---------	-----------------	---------------	---------------	--

		$\begin{array}{c} {\rm Component} \\ {\rm CaO.SiO_2} \end{array}$	6	Eutectic	Ca	Component O.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>
Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	48·2 0·0 51·8	41·4 9·0 49·6	34.1 18.6 47.3	$27 \cdot 27 \cdot 5 \\ 45 \cdot 5$	20 <sup>.</sup> 9 36 <sup>.</sup> 63 43 28
Melting temperature		1540	1436	1299	1484	1550

Melting ter	nperatures o	of the binary system	CaO.Al <sub>2</sub> O <sub>3</sub> .2S	iO2-Al2O
		Component CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>	Eutectic	Comp
Composition	CaO Al <sub>2</sub> O	20·09 36·63	19·3 39·3	10
wt. per cent	d' Å "	10.00	47 4	

43.28

1550

41.4

1547

SiO

Melting

temperature

onent 2O8 0

)0

0

2050

TUDLE X V	Тав	LE	XV	Τ.
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FIG. 13.



Temperature-concentration diagrams of the binary systems Fig. 13. CaO.SiO<sub>2</sub>-CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> and SiO<sub>2</sub>-CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.

TABLE XVI.

Menning temperatures of the binary system 20a0. Al <sub>0</sub> 0 <sub>3</sub> . Si0 <sub>3</sub> -20	Melting	temperatures	of	the binary	system	2CaO.	A1.	O <sub>3</sub> .SiC	-2CaO	.SiO.
---	---------	--------------	----	------------	--------	-------	-----	---------------------	-------	-------

$\begin{array}{c} Component\\ 2CaO,Al_2O_3.SiO_2\end{array}$						Eutectic	Co	Component Ca <sub>2</sub> SiO <sub>4</sub>	
Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	40.83 37.19 21.98	42·3 35·0 22·7	45·8 29·5 24·7	46.6 28.3 25.1	49.6 23.7 26.7	50.7 22. 27.3	65 0 35	
Melting temperature		1590	1588	1574	1564	1545	1625	2130	

TABLE XVII.

Melting temperatures of the binary system CaO. Al<sub>2</sub>O<sub>3</sub>. 2SiO<sub>2</sub>-2CaO. Al<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub>.

Component CaO. Al <sub>2</sub> O <sub>8</sub> .2SiO <sub>2</sub> Eutectic						Component 2CaO.Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>		
Composition Wt. per cent	$\begin{array}{c} \text{CaO} \\ \text{Al}_2\text{O}_3 \\ \text{SiO}_2 \end{array}$	20.09 36.63 43.28	23·2 36·8 40·	30·2 36·8 33·	37.75 37.25 25.	$35.6 \\ 37.1 \\ 27.3$	40.83 37.19 21.98	
Melting temperature		1550	1538	1385	1586	1535	1590	



## TABLE XVIII.

Melting temperatures of the binary system 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>-3CaO.5Al<sub>2</sub>O<sub>3</sub>.

	1	Component 2CaO.Al <sub>2</sub> O <sub>3</sub> .S	Eutecti	c	Component 3CaO.5Al <sub>2</sub> O <sub>3</sub>		
Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	40.83 37.19 21.98	$38\\44\\18$	$35 \\ 50.8 \\ 14.2$	$34.3 \\ 52.7 \\ 13$	$24.78 \\ 75.22 \\ 0.0$	
Melting temperature		1590	1583	1552	1570	1720	

## TABLE XIX.

Melting temperatures of the binary system 2CaO.SiO<sub>2</sub>-5CaO.3Al<sub>6</sub>O<sub>3</sub>.

		$\begin{array}{c} Component \\ 2CaO.SiO_2 \end{array}$		Eutectic	$\begin{array}{c} Component \\ 5CaO.3Al_2O_3 \end{array}$	
Composition Wt. per cent	$\begin{array}{c} \text{CaO} \\ \text{Al}_2\text{O}_3 \\ \text{SiO}_2 \end{array}$	65 0*0 35	54·5 32·0 13·5	$51.3 \\ 41.9 \\ 6.8$	$49.3 \\ 47.7 \\ 3.0$	$47.78 \\ 52.22 \\ 0.0$
Melting temperature		2130	1575	1350	1432	1455

TABLE XX.

Melting temperatures of the binary system CaSiO<sub>3</sub>-CaO.Al<sub>2</sub>O<sub>3</sub>.

$\begin{array}{c} { m Component} \\ { m CaSiO_3} \end{array}$					Eutectic					
Composition Wt. per cent	CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	$48.2 \\ 0.0 \\ 51.8$	48.0 2.0 50.0	$47.0 \\ 6.3 \\ 46.7$	46·3 10· 43·7	45·7 13·2 41·1	44·3 20 <sup>,</sup> 35·7	43·0 26·2 30·8		
Melting temperature		1540	1522	1472	1405	1316	1477	1549		

TABLE XX (C	Continue	d)
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C 2CaC	Compound D.Al <sub>2</sub> O <sub>3</sub> .Si	Eutectic	Component CaO.Al <sub>2</sub> O <sub>3</sub>		
 41	40 83	39.2	37.8	36.7	35.44
36	37.19	$46 \cdot$	52.9	58.1	64.56
23	21.98	14.8	9.3	5.2	0.0
1586	1590	1572	$1512^{-1}$	1549	1600



AM. JOUR. Sci.—Fourth Series, Vol. XXXIX, No. 229.—January, 1915. 4

## 50 Rankin and Wright-Ternary System CaO-Al, O.-SiO.

(b) The straight line lies partially within the fields of the two compounds whose compositions it connects.—For example consider the line joining  $CAS_2$  (CaO.Al<sub>2</sub>O<sub>2</sub>.2SiO<sub>2</sub>) and AS (Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>) in fig. 12. This line does not cross the boundary (1-9) between  $CAS_2$  and AS, so that there is no composition in which  $CAS_2$  and AS are in equilibrium with their own solution; that is, the melting curves  $CAS_2-U$  for  $CAS_2$  and AS-U' for AS do not meet. These melting curves are separated by the line U-U' which crosses the A field and is the melting curve of Al<sub>2</sub>O<sub>3</sub> in solutions of AS and  $CAS_2$ ; in other words, neither  $CAS_2$  nor AS are stable in solutions of the

Ca2 Al2 O7 + Melt CaAl204 + Mel 1600 1600 1500 1500 Melt Ca2 Al2 Si 07 1400 CaSiO<sub>2</sub> 1400 Ca2 A12 SiO7 + Ca A1204 1300 1300 CaSiO3+Ca2Al2SiO7 2 Ca0. Al203. Si02 Ca0. Al2 03 Ca0.SiO2

FIG. 16.

FIG. 16. Temperature-concentration diagram of the binary system  $CaO, SiO_2-CaO, Al_2O_3$ .

compositions on the line U-U'. This is, then, the case in which two compounds stable at their respective melting points and whose fields have a common boundary do not form a binary series because the line joining the compositions of these two compounds crosses the field of another compound. We have three examples of this case; the one already given; the composition line for  $C_2S$  and CA which crosses the field for  $C_2AS$ at X-X'; the composition line for  $C_2AS$  and A which crosses the field for  $C_3A_5$  at V-V'. (Fig. 12.)

(c) The composition line in this case connects a stable and an unstable (at the M.P.) compound.—An example is the line connecting the stable compound  $C_sAS$  and the compound  $C_sS_s$ unstable at the melting point. As is to be expected the stable compound  $C_sAS$  has a melting curve  $C_sAS-Y$  but the unstable compound  $C_sS_s$  has no melting curve, for the composition line does not cross its field of stability. The composition line does however cross the field for  $C_sS$  and the line  $C_sS_s-Y$  is the melting curve of  $C_sS$  in solutions of  $C_sS_s$  and  $C_sAS$ . There is one other example of this case; the composition line for the stable compound  $C_sS$  and the unstable compound  $C_sA$ , which line crosses the fields for  $C_sS$  and  $C_s$ .

## Rankin and Wright—Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 51

(d) The composition line for the compounds  $C_3S$  and  $C_3A$ , both of which are unstable at the melting point, lies entirely within the field for C.—This line, then, is the melting curve of C in solutions of  $C_3S$  and  $C_3A$ .

## CRYSTALLIZATION IN TERNARY SYSTEMS.

The results of this investigation, thus far, have been plotted graphically in diagrams to show the equilibria between the various phases of this system of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. To the end that these data be utilized in practical work it is desirable to know what is the composition of the solid phases which separate when a ternary solution is cooled. The systematic elaboration of the theory of phase separation has been carried out in a paper by W. C. Geer, entitled "Crystallization in Three-Component Systems."\* Instead of giving merely the reference to this important work, it has seemed desirable to present again in some detail his deductions on crystallization in three-component systems as it is a very concise statement of the theory involved; for we believe that crystallization of ternary solutions is not a matter of general knowledge even amongst those most concerned and the theory is of vital importance to an understanding of the behavior of ternary systems. Where Geer has used hypothetical compounds and conditions we have substituted actual data on which to base the deductions. Otherwise the matter presented is in substance identical with Geer's paper, except for a few minor changes in arrangement and in the wording of certain explanations.

For the discussion of the theory of crystallization as applied to solutions made up only of the components CaO,  $Al_2O_3$  and SiO<sub>2</sub>, we will use fig. 17. Within this diagram the same numbers and letters are used for the designation of quintuple and quadruple points as in the previous equilibrium diagrams.

The experimental data represented by this diagram are such that all the possible theoretical types of ternary crystallization discussed by Geer are found therein. Solid solution we shall leave out of account, since it occurs only in the case of CaO.SiO<sub>2</sub> and then only to the extent of 2 per cent with each of the compounds with which it is associated, namely: SiO<sub>2</sub>,  $3CaO.2SiO_2$ , CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>, and 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>.

In taking up this discussion we will consider first the simplest type of crystallization, which at the same time is that most commonly observed in solutions of CaO.  $Al_2O_3$  and  $SiO_2$ . For this purpose it will be convenient to consider that portion of fig. 17 which is included within the triangle formed by the

\*W. C. Geer, J. Phys. Chem., viii, p. 257, 1904.

# 52 Rankin and Wright-Ternary System CaO-Al2O3-SiO2.

lines connecting the compositions of  $S(\text{SiO}_2)$ ,  $CS(\text{CaO.SiO}_2)$ and  $CAS_2$  (CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>) as a separate and distinct ternary system. This provides us with a ternary system in which the three components unite to form no compounds either binary



FIG. 17. Equilibrium diagram to show the course of crystallization when ternary solutions of CaO,  $Al_2O_3$ ,  $SiO_2$  are cooled.

or ternary. From fig. 17 it is obvious that the lines S-CS,  $S-CAS_2$  and  $CS-CAS_2$  represent the three binary systems, A, L, and M representing the eutectics of the respective binary systems, and that point 2 is the quintuple point.

"From the deductions of Alkemade, it is known that the temperatures fall along the sides of the triangle toward the binary eutectics and, so far as this diagram is concerned, toward the ternary eutectic."\* The direction of falling temperature is indicated in the diagram by arrows; fig. 17 is, of course, a projection of the solid model on the horizontal plane.

When a saturated solution, whose composition is represented by any point within triangle  $S-CS-CAS_{3}$  is cooled and a solid crystallizes, the concentration of the solution changes by the amount of the separated phase. In other words, the difference between the number of kilograms of S, CS and  $CAS_{2}$  in the original solution and the number of kilograms of S, CS, and CAS in the residual solution is the number of kilograms of solid crystallized. Now if one starts with any solution and cools, the composition of the residual solution after partial crystallization lies on a straight line which passes through the point giving the composition of the solid separating and the point giving the composition of the initial solution. Such a change of concentration along a straight line through the initial solution and the solid crystallized constitutes the fundamental principle of phase separations. Thus in fig. 17, on cooling a solution which has a composition represented by the point d, on the side of the triangle CS-S, the component S will crystallize, while the solution itself will change concentration in the opposite direction along the line CS-S, and at some temperature, lower than that of the original solution, there exists, in equilibrium with S, a new solution e.

By means of the diagram one can compute the amount of Swhich has separated from the solution and also the amount of S retained in the solution e. The ratio of the line de to the line Se is the percentage of the total composition of the solution dwhich has separated as S in cooling from d to e. The ratio of Sd to Se is the percentage of the total composition corresponding to d which remains in the solution e. For example, let the composition of d be 80 kilograms of S and 20 kilograms of CS, and that of e be 70 per cent S and 30 per cent CS. The number of kilograms that have separated is found by the ratio

$$\frac{de}{Se} \times 100 = \frac{10}{30} \times 100 = 331/3$$
 per cent.

Thus 33 1/3 kilograms have separated as S, and 66 2/3 kilograms of S and CS remain in solution at e. The solution d contains 80 kilograms of S. 80-331/3=46.6 kg. of S remain

\* Geer, ibid., p. 259.

† It is, of course, understood that the process of cooling is slow enough to secure the continuous attainment of equilibrium.

with the original 20 kilograms of CS. The percentage of S and CS in e may be checked from the figures given. Solution e contains 46.6 kg. S + 20.0 kg. CS = 66.6 kg:

$$\frac{46\cdot 6}{66\cdot 6} \times 100 = 70 \text{ per cent } S.$$

$$\frac{20}{66\cdot 6} \times 100 = 30 \text{ per cent } CS.$$

If the solution e is cooled further, S continues to separate until point A is reached. Since this is the eutectic temperature, pure S and pure CS separate together with no further change in the concentration of the solution.

Within the field A-2-L-S, solutions containing the three components will be in equilibrium with S. If a solution represented, for instance, by a point b is cooled, S will crystallize, while the composition of the residual solution will be indicated by a point on a straight line passing through b and the point giving the composition of the phase separating, viz., S, at the apex of the triangle. If the solution is cooled further, each successive, residual solution will have its composition given by a point on the straight line through b and S, until finally a solution b, will appear whose composition is found on the boundary A-2. The line bb, is, therefore, the locus of the points which give the compositions of the successive solutions which are formed from the original solution b, on cooling, with the separation of S as solid phase.

The amount of S which has crystallized from solution b (a ternary solution) is computed in the manner previously indicated for a binary solution. In cooling from b to  $b_1$ ,  $\frac{bb_1}{Sb_1} \times 100$  per cent of the solution having the composition b has separated as S. So, also,  $\frac{bS}{Sb_1} \times 100$  per cent of the original solution b remains as solution having the composition  $b_1$ . From the phase rule definition of univariant systems the solution  $b_1$  is in equilibrium with S and CS; therefore if the temperature be again lowered a mixture of S and CS must crystallize.

It has been stated that a straight line joining the points representing the composition of a solid phase and that of a solution from which it has separated, will pass through the compositions of the residual solutions. The converse, which is also true, is the form in which the principle was applied by Bancroft<sup>\*</sup> in his method of analysis of solid phases. If a given solution is cooled, a straight line joining the successive

\* J. Phys. Chem., vi, 178, 1902.

## Rankin and Wright—Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 55

compositions of the solution will on extrapolation pass through the point which gives the mean composition of the solid which has separated. In the cases thus far considered this mean composition is none other than that of a pure component. However, when two phases separate together, as the components S and SC along the boundary A-2, the mean composition of the solid which separates on cooling, provided no solid is removed during the process, will be found as a point on the line joining the compositions of the constituent phases. In the cases mentioned this line is the side of the triangle S-CS. Such a line may connect pure components, a component and a compound, or two compounds.

Since the mean composition of the total solid separated at a definite temperature is on the line joining the compositions of its constituent phases and also on the extrapolated portions of the line through the compositions of the original and residual solutions, it follows that it lies at the intersection of these two lines. Thus a line joining b and  $b_2$  (in fig. 17) will extrapolate to  $\beta_2$  on the line S-CS, which gives the mean composition of the solid which has separated on cooling the solution b from the temperature of the isotherm through that point to the temperature of the isotherm passing through  $b_2$ . Similarly, in cooling from b to 2 the mean composition of the solid phase is represented by  $\beta_3$ . When the temperature of the quintuple point 2 is reached, the component  $CAS_2$  appears as a phase in the solid; but from the definition of the same composition, so that no further change of concentration occurs.

At any intermediate temperature the same reasoning is applicable. Consider, for example, a solution of concentration  $b_1$  cooled to  $b_2$ . Since the two solutions lie on the boundary curve, S and CS crystallize together. Extrapolation through  $b_1$  and  $b_2$  to the side of the triangle S-CS gives A, which point shows the mean composition, in terms of S and CS, of the solid which has separated during the cooling from  $b_1$  to  $b_2$ .

The *amount* of solid which has separated between the temperatures of b and  $b_2$  is, as above, given by the ratio

$bb_2$	
$\beta_2 \overline{b}_2$	

The fraction of the original solution b which remains in solution  $b_a$ 

 $rac{eta_{_2}b}{eta_{_2}b_{_2}}$ 

From the fundamental principle of solid separation mentioned as well as from geometrical considerations it is obvious that 56 Rankin and Wright-Ternary System CaO-Al, O\_s-SiO\_s.

$$\frac{bb_2}{\beta_2 b_2} + \frac{\beta_2 b}{\beta_2 b_2} = 1$$

Similarly for any other pairs of temperatures (or compositions) within this region.

"The expression *crustallization curve* will be used to denote the locus of points which represent the compositions of the solutions formed on cooling any given solution from any given temperature to the quintuple point at which it becomes solid. under the assumption that no phase is removed during the cooling."\* The crystallization curve discussed begins with b. is a straight line to b., turns sharply at that point and follows the boundary curve to 2. From any point on the crystallization curve a line drawn through the initial solution will extrapolate to the point which represents the mean composition of the solid phase which has separated up to that time in the process of cooling. Thus the line b, to b extrapolates to S:  $b_2$  to b extrapolates to  $\beta_2$ ; etc. When the point 2 is first reached, the solid phase has the composition  $\beta_3$ . As the solution continues to solidify the gross composition of the solid phase changes from  $\beta_{a}$  to b, reaching b as the last drop of solution disappears.

From this study of the crystallization of solution b certain generalizations may be drawn. (1) The crystallization curve for any solution whose composition lies within a field will proceed along a definite straight line to a boundary curve. (2) The mean composition of solid crystallized or of liquid remaining at any point on a crystallization curve, or the amount of solid crystallized, may be determined geometrically from the equilibrium diagram.

We will now consider the nature of the crystallization curve. up to the boundary curve, for any solution of CaO, Al<sub>2</sub>O<sub>3</sub>, SiO. As we have pointed out, the crystallization curve for any solution follows a straight line until this line intersects a boundary curve, and the origin of this straight line is the point representing the composition of the primary phase of the solution. To show the course of the crystallization curves within each field, straight lines have been drawn which radiate from the point representing the composition of the primary phase for each field; these lines end at the boundaries of each of these fields. Thus within the field,  $SiO_{a}-A-2-1-J$ ,  $SiO_{a}$  is the primary phase and the lines radiating from SiO<sub>2</sub> to the lines A-2, 2-1 and 1-J show the direction of the crystallization curves, up to the boundaries, for all solutions whose compositions lie within this field. Within each field in which the primary phase is a compound stable at its melting point, these

\* Geer, ibid., p. 263.
straight lines actually meet at the point representing the composition of the primary phase; but if the compound is not stable at its melting point these lines do not actually meet at the point which is the composition of the primary phase, but the direction of these lines is obtained with this point as an imaginary origin. Thus  $3\text{CaO.2SiO}_2$  is unstable at its melting point and consequently its composition lies outside of its field; and the direction of the crystallization curve for any solution within the field B-B'-4-6 is obtained by drawing straight lines, from the composition  $3\text{CaO.2SiO}_2$  through this field; as is evident from the diagram, these lines do not meet. In the same way lines have been drawn within the field 16-17-18 of the unstable compound  $3\text{CaO.SiO}_2$ , and within the field D-17-16-15-E of the unstable compound  $3\text{CaO.Al}_2\text{O}_3$ .

It is evident, then, that if any solution of  $CaO, Al_2O_3$ .SiO<sub>2</sub> is cooled its crystallization curve follows a definite straight line to a boundary curve, and the direction of falling temperature along such a line is from the origin (the composition of a compound) toward a boundary as represented in fig. 17; on reaching a boundary, the crystallization curve follows the direction of falling temperature as indicated by the arrows.

The crystallization curve for solution b, it will be remembered, on reaching the boundary followed the boundary, along which two phases crystallize, until the ternary eutectic is reached, when three phases crystallize and the solution solidifies completely. All the ternary solutions of CaO,Al<sub>2</sub>O<sub>3</sub>,SiO<sub>2</sub> whose crystallization curves proceed to a boundary which leads directly to a eutectic will have this type of crystallization curve. The ternary eutectics at which this type of crystallization curve will end are those indicated in the diagram by the numbers 1, 2, 5, 6, 7, 12, 14, 15. It follows, therefore, that the crystallization of any solution whose crystallization curve intersects a boundary curve which with falling temperature (i. e. the direction of the arrows) proceeds to one of these eutectics, will be continuous until the solution solidifies completely.

Certain pairs of solid phases behave as binary systems; if a solution of composition lying precisely on the line joining any of these pairs—e. g., f on the line joining 2CaO Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> and CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>—is cooled, 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> will crystallize and the crystallization curve will proceed to the quadruple point N where the solution will go solid,  $C_2AS$  and  $CAS_2$  crystallizing together. There are nine of these binary eutectics, L, M, N, O, P, Q, R, S, and T, included within the ternary system. All crystallization curves which intersect a boundary at one of these points will end at that point.

In the ternary crystallization curves so far considered, crys-

tallization has been continuous from the beginning to the end of the curve which has been a eutectic point where three solid phases crystallize together; on such crystallization curves the composition of the liquid phase at any instant can be made up of the three solid phases which crystallize together at the eutectic. In other words, such a crystallization curve lies entirely within the triangle formed by joining the compositions of the three solid phases present at the quintuple point (eutectic), for the reason that the area within this triangle represents all possible concentrations of these three solid phases. Thus the crystallization curve of solution b begins, of course, at band ends at eutectic 2; its course is entirely within the triangle  $S-CS-CAS_2$ , which represents all possible concentrations of these three components. Therefore all points on it represent solutions of S, CS and  $CAS_2$ .

We now come to the consideration of crystallization curves which lie partially without the triangle formed by the lines joining the compositions of the three solid phases present at the quintuple point (which in such cases is not a eutectic) which is the end of the crystallization curves. For example, consider solution a within the triangle CAS - AS - A (fig. 17). The crystallization curve starts at a and is a straight line to  $a_{i}$ , thence follows the boundary P 9 to point 9, where it ends. From a to a, A crystallizes and from a, to 9 CAS crystallizes The composition of the solution is given by points with A. on the crystallization curve  $a-a_1-9$ ; that of the solid crystallizing is obtained by extrapolation of straight lines through aand points on  $a_1-9$  to intersect the composition line  $CAS_2-A$ . The final solid will, of course, have the gross composition of the original solution a if no solid is removed during the course of crystallization. It will be seen that point 9 lies outside of the triangle  $CAS_2$ -AS-A; that is, point 9 which represents the composition of the solution when the crystallization curve reaches 9 is a composition such that it can not be represented in terms of CAS, AS and A. But we know that solution a goes solid at the temperature of 9 and that the three solid phases present are  $CAS_{a}$ , AS and A. Such being the case, the only way this result may be achieved is for some of the Al<sub>2</sub>O<sub>2</sub> which has crystallized to unite with the SiO<sub>2</sub> which is in solution to form  $AS(Al_{0}O_{1},SiO_{2})$ , and this is what actually happens. As soon as the crystallization curve reaches point 9, Al<sub>2</sub>O<sub>3</sub> unites with SiO<sub>2</sub> in solution to form Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>, the CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> continuing to crystallize. This process goes on until either the SiO<sub>2</sub> disappears from solution or Al<sub>2</sub>O<sub>3</sub> from the solid. In the case under discussion (solution a) the SiO, will disappear first and as the solution solidifies at 9, the composition of the solid phase changes from a, to a, reaching a as the last drop of solution disappears.

## Rankin and Wright—Ternary System $CaO-Al_2O_3-SiO_2$ . 59

If, however, we start with a solution a' whose composition lies within the triangle which represents all possible concentrations of S, AS, and  $CAS_2$ , then, when the crystallization curve  $a'-a_1-9$  reaches point 9 the  $Al_2O_3$  will disappear from the solid before all the SiO<sub>2</sub> from solution is used up and the crystallization curve follows the boundary 9–1, AS and  $CAS_2$  crystallizing together. At point 1 the crystallization ends, the solution going solid, AS, S, and  $CAS_2$  crystallizing together, and the gross composition of the solid phase changes again to a'.

There are several portions of the diagram which represent concentrations such that their solutions have this general type of crystallization curve. Thus all solutions represented by points within the area  $C_2AS-11-A-C_3A_5$  have crystallization curves along which crystallization is continuous until quintuple point 11 is reached. Some of these curves will end at that point, others will follow boundary 11-7 and end at eutectic 7. Following the reasoning applied to the crystallization curve for solutions a and  $a_1$ , it is evident that solutions within triangle  $C_2AS-A-C_3A_5$  have crystallization curves which end at quintuple point 11, and that those solutions within triangle  $C_2AS-11-A$  will pass through point 11, where  $C_3A_5$  completely disappears and continue along boundary 11-7 to point 7, where the crystallization curve ends, A,  $C_2AS$  and  $CAS_2$  crystallizing together.

In the same way it can be shown that crystallization curves for all solutions within the area  $C_2 S - C_2 A S - C A - 14$  will proceed first to quadruple point 13. For those solutions within triangle  $C_2 S - C_2 A S - C A$  crystallization curves will end at 13 and for those within triangle  $C_2 S - C A - 14$  crystallization curves will pass through point 13 and end at eutectic 14.

In all of the crystallization curves so far studied two phases have crystallized together at all points on the boundary curves; in other words, the composition of the solid phase present on a boundary curve could be represented in terms of the two solid phases separating. This has been so because the line joining any two points on a boundary curve on extrapolation has intersected the straight line joining the compositions of the two phases separating. There are cases, however, in which such a line on extrapolation will not intersect the composition line of the two phases separating but will intersect an extension of this composition line.

For example, consider solution r whose composition lies within the triangle  $CS-C_sS_2-C_2AS$ .  $C_2S$  separates until the crystallization curve reaches the boundary curve B'-4 at  $r_1$ , fig. 18 (fig. 18 is an enlarged portion of fig. 17). From the latter point the boundary curve is followed to 4, along which the solid consists of  $C_2S$  and  $C_sS_2$ . As the solution changes composition along the boundary curve B'-4 from  $r_1$  to 4, it is seen from the figure that the mean composition of the total solid separated changes from  $C_2S$  to  $\sigma$ . The mean composition of that portion of the solid which has separated during the cooling from  $r_1$  to 4 is found by extrapolation of the line joining  $r_1$  and 4 and is B'. However, B' lies outside of the line joining the



FIG. 18. An enlarged portion of fig. 17 to illustrate the phenomenon of resorption.

phases which separate, viz.:  $C_2S$ ,  $C_3S_2$ . Thus by no possible combination of  $C_2S$  and  $C_3S_2$  can a mixture be made which has a concentration B'. Therefore,  $C_2S$  and  $C_3S_2$  can not both have separated during the cooling from r, to 4, but in reality  $C_3S_2$  has been separating alone, while  $C_2S$  has been disappearing. If more  $C_2S$  disappears from the solid than unites with the CS in solution to form  $C_3S_2$ , then  $C_2S$  must in reality be dissolving. From the solution r, then,  $C_2S$  will crystallize until the crystallization curve intercepts the boundary B'-4 at  $r_1$ . From  $r_1$  to 4,  $C_2S$  will, wholly or in part, disappear and  $C_3S_2$ will crystallize. On reaching 4 the concentration of the solid is  $\sigma$ . The temperature will now remain constant while  $C_2AS$ crystallizes with  $C_3S_2$ ; the solid  $C_2S$  is used up in forming  $C_3S_2$ before the CS in solution disappears, since the concentration of CS in the solution is high. Consequently crystallization will proceed along boundary 4-6,  $C_2AS$  and  $C_3S_2$  separating. At 6, CS will crystallize with the  $C_2AS$  and  $C_3S_2$  and the crystallization curve ends at that point.

In the case just discussed a phase which had crystallized partially disappeared as the crystallization proceeded along a boundary curve. There are types of solutions in which a phase which has crystallized will entirely disappear as the crystallization curve follows a boundary curve. Such a solution is that represented by point t (fig. 18) within the triangle  $CS-C_{-}S_{-}$ CAS. Since solution t lies within the field for  $C_{o}S$ ,  $C_{o}S$  will be the first solid to appear as the solution is cooled. As in the former cases the composition of the solution changes along a straight line and intercepts the boundary B'-4 at  $t_1$ . This solution is saturated with respect to both  $C_{a}S$  and  $C_{a}S_{a}$  and hence when the temperature corresponding to  $t_{a}$  is reached, the solid consists of both  $C_sS$  and  $C_sS_s$ , and its mean composition is  $a_s$ . On continued cooling a point  $t_s$  is reached at which the composition of the solid is that of the compound  $C_s S_s$ . During the cooling of the solution t through the points  $t_1, t_2, t_3$ , extrapola-tion to the line joining the compositions of the pure phases separating, shows that the percentage of  $C_2S$  in the crystal mass has been steadily decreasing. Since the solid phase which originally consisted of pure  $C_2S$  changes continuously to that called for by the composition of the compound  $C_s S_s$ , while  $C_s S_s$  and  $C_s S$  separate together, it must follow that this change means that pure  $C_{o}S$  disappears faster than it crystallizes; in other words, the compound  $C_sS$ , which has separated in cooling along the curve from t to  $t_i$ , has disappeared in cooling from  $t_1$  to  $t_2$ , while the compound  $C_2S_2$  has crystallized. With the solution  $t_{\rm o}$ , then, there exists in equilibrium only the compound  $C_{3}S_{2}$ .

When the solution  $t_s$  is cooled again there seems to be one of two courses for the crystallization curve. It might follow the boundary curve, as in the preceding cases, to the quintuple point 4; in which case the mean composition of the solid in equilibrium with the solution would be given by points along  $C_2S-CS$ , but on the side of  $C_3S_2$  away from  $C_2S$ . Such a course, however, is impossible, because there is no mixture of  $C_2S$  and  $C_3S_2$  which, by any possible combination, can be made to contain an amount of  $C_2S$  less than that required for the composition of  $C_3S_2$ . Therefore, the crystallization curve cannot follow the boundary curve B'-4 to the quintuple point 4. That this conclusion is the correct one is evident also from a consideration of the following facts : since  $C_2S$  disappears during the cooling from  $t_1$  to  $t_3$ , and since there is no more  $C_2S$  to so change and since  $C_3S_2$  is stable at the temperatures in question, the crystallization curve cannot follow the boundary beyond  $t_3$ . Consequently, on further cooling the crystallization curve takes the only other possible course.  $C_3S_2$  continues to separate, the crystallization curve leaves the boundary, crosses the field B'-B-4-6, wherein  $C_3S_2$  is the solid phase, and intercepts the boundary B-6 at  $t_4$ . In accordance with the principles of equilibrium, the solution  $t_4$  is saturated with respect to CS as well as to  $C_3S_2$ . Hence, on cooling the solution, the crystallization curve passes along the boundary B-6, with separation of CS and  $C_3S_2$ . The mean composition of the solid at  $t_4$  is  $C_3S_2$ , and at 6, which is the end of the curve, it is  $a_4$ .

Thus in the course of the cooling of solution t there have appeared consecutively pure  $C_2S$ ;  $\tilde{C}_2S$  and  $C_3S_2$ ; pure  $C_3S_2$ ;  $C_3S_2$  and CS, and finally  $C_3S_2$ , CS and  $C_2AS$ . It is seen, therefore, that whenever there exists a ternary system which contains a compound unstable at its melting point (in this case  $C_sS_s$ ), solutions can be found in which crystallization curves do not follow the first boundary curve intercepted to its quintuple point, but which may pass into the field for the compound and follow some other boundary to another quintuple point. From a consideration of fig. 18 it is evident that the crystallization curve can leave the boundary only when there is reached some point from which the line drawn through the point giving the composition of the original solution, passes also through the composition of the compound in question. Solutions for which this condition holds lie within a limited field. By an inspection of fig. 18 one observes that such solutions involving  $C_s S_s$ are possible only within the limits of the triangle  $C_3S_3-B'-4$ . These considerations obviously apply equally well to binary and ternary compounds.

In the study of the crystallization curves which proceed to a boundary along which one solid phase wholly or partially disappears, we have considered the case in which the boundary curve separating the field of a compound stable at its melting point from that of a compound unstable at its melting point is a straight line. The same theory is also applicable when the boundary is a curved line and holds whether the boundary separates the fields for compounds stable or unstable at their respective melting points.

For the study of curved boundary lines of this class consider the boundary curve 9-I (fig. 17). The boundary curve 9-I separates the fields of A and AS, each of which is stable at its melting point. If then a solution of the composition U on the boundary 9-I is cooled, A and AS will separate and the crystallization curve will follow the boundary I-9. The composition of the solution will be given by points on I-9, that of the solid by a series of points on the line A-AS, the position of each of which is determined by extrapolation of a line through U and points on I-9 to intercept the composition line A-AS. Further, the mean composition of the solid which has separated between any two points, such as U and V, is determined by extrapolation of a line through U and V to the composition line A-AS. If now the points U and V be made to approach each other along the curve 9-I then the line extrapolated through U and V approaches the position of a tangent, and finally becomes tangent to the boundary curve; hence at any point the tangent will intercept the line joining the two phases and thus give the mean composition of the solid which separates at that point. It will be seen from the diagram that all tangents to the boundary 9-I at points between V and U will intercept the composition line A-AS, but that all tangents to 9-I between 9 and V will intercept an extension of the composition line A-AS away from A. It follows, therefore, that on the boundary 9-I, A and AS will separate together from U to V, but that from V to 9, A will wholly or partially disappear while AS crystallizes. The boundary curve 9-I is of that type along which two solid phases separate together over a part of the curve and one solid phase disappears while the other crystallizes over another part of the curve. The changes which take place along the boundary 9-I from V to 9 are essentially the same as those along boundary B'-4, except that in the case of boundary 9-I the mean composition of the solid phase which separates will vary, while for boundary B'-4 the mean composition of the solid phase which separates at any point is constant (the composition of B') because a tangent to any point on B'-4, which is a straight line, is that line itself.

There are three other boundary curves similar to the boundaries B'-4 and 9-I, namely, D-17, 18–17 and 18–16. Along at least a part of each of these three one solid disappears while the other crystallizes. Along the boundary D-17, CaO wholly or partially disappears while  $3\text{CaO.Al}_2\text{O}_3$  separates during the course of any crystallization curve which follows this boundary. Along the boundary 18–17, from 18 to Y, CaO wholly or partially disappears while  $3\text{CaO.SiO}_2$  crystallizes and from Y to 17 CaO and  $3\text{CaO.SiO}_2$  separate together. Along the boundary 18–16 from 18 to Z 2CaO.SiO<sub>2</sub> and  $3\text{CaO.SiO}_2$  separate together while from Z to 16 2CaO.SiO<sub>2</sub> disappears while  $3\text{CaO.SiO}_2$  disappears while  $3\text{CaO.SiO}_2$  disappears.

There are, therefore, five boundary curves of this type, B'-4, 9-1, D-16, 18-17 and 18-16, along each of which crystallization curves of the several different types described for boundary These different types of crystallization B'-4 will proceed. curves are: (1) a crystallization curve which, proceeding to a boundary curve along which one solid phase partially disappears while the other crystallizes ends at the quintuple point for that boundary; (2) a crystallization curve which proceeds in the same manner as (1) to a quintuple point, but at that point one solid phase entirely disappears and the crystallization curve proceeds along a boundary to another quintuple point; (3) a crystallization curve which proceeds to a boundary along which one solid phase wholly disappears before a quintuple point is reached, wherefore it leaves the boundary and crosses a field to another boundary curve along which it proceeds to a quintuple point.

Which one of these three types of crystallization curves any given solution when cooled will follow depends, as has been shown, on the original composition of the solution. We will give here merely the areas (fig. 17) which represent the compositions of solutions for each of these types of crystallization curve and the particular solid phases in order as they appear or disappear from a cooling solution.

(1) There are 4 areas which represent the compositions of solutions which on cooling have crystallization curves of type (1). (a) Triangle  $C_sS_2-C_2AS-C_4S$ ; from solutions whose crystallization curves intersect boundary B'-4 there will appear consecutively pure  $C_2S$ ;  $C_2S$  and  $C_3S_2$  together; and finally  $C_4S$ ,  $C_sS_2$  and  $C_2AS$ . (b) Triangle  $CAS_2-AS-A$ ; from solutions whose crystallization curves intersect boundary 9-I there will appear consecutively pure A; A and AS; and finally A, AS and  $CAS_2$ . (c) Triangle  $C_2S-Z-18$  in which there will appear consecutively  $C_2S$ ;  $C_2S$  and  $C_3S_3$ ; and finally  $C_2S$ ,  $C_3S_3$  and  $C_3A$ . (d) Triangle  $CaO-X-C_3A$ ; from those solutions whose curve intersects boundary 18-17 there will appear consecutively: CaO; CaO and  $C_3S$  and finally CaO,  $C_2S$  and  $C_3A$  and from those which intersect boundary 17-D, CaO; CaO and  $C_3A$  and finally CaO,  $C_2A$  and finally CaO,  $C_3A$  and finally CaO,  $C_3A$  and finally CaO,  $C_3A$  and  $C_3A$ .

(2) There are 8 areas which represent the compositions of solutions which exhibit crystallization curves of type (2). (a) Triangle  $C_sS_2-C_2AS-4$ ; from those solutions whose crystallization curves intersect boundary B'-4 there will appear consecutively: pure  $C_2S$ ;  $C_2S$  and  $C_3S_2$ ;  $C_2S$ ,  $C_3S_2$  and  $C_2AS$ ;  $C_3S_2$  and  $C_2AS$ ;  $C_3S_2$  and  $C_2AS$ ;  $C_4S$  and finally  $C_3S_2$ ;  $C_2AS$  and CS. (b) In triangle  $CAS_2-9-AS$  from those solutions whose crystallization curves intersect boundary 9-I there will appear consecutively: pure A; A and AS; A, AS and  $CAS_2$ ;  $CAS_2$  and AS; and finally

## Rankin and Wright-Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 65

 $CAS_2$ , AS and S. (c) Triangle  $C-C_2S-18$ ; there will appear consecutively: pure  $C_2S$ ;  $C_2S$  and CaO;  $C_2S$ , CaO and  $C_3S$ ;  $C_2S$  and  $C_3S$  and finally  $C_2S$ ,  $C_3S$  and  $C_3A$ . (d) Triangle  $C_3S-18-C$ ; there will appear consecutively: pure CaO; CaO and  $C_2S$ ;  $C_2S$ , CaO and  $C_3S$ ;  $C_2S$  and  $C_3S$ ; and finally  $C_2S$ ,  $C_3S$ and  $C_3A$ . (e) Triangle CaO- $X-C_3S$ ; there will appear consecutively: pure CaO; CaO and  $C_2S$ ; CaO,  $C_2S$  and  $C_3S$ ; CaO and  $C_3S$ ; and finally CaO,  $C_3S$  and  $C_2A$ . (f) Triangle  $C_3S-Z-16$ ; there will appear consecutively:  $C_2S$ ;  $C_2S$  and  $C_3S$ ;  $C_2S$ ,  $C_3S$  and  $C_3A$ ;  $C_2S$  and  $C_3A$ ; and finally  $C_2S$ ,  $C_3A$ and  $C_5A_3$ . (g) Area  $C_3S-C_3A-Y$ ; there will appear consecutively: pure CaO; CaO and  $C_3S$ ; CaO,  $C_3S$  and  $C_3A$ ;  $C_3S$  and  $C_3A$ ; and finally  $C_3S$ ,  $C_3A$  and  $C_3A$ ;  $C_3O$  and  $C_3A$ ;  $C_3O$  and  $C_3A$ ;  $C_3C$  and  $C_3A$ ;  $C_3S$  or CaO and  $C_3A$ ; CaO,  $C_3S$  and  $C_3A$ ;  $C_3S$  and  $C_3A$ ;  $C_3S$  or CaO and  $C_3A$ ; CaO,  $C_3S$  and  $C_3A$ ;  $C_3S$  and  $C_3A$ ;  $C_3S$  or CaO and  $C_3A$ ; CaO,  $C_3S$  and  $C_3A$ ;  $C_3S$  and  $C_3A$ ;  $C_3S$ ,  $C_3A$  and  $C_2S$ ;  $C_2S$  and  $C_3A$ ; and finally  $C_3A$ ,  $C_2S$  and  $C_3A_3$ .

(3) There are four areas which represent the compositions of solutions which have crystallization curves of type (3). (a) Triangle  $C_3S_2$ -4-B'; there will appear consecutively: pure  $C_2S$ ;  $C_2S$  and  $C_2S_2$ ; pure  $C_3S_2$ ;  $C_4S_2$  and CS; and finally  $C_3S_2$ , CS and  $C_2AS$ . (b) Area 9-U-V; there will appear consecutively: pure A; A and AS; pure AS; AS and  $CAS_2$  and finally AS,  $CAS_2$  and S. (c) Triangle  $C_3S$ -18-Y; if the crystallization curve intercepts the boundary between 18 and C, there will appear consecutively: CaO; CaO and  $C_2S$ ; CaO,  $C_3S$  and  $C_3A$ ; or if solutions intercept boundary between 18-Y, there will appear : pure CaO; CaO and  $C_3S$ , pure  $C_3S$ ;  $C_3S$  and  $C_2S$ ; and finally  $C_3S$ ,  $C_2S$  and  $C_2A$ ; or if solutions intercept boundary between 18-Y, there will appear consecutively: pure CaO; CaO and  $C_3S$ , pure  $C_3A$ . (d) Area  $C_3A$ -17-D; there will appear consecutively: pure CaO; CaO and  $C_3A$ , if and finally  $C_3A$ ,  $C_3S$  and  $C_2A_3$ .

General Conclusions as to the Nature of Crystallization in Ternary Solutions of  $CaO-Al_2O_3-SiO_3$ .—The nature of the crystallization of a ternary solution depends upon the original composition of the solution and the class of boundary curve which the crystallization curve intersects. There are two general classes of boundary curves :

1. Boundary curves along which two phases crystallize together. A tangent drawn at any point on a boundary curve of this class will intersect the line joining the compositions of each of the two phases. This class is illustrated by all those boundary curves of which one end is a eutectic point. For example, in fig. 17, boundaries A-2, J-1, M-5, 11-7, 16-15, 13-14, F-14, etc.

2. Boundary curves along which one phase crystallizes while AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 229.—JANUARY, 1915.

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the other partially or wholly disappears. A tangent drawn at any point on a boundary curve of this class will intersect a prolongation of the line joining the compositions of each of the two phases. This class is illustrated by the boundaries 9-V, B'-4, Z-16, 18-Z, and D-17.

Knowing, then, the original composition of a ternary solution and the class of boundary curve to which crystallization proceeds on cooling the solution, one can ascertain from a study of the equilibrium diagram precisely which phases separate, their order of crystallization and the final product of crystallization.

The final product of crystallization of ternary solutions of CaO,  $Al_2O_3$  and SiO<sub>2</sub> always consists of three solid phases whose fields of stability are adjacent. The same three solid phases will be the final product of crystallization from any solution whose composition lies within the triangle formed by lines joining the compositions of these three phases.

A recognition of the above facts is of considerable importance in the study of ternary systems. If one is locating the boundary curve and quintuple point temperatures by the discontinuities in, say, a time curve of cooling, it is quite necessary to know the cause of each break (energy change). Ordinarily one starts with an unsaturated solution, so that the first break is at the freezing-point of the first phase; the second break occurs at the intersection of the boundary curve, and the third break, in such a case, is at the quintuple point. Solutions of silicate mixtures, however, undercool to such an extent that a time curve of cooling is valueless; hence for experimental work of this nature, the time curve of heating is used, in the course of which the solid phases melt in the reverse order of crystallization. Even with heating curves, however, the breaks obtained for the melting of certain silicates are not sharp; in such cases the quenching method, with which one is able to determine the optical properties of a phase and its temperature of melting, is more suitable.

With this quenching method we have made actual observations from which one can deduce what would take place under the ideal conditions for crystallization of cooling solutions of CaO,  $Al_sO_s$  and SiO<sub>2</sub>. The results thus obtained, which give the phases present and their temperature range of stability for certain solutions, illustrate all types of crystallization curves described; they are presented in Tables XXI-XXIV.

The data in Table XX1 illustrate that type of crystallization curve which follows a boundary directly to a entectic. Thus in the solution of the composition CaO 38, Al<sub>2</sub>O<sub>3</sub> 51.5, SiO<sub>2</sub> 10.5, 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> starts to crystallize at a temperature between 1540° and 1520°; at a temperature of 1515° the

## Rankin and Wright-Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 67

crystallization curve has reached the boundary curve 13–12 (fig. 17) along which  $2CaO.Al_2O_3.SiO_2$  and  $CaO.Al_2O_3$  crystallize together; until at a temperature of 1505° the eutectic 12 is reached, when  $2CaO.Al_2O_3.SiO_2$ ,  $CaO.Al_2O_3$  and  $3CaO.5Al_2O_3$  separate together.

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Examples of crystal phases present during the course of a crystallization curve of the simplest type for a ternary system.

Composition weight percentage CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>			Temp.	Phases Present
38	51.5	10.5	1540	Glass
			1520	$Glass + 2CaO.Al_{0}O_{0}.SiO_{0}$
			1515	$Glass + 2CaO.Al_OSiO_+CaO.Al_O$
			1505	$Glass + 2CaO.Al_OSiO_ + CaO.Al_O +$
				3CaO.5Al <sub>2</sub> O <sub>3</sub>
52	38	10	1470	Glass
			1450	$Glass + Ca_SiO_i$
			1410	$Glass + Ca_SiO_i$
			1340	$Glass + Ca_SiO_+ 5CaO_3Al_O_$
			1330	$Ca_{3}^{2}SiO_{4}^{2} + 5CaO.3Al_{2}O_{3}^{2} + CaO.Al_{2}O_{3}$
52.5	42.5	5	1405	Glass
			1380	$Glass + 3CaO.Al_{2}O_{2}$
			1350	$Glass + 3CaO.Al_{a}O_{a} + 5CaO.3Al_{a}O_{a}$
			1325	3CaO.Al <sub>a</sub> O <sub>a</sub> + 5CaO.3Al <sub>a</sub> O <sub>a</sub> + Ca <sub>a</sub> SiO <sub>a</sub>

The data in Table XXII illustrate that type of crystallization which follows a boundary to a quintuple point not a eutectic. So far as the data show, this type of curve is the same as that given in Table XXI; the only difference is that when the temperature  $1380^{\circ}\pm 5^{\circ}$  of the quintuple point (13) is reached, the compound  $2\text{CaO.Al}_2\text{O}_3.\text{SiO}_2$  partially disappears while  $2\text{CaO.SiO}_4$  crystallizes.

TABLE XXII.

Examples of crystal phases present during the course of a crystallization curve which ends at a quintuple point not a eutectic.

CaO CaO	omposit ht—per Al <sub>2</sub> O <sub>3</sub>	tion centage SiO <sub>2</sub>	Temp.	Phases Present
45	43.5	11.2	$     \begin{array}{r}       1490 \\       1450 \\       1385 \\       1375     \end{array} $	$\begin{array}{l} Glass+2CaO.Al_2O_3.SiO_2\\ Glass+2CaO.Al_2O_3.SiO_2+CaO.Al_2O_3\\ Glass+2CaO.Al_2O_3.SiO_2+CaO.Al_2O_3+Ca_2SiO_4\\ 2CaO.Al_2O_3.SiO_2+CaO.Al_2O_3+Ca_2SiO_4\\ \end{array}$
47.5	37.5	15	$1500 \\ 1475 \\ 1400 \\ 1350$	$\begin{array}{l} Glass+2CaO.Al_2O_3.SiO_2\\ Glass+2CaO.Al_2O_3.SiO_2+Ca_2SiO_4\\ Glass+2CaO.Al_2O_3.SiO_2+Ca_2SiO_4\\ 2CaO.Al_2O_3.SiO_2+Ca_2SiO_4+CaO.Al_2O_3\end{array}$

## 68 Rankin and Wright-Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>3</sub>.

The data in Table XXIII illustrate that type of crystallization curve in which a solid phase wholly disappears at a quintuple point. Thus for a solution of the composition CaO 48.5,  $Al_2O_3$  12,  $SiO_2$  39.5 at a temperature of 1340° the crystallization curve has reached the boundary curve S-4, 2CaO.SiO<sub>2</sub> and 2CaO.Al\_2O\_3.SiO\_2 crystallizing together; at 1330° it has passed through quintuple point 4 and proceeded along boundary 4-6, 2CaO.Al\_2O\_3.SiO\_2 and 3CaO.2SiO\_2 separating together; at 1310° it has reached eutectic point 6 and the solution has solidified to CaO.SiO\_3, 3CaO.2SiO\_4 and 2CaO.Al\_2O\_5.SiO\_5.

#### TABLE XXIII.

Examples of crystal phases present during the course of a crystallization curve which passes through a quintuple point and ends at a eutectic.

Composition weight percentage CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>			Temp.	Present
48.5	12	39.5	1340	$Glass + 2CaO. Al_{0}O_{\bullet}.SiO_{0} + 2CaO.SiO_{0}$
			1330	$Glass + 2CaO.Al_{0}O_{2}.SiO_{1} + 3CaO.2SiO_{1}$
			1310	$CaO.SiO_{a} + 2CaO.Al_{a}O_{a}.SiO_{a} +$
				3CaO.2SiO
60	32.5	7.5	1480	Glass + CaO
			1460	$Glass + 3CaO.Al_{a}O_{a} + 3CaO.SiO_{a}$
			1440	$Glass + 3CaO.Al_2O_3 + Ca_2SiO_4$
59	32.5	8.5	1470	Glass + 3CaO SiO
			1455	$Glass + 3CaO.SiO_{a}^{2} + 3CaO.Al_{a}O_{a} + Ca_{a}SiO_{a}$
			1440	$Glass + 3CaO Al_2O_3 + Ca_2SiO_4^{2}$

The data in Table XXIV illustrate that type of crystallization curve in which a solid wholly disappears on a boundary and the curve proceeds across a field to another boundary.

#### TABLE XXIV.

Examples of crystal phases present during the course of a crystallization curve which passes across a field.

Composition weight percentage CaO Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>			Temp.	Phases Present
53	4	43	1420 1415 1410	$Glass + 2CaO.SiO_2$ $Glass + 2CaO.SiO_2 + 3CaO.2SiO_2$ $Glass + 3CaO.2SiO_3$
14	38•5	47.5	$1574 \\ 1570 \\ 1550 \\ 1545$	$\begin{aligned} Glass + Al_{2}O_{3} \\ Glass + Al_{2}O_{3} + Al_{2}SiO_{5} \\ Glass + Al_{2}O_{3} + Al_{2}SiO_{5} \\ Glass + Al_{2}SiO_{5} \end{aligned}$
63	25	12	$1610 \\ 1500 \\ 1475 \\ 1425$	$ \begin{array}{l} Glass + CaO + 3CaO.SiO_2 \\ Glass + 3CaO.SiO_2 \\ Glass + 3CaO.SiO_2 + Ca_2SiO_4 \\ Glass + Ca_2SiO_4 + 3CaO.Al_2O_3 \end{array} $

Thus in a solution of the composition CaO 53, Al<sub>2</sub>O<sub>3</sub> 4, SiO<sub>2</sub> 43 at a temperature of 1420°, 2CaO.SiO<sub>2</sub> crystallizes; at 1415° the crystallization curve has reached the boundary B'-4 where 2CaO.SiO<sub>2</sub> disappears and 3CaO.2SiO<sub>2</sub> separates; at 1410° the 2CaO.SiO<sub>2</sub> has all disappeared and the crystallization curve has left the boundary B'-4 and entered the field B'-4-6-B in which pure 3CaO.2SiO<sub>2</sub> separates.

# THE APPLICATION OF EQUILIBRIA WITHIN THE SYSTEM CAO, AL<sub>2</sub>O<sub>3</sub>, SIO<sub>2</sub> TO PROBLEMS INVOLVING THESE THREE OXIDES.

It is not our purpose to discuss, here, all the possible applications of the equilibrium diagram for CaO,  $Al_2O_3$  and  $SiO_2$  to problems involving these three oxides. We merely wish to show how this diagram may be applied, and to consider briefly its application to the study of portland cement clinker and certain geological inquiries.\*

In order to obtain this diagram it has been necessary to determine experimentally the equilibrium conditions for the existence of the components, pure or in mixtures, and of the various compounds. These equilibrium conditions have been presented in diagrams which have shown principally the conditions at the liquidus; in other words, we have shown the conditions under which the solid components and compounds exist in equilibrium with solutions. The diagram (fig. 17) illustrates how these components and compounds crystallize from solutions; that is, it enables us to state the order in which they crystallize, and to specify the final product obtained when the solutions have completely crystallized.

These final products of crystallization of solutions of CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, which are the only essential data required to elucidate most of the problems in which this system is concerned, are given in fig. 19, which, it will be seen, is composed of a large number of triangular areas. Each of these triangles represents all possible mixtures of those three compounds whose compositions are represented by the apices of the triangle. Though three certain, definite compounds can exist together in only *one* triangle, yet, as can be seen in the diagram, any one of these three compounds may be found in a number of different triangles.

In applying the data presented in fig. 19 to any problem involving a part or all of this diagram, it must be remembered that this diagram represents equilibrium conditions, that is, this diagram represents the components and compounds as they would occur together in mixtures if time were allowed for all

\* Each of these applications will be taken up more fully in papers to be published in the near future.

reactions to go to completion. In the problems to which we wish to apply this diagram, we know that the reactions involved are not always completed, that equilibrium conditions are not attained. It does *not* follow, however, that this diagram is



FIG. 19. Diagram to show final products of crystallization of solutions of CaO,  $Al_2O_3$  and  $SiO_2$ .

worthless in its application to such problems. On the contrary, it simply means that this diagram must be studied in order to determine the possible conditions which may exist if equilibrium is not reached. For example, if one possessed a charge of material whose CaO,  $Al_2O_3$ , SiO<sub>2</sub> content approximated that of some point within the diagram fig. 19, one might expect that the compounds of these three oxides present would be, to a large extent, those given in the small triangle in which that point occurred; if, however, other compounds were found one would expect these compounds to be included within adjacent triangles.

Application to Portland Cement Clinker.—It is a wellknown fact that portland cement can be made from the pure oxides CaO,  $Al_2O_3$  and SiO<sub>2</sub>. According to Richardson's data, cement clinker can be made from mixtures of these three oxides whose compositions are represented by points within the area V-X-Z-Y (fig. 19)—an area which lies almost entirely within the triangle  $C_2S-C_3S-C_3A$ . Therefore a cement clinker made from pure CaO,  $Al_2O_3$  and SiO<sub>2</sub>, burned at a high enough temperature for a sufficiently long time, would consist of the three compounds 2CaO.SiO<sub>2</sub>, 3CaO.SiO<sub>2</sub> and 3CaO.Al<sub>2</sub>O<sub>3</sub>. If, however, equilibrium was approached but not reached we would expect to find, in addition to these three compounds, either free CaO or the compound 5CaO.3Al<sub>2</sub>O<sub>3</sub> or both.

Commercial portland cement clinker has a CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> content of over 90 per cent and is manufactured by methods which one would expect to produce a condition approaching equilibrium; so that it would seem possible to predict from fig. 19 what compounds of CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are formed when the raw material for portland cement is burned. From these data we made the prediction that portland cement clinker consists largely of 3CaO.SiO, 2CaO.SiO, 3CaO.Al,O, 5CaO. 3Al<sub>2</sub>O<sub>3</sub>, with, possibly, a small amount of free line, and the subsequent work of the Bureau of Standards at Pittsburg\* has demonstrated the applicability of these criteria to commercial clinkers and has completely borne out this prediction. In making this prediction as to the probable constitution of portland cement clinker we believed (and it subsequently proved to be so) that the components other than CaO.Al<sub>2</sub>O<sub>2</sub> and SiO<sub>2</sub> were practically negligible. We do not mean by this that the other components such as MgO, Fe<sub>2</sub>O<sub>3</sub>, etc., may not be important in cement as cementing material, but that the MgO, Fe<sub>2</sub>O<sub>2</sub>, etc., are present in such small quantities in the raw cement material that it seemed probable that the clinker would consist largely of compounds of pure lime, alumina and silica. It is not, however, permissible to apply directly the data in fig. 19 to problems involving CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> unless one is sure that the other components present are negligible and that equilibrium conditions were substantially attained.

#### Application of the Results to Certain Geological Inquiries.

In applying the results of this investigation to problems involving natural minerals composed substantially of CaO,  $Al_2O_3$ , and SiO<sub>2</sub>, one must proceed with caution because the

<sup>\*</sup>The Constitution of Portland Cement, by P. H. Bates. Concrete-Cement Age (cement mill section), 2, 3.

conditions of natural formation are very different from those under which this system was studied in the laboratory. The main differences are two: (1) That under geologic conditions the reactions take place under high pressure (which moreover is probably not constant or uniform during the process); (2) the complexity of the mineral solution, particularly the presence of volatile ingredients, especially water, at unknown concentration (pressure); both of these factors would exert an influence of unknown magnitude upon the configuration of the various fields of stability, and might well change their number and character.\* For this reason we find in nature minerals made up substantially of CaO, Al<sub>a</sub>O<sub>a</sub>, SiO<sub>a</sub> (e. g. kvanite) which have not been produced in the laboratory; on the other hand, compounds of these oxides which have not been observed hitherto by petrologists may be made synthetically (e. g. CaO, Al<sub>2</sub>O<sub>2</sub>); but from these circumstances we should conclude-presuming that none of this compound does in fact occur in the earthmerely that the compound may have formed and subsequently disappeared, forming compounds more stable under the particular conditions. In any case the first step in a complete investition—which would include the effects of pressure, of presence of water, etc.,---is a thorough study of the relations of the pure components and of the compounds formed under the least complicated experimental conditions.

Some of the possible applications to geologic problems will be treated in a later paper; for the present, we desire merely to emphasize the fact that these very important differences affect the validity of all deductions made from the behavior and mutual relations of the pure, dry oxides at high temperatures and at atmospheric pressure.

The synthetic minerals composed of CaO, Al<sub>2</sub>O<sub>3</sub>,SiO<sub>2</sub> which we have prepared are: quartz, tridymite and cristobalite (SiO<sub>2</sub>): corundum (Al<sub>2</sub>O<sub>3</sub>); wollastonite (CaO.SiO<sub>2</sub>); sillimanite (Al<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub>); anorthite (CaO.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>); all of which have the same compositions and practically the same optical characteristics as the natural minerals. The compound 2CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> has the same optical characteristics but not the same composition as has been assigned to the natural mineral gehlenite, but the analyses of the natural mineral vary within such wide limits that it seems reasonable to suppose that the true composition of natural gehlenite is  $2CaO_2Al_2O_3$ .SiO<sub>2</sub>. The compounds which are synthetic minerals are underlined in fig. 19; from which one sees that there are five triangles in each of which the only compounds present are synthetic minerals, each triangle

\* For a discussion of some of these points see Johnston and Niggli, J. Geology, xxi, 589-99, 1913.

being the region of stability of a group of 3. In the triangles in which SiO<sub>2</sub> occurs, it will be present either as quartz, tridymite or cristobalite, depending on the temperature.

#### Summary.

The foregoing pages are a record of a thorough investigation of the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, an investigation which necessitated some 7000 heat treatments and subsequent optical examinations of the products. This ternary system proved to be complicated, the equilibrium diagram, which represents the stability relations of components and compounds possible at atmospheric pressure, containing no fewer than 14 separate fields. The mapping of the boundaries of the various fields was possible only by application of the phase rule; the result shows that this principle is just as applicable to mixtures of oxides, which are liquid only at high temperatures, as it is to ordinary solutions.

The relations found to subsist between components and the various compounds in each of the three binary systems and in the ternary system are exhibited in a series of temperatureconcentration diagrams. A list of these compounds, with their respective compositions, and optical characteristics, inversion, melting or dissociation points, and of the co-ordinates (temperature and composition) of the various quadruple and quintuple points, is appended. From these data the theory of crystallization curves enables one, as we have shown, to predict which substances will separate out from any slowly cooling solution containing only CaO,  $Al_2O_3$ , and  $SiO_2$ , the order in which they separate, and the corresponding temperatures.

Moreover, although the diagram exhibiting the final products of crystallization presupposes the continuous attainment of equilibrium, yet it is possible to predict with considerable certainty the final product of reaction in mixtures of the three pure oxides, even when the reaction has not proceeded to completion. This occurs with portland cement clinker, which, if made in the ordinary way from the pure oxides, would be essentially a mixture of 3CaO.SiO<sub>2</sub>, 2CaO.SiO<sub>2</sub>, 3CaO.Al<sub>2</sub>O<sub>3</sub>, with some 5CaO3Al<sub>2</sub>O<sub>3</sub>, and, possibly, a small amount of free CaO; a conclusion which has been confirmed by the work of the Bureau of Standards on commercial clinkers.

Remarks	Crystals often show op- tical anomalies.	Crystallizes readily.	Stable below 575°.	Stable between 575° and 870°. Inverts on cool- ing to <i>a</i> -quartz.	Exists below 117°. Usu- ally finely intergrown aggregates.	Exists only above 117°. Inverts on cooling to <i>a</i> -tridymite.	Exists below 140°.	Exists only above 140°. Inverts on cooling to <i>a</i> -tridymite.	Resembles natural min- eral in every respect.	Polysynthetic twinning not uncommon. Ex- tinction angles small.		Obtainable only as fine powder. Plane of optic axes normal to cleav- age direction.
Optic axial angle		uniaxial	uniaxial	uniaxial	large	uniaxial			$2 E = 70^{\circ}$	very small	large	$2 E = 52^{\circ}$
Орtical сharacter		1	+	+	+	+	1		1	+	+	1
~	1.83	1.768	1.553		1.473		1.487		1.631	1.654	1.650	1.654
Ø									1.629	1.611		1.645
a		1.760	1.544		1 • 469		1.484		1.616	1.610	1.641	1.642
Optical orienta- tion		c = a	$c \equiv \gamma$	$c = \gamma$		c ≡ γ	c = a		$b = \beta$ c: a = +32			$\mathbf{b} = \beta$ $\mathbf{c} : \gamma = 3^{\circ} (\mathbf{i})$
Elongat'n			~	×					γ			a X
Rardness	3-4	6	2		6.5				n	20		
Cleavage	perfect (100)								g (100) d (001)			g (001) g (100)
Cryst <b>a</b> l habit	unmodified cubes	thin hexagonal plates	pyramidal	pyramidal	thin pseudohex. plates	hexagonal plates	equaint grains	equaint grains	plates laths	equaint grains	irregular grains	prismatic
Crystal system	isometric	hexagonal	hexagonal trapezohedral tetartohedral	hexagonal trapezohedral hemihedral	orthorhombic	hexagonal	probably tetragonal	isometric	monoclinic	monoclinic (pseudohex- agonal)	probably orthorhombic	probably monoclinic
Composition	CaO	Al <sub>2</sub> O <sub>3</sub> corundum	SiO2 a-quartz	β-quartz	a-tridymite	$\beta$ -tridymite	a-cristobalite	β-cristobalite	$\beta$ -CaO.SiO <sub>2</sub> wollastonite	<i>a</i> -CaO.SiO <sub>2</sub> pseudo- wollastonite	3Ca0.2Si02	$\gamma$ -2CaO.SiO <sub>2</sub>

Optical-crystallographical properties of the compounds.

TABLE.

74

Rankin and Wright-Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. 75

	Remarks	Plane of optic axes	Intricate polysynthetic twinning is character-	istic of this form. Birefringence very weak.	Birefringence very weak Twinning lamellae not uncommon.	Refractive indices slightly lower than in natural mineral.	Occasionally gray inter- ference colors appear as result of strain.	Stable form.	Plane of optic axes parallel with fiber elongation.	Complex twinning is a characteristic feature	Indications of small 2 H	A vial dispersion strong $2V_r > 2V_v$ . Plane of optic axes parallel with fiber elongation.	Polysynthetic twinning characteristic.	Crystallizes readily.		Usually in fine fibrou aggregates. Plane o optic axes parallel to
	Optic axial angle	large	large	small or uniaxial(?)	small or uniaxial	small			large	$2V=36^{\circ}$		$2V=35^{\circ}$	large	uniaxial		large
	Optical character	+-	+	+	1	+			(1)	1	+	1	1	1		+
	~	1.735	1.737	1.715	1.715	1.653	1.710	1.608	1:692	1.663	1.652	1.674	1.589	1.669		1.685
	B		1.730			1.642				1.655		1.671	1.585			
and the second second	a	1.717	1.715			1.638			1.687	1.643	1.617	1.662	1.576	1.658		1.675
	Optical orienta- tion		$c:a'=18^{\circ}$		$c=\gamma$	$b \equiv a$ $c \equiv \gamma$					c=y	-	a:a'  on $001 = -35^{\circ}$	<u>c=a</u>		-
-	a'tsgnolA					~			a		$\left  \right\rangle$	~				×
	asenbrsH	5-6	5-6			2-9	9	5	õ	6.5	6.5	5.5	9	9		
	Cleavage	poor				g (100)	$p_{\rm or}^{(111)}$		p. pris- matic	pris- matic			g (001) g (010)	d (001)		
	Crystal habit	irreg. grains	jrregular	equant gr.	equant grains	fibers prisms	equant grains	equant	grams fibers prisms	irreg. grains fibers	equant	grains fibers prisms	laths	equant	grains	fibers
	Crystal system	orthorhombic	Inonoclinic or		monoclinic (?)	orthorhombic	isometric	isometric	probably orthorhombic	probably monoclinic	tetragonal	probably orthorhombic	triclinic	tetragonal		orthorhombic (?)
and the second s	Composition	$\beta$ -2CaO.SiO <sub>2</sub>	a-2CaO.SiO <sub>a</sub>	$\beta'$ -2CaO.SiO <sub>2</sub>	3CaO.SiO2	Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> sillimanite	3CaO.Al2O3	5CaO.3A12O8	5CaO.3Al2O3 unstable	CaO.Al <sub>2</sub> O <sub>3</sub>	3CaO.5A12O3	stable 3CaO.5Al <sub>2</sub> O <sub>3</sub> unstable	$CaO.Al_2O_3.$ $2SiO_3.$ anorthite	2Ca().Al <sub>2</sub> O <sub>3</sub> .	gehlenite	3CaO.Al <sub>2</sub> O <sub>8</sub> . SiO <sub>2</sub> .

	Weig	ht percei	ntage		
Formula	CaO	$A\hat{l}_2O_2$	SiO <sub>2</sub>	Transformation	Temp.
CaO	100.			Melting	2570°*
Al.O.		100.		"	2050°*
SiO.			100.	66	1625°†
SiO			100.	Tridymite to	1470°+
2				cristobalite	,
				and reverse	
aCaO.SiO	48.2		51.8	Melting	$1540^{\circ} \pm 2^{\circ}$
CaO.SiO	48.2		51.8	a to $\beta$ and reverse	$1200^{\circ}\pm2^{\circ}$
a2CaO.SiÔ	65.		$35 \cdot$	Melting	$2130^{\circ} \pm 20^{\circ}$
2CaO.SiO	65.		$35 \cdot$	$\gamma$ to $\beta$ and reverse	$675^{\circ} \pm 5^{\circ}$
2CaO.SiO	65.		$35 \cdot$	$\beta$ to a and reverse	$1420^{\circ} \pm 2^{\circ}$
3CaO. $2$ SiÕ <sub>2</sub>	58.2		41.8	Dissociation into	$1475^{\circ}\pm5^{\circ}$
				$a2CaO.SiO_{2}$	
				and liquid	
3CaO.SiO <sub>2</sub>	73.59		26.41	Dissociation into	$1900^{\circ} \pm 20^{\circ}$
				$a2CaO.SiO_{2}$	
				and CaO	
3CaO.Al <sub>2</sub> O <sub>3</sub>	62.22	37.78		Dissociation into	$1535^\circ \pm 2^\circ$
				CaO and liquid	
5CaO. $3$ Al <sub>2</sub> O <sub>3</sub>	47.78	52.22		Melting	$1455^\circ \pm 5^\circ$
$CaO.Al_2O_3$	35.44	64.56		"	$1600^{\circ} \pm 5^{\circ}$
3CaO. $5$ Al <sub>2</sub> O <sub>3</sub>	24.78	75.22		٠٠ ،	$1720^{\circ} \pm 10^{\circ}$
$Al_2O_3.SiO_2$		62.85	37.15	"	$1816^{\circ} \pm 10^{\circ}$
CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>	20.09	36.63	43.28	"	$1550^{\circ} \pm 2^{\circ}$
2CaO.Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	40.83	37.19	21.98	"	$1590^{\circ} \pm 2^{\circ}$
3CaO.Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	50.9	30.9	18.2	Dissociation into	$1335^{\circ} \pm 5^{\circ}$
				$\beta$ CaO.SiO <sub>2</sub>	
				and $CaO.Al_2O_3$	

A. Compounds-Transformation Points.

\*Kanolt, J. Wash. Acad. Sci., iii, 315, 1913. † Fenner, this Jour. (4), xxxvii, 331-384, 1913.

Crystalline Phases	Weig CaO	ght percen Al <sub>2</sub> O <sub>3</sub>	$tage SiO_2$	Temp.
$\overline{\operatorname{aCaO.SiO}_2}$	37.		63•	1436°± 5°
$aCaO.SiO_{2}$ 3CaO.2SiO_{2}	54•5		45.5	$1455^{\circ}\pm 5^{\circ}$
$a2CaO.SiO_{2}$	67.5		32.5	$2065^{\circ} \pm 10^{\circ}$
$ \begin{array}{c} 3CaO.Al_2O_3 \\ 5CaO.3Al_2O_3 \end{array} $	50.	50.		$1395^{\circ}\pm 5^{\circ}$
${}^{5\text{CaO.3Al}_{2}\text{O}_{3}}_{\text{CaO.Al}_{2}\text{O}_{3}}$	47.	53.		1400°± 5°
CaO.Al <sub>2</sub> O <sub>3</sub> ) 3CaO.5Al <sub>2</sub> O 5	33.2	66•5		$1590^{\circ}\pm 5^{\circ}$
$\left. \begin{array}{c} 3\mathrm{CaO.5Al_{2}O_{3}} \\ \mathrm{Al_{2}O_{3}} \end{array} \right\}$	24•	76.		$1700^{\circ}\pm10^{\circ}$
$Al_2O_3.SiO_2$ SiO <sub>2</sub>		13.	87.	$1610^{\circ}\pm10^{\circ}$
$ \begin{array}{c} \operatorname{Al}_{2}\operatorname{O}_{3}.\operatorname{SiO}_{2} \\ \operatorname{Al}_{2}\operatorname{O}_{3} \end{array} \right\} $		64.	36•	$1810^{\circ}\pm10^{\circ}$
$ \begin{array}{c} \operatorname{CaO} \operatorname{Al}_2 \operatorname{O}_{\mathfrak{s}}.2 \operatorname{SiO}_{\mathfrak{s}} \\ \operatorname{aCaO}.\operatorname{SiO}_{\mathfrak{s}} \end{array} \right\} $	34.1	18.6	47.3	$1299^{\circ}\pm 5^{\circ}$
$\begin{array}{c} \operatorname{CaO.Al}_{2}O_{3}.2\operatorname{SiO}_{2} \\ \operatorname{SiO}_{2} \end{array} \right\}$	10.5	19.5	70.	1359°± 5°
$ \begin{array}{c} 2\text{CaO.Al}_2\text{O}_3\text{.SiO}_2 \\ a2\text{CaO.SiO}_2 \end{array} \right\} $	49.6	23.7	26.7	$1545^{\circ}\pm 5^{\circ}$
$\begin{array}{c} \text{CaO.Al}_2\text{O}_3\text{.2SiO}_2 \\ \text{Al}_2\text{O}_3 \end{array} \right\}$	19.3	39.3	41•4	1547° <b>±</b> 5°
$ \begin{array}{c} 2\text{CaO.Al}_2\text{O}_3.\text{SiO}_2 \\ \text{CaO.Al}_2\text{O}_3 \end{array} \right\} $	37.8	52.9	9.3	$1512^{\circ}\pm 5^{\circ}$
$\begin{array}{c} 2\text{CaO.Al}_2\text{O}_3\text{.SiO}_2\\ 3\text{CaO.5Al}_2\text{O}_3 \end{array}$	35.	50•8	14.2	$1552^{\circ}\pm 5^{\circ}$
$CaO.Al_2O_3.2SiO_2$ $2CaO.Al_2O_3.SiO_2$	30•2	36•8	33•	$1385^{\circ}\pm 5^{\circ}$
2CaO.Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> $\alpha$ CaO.SiO <sub>2</sub> }	45.7	13.2	41.1	$1316^{\circ}\pm 5^{\circ}$
$\beta$ 2CaO.SiO <sub>2</sub> 5CaO.3Al <sub>2</sub> O <sub>3</sub> $\}$	51.3	41.8	6.9	$1350^{\circ}\pm 5^{\circ}$

B. Binary Eutectics-Melting Points.

Crystalline	Wei			
Phases	CaO	$\operatorname{Al}_2O_3$	$SiO_2$	Temp.
3CaO.2SiO <sub>2</sub> } a2CaO.SiO <sub>2</sub> }	55.2		44.5	1475°±5°
CaO $3CaO.Al_2O_3$	57.	43 <b>·</b>		$1535^{\circ}\pm 2^{\circ}$

# C. Quadruple Points other than Eutectics.

Crystalline	We	eight percen		
Phases	CaO	$Al_2O_3$	SiO2	Temp.
$\overbrace{\substack{\text{CaO.Al}_{2}O_{3},2\text{SiO}_{2}\\\text{SiO}_{2}\\\alpha\text{CaO.SiO}_{2}}}^{\text{CaO.Al}_{2}O_{3},2\text{SiO}_{2}}$	23.25	14.75	62.	$1170^{\circ}\pm5^{\circ}$
$\left. \begin{array}{c} \operatorname{CaO.Al}_2\operatorname{O}_3.2\operatorname{SiO}_2\\ \operatorname{Al}_2\operatorname{O}_3.\operatorname{SiO}_2\\ \operatorname{SiO}_2 \end{array} \right\}$	9.8	19.8	70.4	$1345^{\circ}\pm5^{\circ}$
$\begin{array}{c} 2\text{CaO.Al}_{2}\text{O}_{3},\text{SiO}_{2}\\ 3\text{CaO.2SiO}_{2}\\ \alpha\text{CaO.SiO}_{2} \end{array} \right\}$	47.2	11.8	41•	$1310^{\circ}\pm5^{\circ}$
$\left.\begin{array}{c} 2\text{CaO.Al}_{2}\text{O}_{3}\text{.SiO}_{2}\\ \text{CaO.Al}_{2}\text{O}_{3}\\ 3\text{CaO.5Al}_{2}\text{O}_{3} \end{array}\right\}$	37.5	53.25	9.25	$1505^{\circ}\pm5^{\circ}$
$\left. \begin{array}{c} \operatorname{CaO.Al}_{2}\operatorname{O}_{3}.2\operatorname{SiO}_{2} \\ \operatorname{2CaO.Al}_{2}\operatorname{O}_{3}.\operatorname{SiO}_{2} \\ \operatorname{\alphaCaO.SiO}_{2} \end{array} \right\}$	38.	20.	42.	$1265^{\circ}\pm5^{\circ}$
$\left. \begin{array}{c} \operatorname{CaO.Al}_{2}\operatorname{O}_{3}.2\operatorname{SiO}_{2} \\ \operatorname{2CaO.Al}_{2}\operatorname{O}_{3}.\operatorname{SiO}_{2} \\ \operatorname{Al}_{2}\operatorname{O}_{3} \end{array} \right\}$	29.2	39.	31.8	$1380^{\circ}\pm5^{\circ}$
$ \left. \begin{array}{c} \beta 2 \text{CaO.SiO}_2 \\ \text{CaO.Al}_2 \text{O}_3 \\ 5 \text{CaO.3Al}_2 \text{O}_3 \end{array} \right\} $	49.5	43.7	6.8	1335°±5°
$ \begin{array}{c} \beta 2 \text{CaO.SiO}_{2} \\ 3 \text{CaO.Al}_{2} \text{O}_{3} \\ 5 \text{CaO.3Al}_{2} \text{O}_{3} \end{array} \right\} $	52.	41.2	6.8	$1335^{\circ}\pm5^{\circ}$

## D. Ternary Eutectics-Melting Points.

Crystalline	We	tage		
Phases	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Temp.
$\overbrace{\mathbf{CaO.Al_2O_3.2SiO_2}}_{Al_2O_3} \left\{ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	15.6	36•5	47.9	$1512^\circ \pm 5^\circ$
$\left.\begin{array}{c} 2\text{CaO.Al}_{2}\text{O}_{3}\text{.SiO}_{2}\\ \beta 2\text{CaO.SiO}_{2}\\ \text{CaO.Al}_{2}\text{O}_{3} \end{array}\right\}$	48.3	42·	9.7	$1380^\circ \pm 5^\circ$
$\begin{array}{c} 2\text{CaO}, \text{Al}_{2}\text{O}_{3}, \text{SiO}_{2} \\ 3\text{CaO}, 2\text{SiO}_{2} \\ \beta 2\text{CaO}, \text{SiO}_{2} \end{array} \right\}$	48.2	11.9	39.9	$1335^\circ\pm5^\circ$
$\left.\begin{array}{c} 3\mathrm{CaO.5Al_2O_3}\\ 2\mathrm{CaO.Al_2O_3,SiO_2}\\ \mathrm{Al_2O_3} \end{array}\right\}$	31.2	44.5	24.3	$1475^\circ\pm5^\circ$
$3CaO.SiO_2$ $3CaO.Al_2O_3$ $a2CaO.SiO_2$	58.3	33.	8.7	$1455^\circ\pm5^\circ$
$\left. \begin{array}{c} CaO\\ 3CaO.SiO_{a}\\ 3CaO.Al_{2}O_{a} \end{array} \right\} =$	59.7	32.8	7.5	$1470^{\circ}\pm5^{\circ}$
$\left. \begin{array}{c} CaO\\ a2CaO.SiO_2\\ 3CaO.SiO_2 \end{array} \right\}$	68.4	9.2	22.4	$1900^{\circ} \pm 20^{\circ}$

E. Quintuple Points other than Eutectics.

In closing this record of a long and, in many of its phases, very exacting investigation, the authors take especial pleasure in expressing their gratitude to Prof. W. D. Bancroft for many helpful suggestions, and to their colleagues, Dr. John Johnston, Mr. E. S. Shepherd, and Mr. J. B. Ferguson, for most valuable assistance which was often asked and always freely given.

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## ART. II.—Note on a New Meteoric Iron from Sams Valley, Jackson Co., Oregon; by W. M. FOOTE.

THE mass of iron described below was found in 1894 by Mr. George P. Lindley, since deceased. The specimen then passed into the hands of his son, Mr. Nolo M. Lindley, under the belief that it was a meteorite. Later it came to the attention of Mr. E. W. Liljegran. All were, or are, residents of the town of Medford, Oregon. Through the latter gentleman, the mass was secured in October, 1914, by the Foote Mineral Company of Philadelphia. It was found in the Sams Valley. a farming and ranching region about ten miles northwesterly from Medford. The ground here possesses a wavy and flat surface, gradually rising into foothills to the north; Mt. Pitt is about thirty-five miles to the east, with an elevation of 9760 feet. The location of the find is approximately 123° E. longitude and 42° 30' N. latitude. The iron was found on the nearly level surface of the rocky soil which characterizes this locality. The exact position of the mass was not recorded. No other pieces are known to have been found, nor are there any local rumors of the observation of the fall of such a meteorite. The writer is indebted to Mr. Liljegran for the preceding data.

The designation "Sams Valley" is used for the meteorite, as there is now a small post office town of that name at this point.

As will be seen by figs. 1 and 2, the mass is irregularly lenticular in contour. On the lower left corner of fig. 1 a sawed sample of 30 grams was replaced, as shown; the upper end has been reconstructed as indicated, where a sample of about 15 grams was sawed off at Medford and lost. In the extreme right center of fig. 2 is seen a much oxidized depression of crystalline cleavage, where a sample of perhaps 35 grams was long since cut and fractured off with a tool. The mass, when received at Philadelphia, weighed 6810 grams, which, with the weight of samples and loss in sawing two of them, brings the total weight when found to about 6900 grams ( $15\frac{1}{4}$  lbs.). After sawing and etching, the various pieces had a total net weight of 5,517 grams. The surface exhibits no effects of fusion, nor are its irregularities probably due to aerial pitting. The terrestrial weathering has left broad shallow depressions and a hole of about  $8 \times 8^{mm}$  in a troilite nodule of about  $23^{mm}$  diameter, shown in the center of fig. 1. The mass is thinly oxidized, the rust being from about 0.1 to  $0.5^{mm}$  thick. Crystalline lamellæ and schreibersite are slightly in evidence on the surface.

The greatest dimensions of the mass are about  $17 \times 12 \times 9^{\text{cm}}$ .



FIG. 1. Broadside view.  $\times 4/5$  diameter.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 229. – January, 1915. 6

F1G. 2.



## W. M. Foote-Meteoric Iron from Sams Valley, Oregon. 83

After making a plaster model, the iron was sawed at Philadelphia into four slices of the largest possible area and about 5 to 10<sup>mm</sup> thickness, as well as two large end-pieces. Polished and etched with a weak solution of nitric acid, the crystallization of a medium octahedrite is clearly brought out. The sawing was done parallel to the plane of two of the three cubic axes. The lamellæ forming the octahedral units of the crystalline mass are therefore sectioned so as to meet at right angles, thus affording a network of rectangular figures (fig. 4). In sawing irons the plane of sawing usually intersects a plane formed by two of the crystal axes; the etching thus exhibits rhomboidal and triangular figures. Both rectangular and other figures are shown in the same piece by FIG. 3.

etching in different planes, as in fig. 3.

Fig 4 is an end-piece, the reverse side of which is shown in fig. 1. The troilite nodule, measuring 25<sup>mm</sup> in longest diameter, is the only one met with in the mass, except one already mentioned and indicated by the hole at the center of the reverse side of this end-piece. The two may form part of a nodule between 40 and 50<sup>mm</sup> long and 20 to 25<sup>mm</sup> thick. In the adjoining slice, 2<sup>mm</sup> distant, the nodule is slightly smaller, and on the reverse of this slice, 5<sup>mm</sup> beyond, it has disappeared. The etching at angles of 45° to polished nodule bears a central inclusion one another. of nickel iron.

Schreibersite is abundant in small masses, but mostly in the form of broad, thin plates showing on the etched surface as slender rods of about 0.1 to 1<sup>mm</sup> width and 10 to 30<sup>mm</sup> length. These plates sometimes lie between the kamacite lamellæ, but more often cut across the squares prominently at various angles. In either case they are paralleled for their entire length by the typical and familiar swathing kamacite of Brezina. The bands are about double the thickness of the normal kamacite forming the crystalline mass.

The kamacite bands are quite regular, except for those paralleling the schreibersite plates, and range mostly from 0.5 to 1<sup>mm</sup> diameter; their length varies greatly, many being only 1 to  $2^{\text{mm}}$ , while others reach 25 to  $30^{\text{mm}}$ . The characteristic and very thin lamellæ of nickel-rich tænite outline all of the kamacite bands, and are prominent in certain lights. The groundmass consists of abundant fields of the nickel-poor plessite.

The chemical analysis was made by Mr J. Edward Whitfield of the firm of Booth, Garrett & Blair, Philadelphia. The



FIG. 3. Two planes of



FIG 4. Polished and etched surface. Natural size.

# W. M. Foote-Meteoric Iron from Sams Valley, Oregon. 85

specific gravity was found to be 7.794. Mr. Whitfield obtained the following results on analysis of clean unoxidized drillings:

Silicon	0.009%
Sulphur	0.056
Nickel	9.160
Cobalt	0.640
Copper	0.016
Carbon	0.100
Iron	83.800
	93.781
Schreibersite	6.194
	99.975%
	00 01 0/0

"There was no indication of phosphorus in the metal of this iron other than that composing the schreibersite. This mineral, amounting to 6.194 per cent, was analyzed separately with the following results:

Iron	65.13%
Nickel	20.93
Phosphorus	13.94

There was no manganese present in this iron, nor could any of the rare or unusual elements be identified."

A recalculation of the above figures, excluding the schreibersite, gives the following results. For comparison the Mount Edith (West Australia) analysis by Whitfield is given in the second column.

	Sams Valley	Mt. Edith
Silicon	0.009%	0.005%
Sulphur	0.059	0.005
Nickel	9.762	9.450
Cobalt	0.682	0.625
Copper	0.012	0.013
Carbon	0.106	0.017
Iron	89.357	89.500
Phosphorus	None	0.316
	99.992%	99.931%

Estimating all the phosphorus in Mt. Edith as composing schreibersite, 2<sup>·10</sup> per cent of this mineral would be indicated. The striking crystallographic similarity of Sams Valley with

Mt. Edith, described by the present author in May last.\* is supplemented by chemical likeness to a degree which is rarely encountered. Indeed, the chemical difference between these two geographically distant falls is far less than is often noted in different portions of the same mass of meteoric iron. Their analyses confirm what has long been known: namely, that chemical composition alone cannot be relied upon to distinguish two clearly distinct meteorites. An important physical feature which easily differentiates the two irons is the schreibersite content. Etched plates of Sams Valley show two or three times as much of this mineral in prominent patches and rods as does Mt. Edith. The two analyses, affording respectively 2.10 per cent and 6.1 per cent schreibersite, tend to confirm this appearance. Moreover, an abundance of straight capillary "Brezina lamellæ" of schreibersite, often in parallel groups, characterizes Mt. Edith, while their entire absence is noted in Sams Valley. A minor distinction is to be found in occasional low crystalline ridges on the Sams Valley, due to the kamacite lamellæ resisting unequally the attack of terrestrial agencies. Such structural indications are absent on the Mt. Edith.

In an examination of the analyses of meteoric irons, Dr. O. C. Farrington has already demonstrated that uniformity of composition is accompanied by a similarity in crystalline structure.

Sams Valley's nearest geographical neighbors among the siderites are Willamette (200 miles north, in Oregon), a medium octahedrite of totally different crystalline aspect, and Oroville (200 miles south, in California), another medium octahedrite. A comparison by Dr. Farrington shows the latter to contain less schreibersite and plessite than Sams Valley. The Oroville lamellæ are more swollen than those of Sams Valley, whereas there are far more repeating lamellæ in Sams Valley. The differences are such that the two falls could probably be distinguished on any etched sections. While there are doubtless other irons which Sams Valley closely resembles physically, it may be unquestionably accepted as a distinct fall.

Philadelphia, Pa.

\* This Journal, vol. xxxvii, pages 391-8.

## ART. III.—A New Longirostral Mastodon, Tetrabelodon lulli. Preliminary Notice; by ERWIN H. BARBOUR.

DURING the field season of 1914, the Nebraska Geological Survey, while exploring the Pliocene exposures along the Minichaduza, Niobrara, and Snake rivers, in Cherry County, obtained a new and unusual longirostral mastodon. It was found near Burge in the deposits bordering a stream variously termed Snake Creek and Snake River. The latter name is preferable since it avoids confusion with Snake Creek, and the Snake Creek beds, in Sioux County. The beds around Burge are equivalent to the well-known Snake Creek, and it might be sufficiently distinctive, as well as associative, to call these deposits the Snake River stage.

The gradient of the streams at this point is rather steep, and the land surfaces are well washed and gullied. There are bare canyon walls of Loup Fork two hundred feet high, heavily capped by sand hills. Large numbers of bones, mostly proboscidean, have been more or less completely washed out. Unfortunately the bulk of them are fragmentary. These deposits might well be called the mastodon beds, because mastodon bones are found in such abundance for a distance of almost two hundred miles. It should be explained, however, that much of this area is deeply covered and obscured by sand.

On one talus slope, the number of mastodon bones led the party to explore the canyon walls well to the top. Here a tusk and associated bones were found, together with the mandible shown in the accompanying figure. It is assumed that these associated bones are related. Work will be resumed later in this spot, and it is believed that the skull, missing tusk, and other parts of this individual may be recovered.

The mandible is uncommonly large, and remarkably well preserved. Unfortunately the very tip of the rostrum, as well as any tusks which it may have borne, are wanting. The great length of the rostrum would, in itself, be sufficient to warrant the assumption that inferior tusks were present in life. The alveolus also suggests the probability of their presence, although they must have been slim. Dr. Richard S. Lull, who examined this specimen, concurs in the belief that the mandible probably bore tusks.

We wish to propose the name, *Tetrabelodon lulli*, for this new species; in honor of Professor Richard Swann Lull of Peabody Museum, Yale University. It is probably entitled to rank as a new subgenus.

Measured from the condyle, the length of the mandible, as found in the quarry, exclusive of tip and tusks, is 52 inches



Fig. 1. Mandible of Tetivabelodon lulli. Side view  $\times 1/10$ . The portion in front of the dotted line is restored. Geological collections of Honorable Charles H. Morrill, Nebraska State Museum.



F1G. 2.



Mandible of *Tetrabelodon lulli*. Crown view  $\times 1/10$ . The portion in front of the dotted line is restored. FIG. 2. (1,322<sup>mm</sup>). Three large fragments of the tip, found at the end of the mandible, when set in position, increase the length to about 56 inches (1,424<sup>mm</sup>). Its total restored length, including the tusks, is 69 inches  $(1,754^{\text{mm}})$ . There is every probability that the length could not have been less than two full meters. Dr. Lull is undoubtedly right in believing that the tusks, as restored, are too short. We fully agree that they may have been two or three times as long as shown in the accompanying figures. In any event, the length of the tusks must be assumed. Accordingly a very moderate size was chosen. The great size and strength of the ascending ramus, and especially the large roughened coronoids, suggest longer tusks. It is much larger than either of the Tetrabelodons, longirostris or angustidens, and is of different proportions. In the best known specimen of Tetrabelodon angustidens the mandible is about 46 inches  $(1,169^{\text{mm}})$  long, or with tusks included, about 52 inches  $(1,322^{\text{mm}})$ . In *Tetrabelodon longirostris*, the symphys is is not greatly produced, and the inferior tusks are relatively large.

*Tetrabelodon campester* is much smaller, the symphysial prolongation is much shorter, the ramus thin, and the inferior border curves without angle into the ascending ramus.

The rostrum of this new mastodon is greatly elongated and noticeably decurved. The rami diverge by curves the convexity of which is outward; while in *angustidens* it is inward. The lingual groove is 2 inches  $(51^{mm})$  deep, and 3 inches  $(76^{mm})$ broad, growing shallower toward the tip, and is bounded on the sides by narrow rounded edges. The long attenuated symphysis is ancestral, and its maximum development seems to have been reached in this species. The narrowed and reduced alveolus seemingly marks a decline in the mandibular tusks, and consequent to their reduction and loss, follows the reduction and final suppression of the prolonged rostrum.

The ramus is massive and powerful, being 31 inches (788<sup>mm</sup>) from the bifurcation to the condyle, by 8 inches (203<sup>mm</sup>) deep, and 4 inches (102<sup>mm</sup>) thick at the molars. Immediately back of the molars the thickness increases to 5 inches (127<sup>mm</sup>). The symphysial prolongation is  $28\frac{1}{2}$  inches (724<sup>mm</sup>). It is 5 inches (127<sup>mm</sup>) deep at the entrance of the mental foramen, by 4 inches (102<sup>mm</sup>) wide. This makes a very narrow rostrum. *Tetrabelodon angustidens*, measured at the same point, is about 4 inches (102<sup>mm</sup>) deep, by 5 inches (127<sup>mm</sup>) wide. The inferior mandibular border is thick and round under the molar, but narrows rapidly toward the angle. The angle is thin and pronounced, and flares outward very unlike modern and fossil elephants.

The ascending ramus is very broad and erect, and rises well above the level of the molars, but not as high as in *Tetrabelodon*  angustidens. The condyloid process is constricted into a distinct neck below the condyle. The condyle is large, elliptical in outline and noticeably convex. This is very unlike *Eubelodon morrilli*,\* in which the convexity is extremely low. The condyle measures  $4\frac{1}{2}$  inches  $(114^{\text{mm}})$  transversely, by  $2\frac{3}{4}$ inches  $(69^{\text{mm}})$  postero-anteriorly. The condylar surface lies  $7\frac{1}{2}$  inches  $(191^{\text{mm}})$  above the crown of the molars. The extreme distance across the condyles is  $23\frac{1}{2}$  inches  $(597^{\text{mm}})$ .

The coronoid process resembles that of a typical mammal, but differs widely from any living or fossil elephant with which we are familiar. It is deeply roughened for ligamentous attachment, and is strongly recurved. The lower of the three mental foramina is produced into a deep, narrow fossa 10 inches  $(254^{mm})$  long. The foramen itself is noticeably large, and must have admitted great nerves and vessels. The same condition obtains in the new mastodon, *Eubelodon morrilli*, from Brown County. In *Tetrabelodon willistoni*,<sup>+</sup> from the same beds, the foramen is large and elliptical, but only moderately produced. In *Mastodon americanus*, the mental foramen ordinarily lies below the front edge of molar No. 2. In the mammoths and modern elephants, these foramina are small, in many cases numerous, and close to the symphysial line.

The mandible of *Tetrabelodon lulli* is from an individual advanced in age. The teeth are worn flat and low and are deeply cupped at each of the four transverse ridges. Two cones, indicated by concentric rings, are discernible in each ridge, but no secondary cones are apparent. Contrary to the usual order, the teeth are ground with an inward and backward slant. The back slant on the last transverse ridge is noticeably steep. The molars are  $8\frac{3}{4}$  inches ( $222^{mm}$ ) long, by  $3\frac{1}{2}$  inches ( $89^{mm}$ ) wide.

After an immeasurably extended period of survival, wide migrations, and various modifications, the longirostral mastodons gradually merged into the brevirostral. Many stages of development are already known, and many more are to be discovered. The Nebraska beds seem destined to furnish many links in the phylogeny of the Proboscidea. It seems certain also that many subdivisions must be made in the group. Even after the mastodons became short-jawed, they continued to bear one or two dwarfed mandibular tusks. This obtains in the case of *Mastodon americanus*, which survived almost to modern times, and in which one or two small lower tusks are occasionally found.

The maxillary tusk found associated with this mandible is \*Barbour, Erwin H.: Mammalian Fossils from Devil's Gulch, Nebr. Geol.

Survey, vol. iv, pt. 11, No. 33.

† Idem.

92

slightly decurved, is  $5\frac{1}{2}$  feet  $(1.678^{\text{mm}})$  in length, and  $4\frac{1}{2}$  inches (114<sup>min</sup>) in diameter. Unlike Eubelodon morrilli, the tusk has an enamel band, although narrow and almost vestigial, and the tip is worn to a very obtuse wedge. The two associated humeri seem uncommonly short and stout. They are scarcely more than 30 inches (763<sup>mm</sup>) in length. It seems worthy of notice that, in the case of the Brown County mastodons, the acetabula have bold, cotyloid notches, and singularly deep, broad cotyloid fossæ, which are roughened and deeply pitted. This indicates that the round ligaments were present, that they were uncommonly large. The heads of the femora show unmistakable scars. With so many examples at hand, it seems beyond the limit of probability that this is coincidence. Contrary to the usual rule, all of these mastodons seem to have had the ligamentum teres strongly developed. In the case of the acetabula of Tetrabelodon lulli, the fossæ are narrow and deep, and the heads of the femora have corresponding scars. In *Élephas*, the acetabular fossæ are nearly obliterated, and the heads of the femora are without scars. Absence of this ligament has been counted a character of the Proboscidea, but the Brown and Cherry County mastodons seem to be exceptions to the rule.

The following associated fossils have been noted: Testudoorthopygia, Testudo indet., Alticamelus, Camel indet., Parahippus, Hipparion, Neohipparion, Teleoceros fossiger, and Merycodus necatus.

In the Nebraska State Museum, the following proboscideans from Nebraska are represented: Tetrabelodon lulli, Tetrabelodon willistoni, Eubelodon morrilli, Tetrabelodon euhypodon, Mastodon merificus, Mastodon americanus, Elephas columbi, Elephas imperator, Elephas primigenius, and several undetermined forms believed to be distinct.

The University of Nebraska,

Lincoln, September 15, 1914.
# ART. IV.—The Repulsion of Two Metallic Disks, nearly in Contact ;\* by C. BARUS.

1. Apparatus.—The apparatus shown in fig. 1 was originally constructed with the expectation of adapting the horizontal pendulum for the measurement of the Newtonian constant; or conversely to graduate the horizontal pendulum by means of that constant. Here AB suggests the parts of a Fraunhofer slide micrometer, capable of moving the slide about 6cm and graduated in  $\cdot 0001^{\text{cm}}$ . On this the two brass disks, DD, originally 15<sup>cm</sup> in diameter and about 6<sup>cm</sup> thick, are mounted in parallel, rigidly, normally and vertically. To adjust the disks the steel plugs cc are provided, fitting radial holes in the plate. They are further held by the semi-circular frame ee. screwed to the slide below and attached above to the disks by aid of the pairs of screws a and b on opposite sides of the diameter. The screw a is sunk into the disk while b presses against its outer surface. As the disks are to be fitted nearly true to the slide and the frame, but slight adjustment at a and b is needed. The interior of the smaller disk, d, about  $10^{\text{cm}}$  in diameter and  $\cdot 6^{\rm cm}$  thick, is suspended vertically by two fine wires f, from the end of the arm HH', fig. 2, of the horizontal pendulum, just below the grating. The disks D, d, D', are coaxial, while d is relatively stationary; D or D' may be brought by aid of the slide micrometer as near to d as desirable, the other disk being removed at the same time.

The method of attachment of the disk d to the horizontal pendulum is shown on a smaller scale in fig. 2. Here G is the grating, secured by three adjustment screws to the table T, the cylindrical stem of which is grasped in a clamp P (open form), of the horizontal pendulum H, PH'. To the bottom of the stem in question, a cross piece, hgh, is screwed and fastened with a lock nut. The two metallic fibers ff which support the disk d are wound above around the screws hh and thus adequate vertical adjustment of disk d is available.

The slide micrometer is attached to the pier by a firm horizontal rail capable of adjustment forward and rearward. A strong clamp attaches the base of the slide micrometer to this rail, so that the whole instrument may also be adjusted to the right or left, roughly. The fine adjustment is secured at the slide micrometer itself.

Finally, a case is provided covering the disks D and d and part of the micrometer, so that only the drum head and scale

<sup>\*</sup> Abridged from a forthcoming Report to the Carnegie Institution of Washington, D. C. See note, this Journal, xxxvii, p. 350.

projects. The apparatus was found to work satisfactorily. It is quite possible to rely solely on the effective air damping produced when the disk d is very close to D or D'. In fact, the tin cover in this case was all but superfluous. D could be shifted from end to end of its course without materially interfering with the visibility of the ellipses in the spectrum of the interferometer. The occurrences unfavorable to the gravitational measurement were all incidental; due either to the change in inclination of the pier, a, or to changes in the mag-



netic field (inasmuch as the pendulum was preliminarily constructed on steel tubing), or to the phenomena discussed in this paper. For what was found was not an attraction at all, but a repulsion much larger in absolute value than the attraction anticipated.

2 Equations.—The chief equations to be used in the present work have already been given in the former paper.\* It is merely necessary to add those which bear upon the sensitiveness of the method. Since the disk of mass m is added at the mean distance R to the mass of the pendulum M, the force at R from the axis is now

$$F'_{\rm R} = F_{\rm R}^{\rm c} (1 + mR/Mh)$$

\* Barus : This Journal, xxxvii, 1914, p. 501, et seq.

91

The gravitational attraction  $f^*$  of the disks necessarily involves spherical harmonics, but may be written temporarily as

$$f' = \gamma \, mm' / f(d)$$

where m' is the mass of the stationary disk at a mean distance d from m. Equating these forces and inserting the value of  $F_{\rm R}$ , the equation for  $\Delta N$ , the displacement at the micrometer, becomes

$$\Delta N = \frac{\gamma m' 2 R^2 m/M}{f(d) g \phi h (1 + mR/Mh)}$$

In the first place, therefore, the lightest available pendulum and the heaviest admissible disk is to be selected, although the increase of sensitiveness is not quite proportional to m/M. This procedure, even when the float<sup>\*</sup> is used, is relatively inefficient.

It is much more effective, since the disks are all but in contact on measurement, to increase their area and decrease their thickness. Equation 3, if equal disks of radius r and thickness t and density  $\rho$  are employed, and if  $f(d) = d^2 = t^2$  takes the form

$$\Delta N = \frac{\pi^2 \gamma r^4 \rho^2 2 R^2}{g \phi h M (1 + m R/Mh)}$$

so that for disks and pendulum of an invariable mass,  $\Delta N$  increases roughly as the fourth power of the radius of the disks. Inasmuch as this is also the case in which the gravitational attraction may be much more easily computed, it is, therefore, the direction which the experiment should take. Thus, if the above disks for constant mass be decreased in area and increased in thickness and be placed all but in contact, the estimated value of  $\Delta N$  should be at least

r =	5	10	15
r' =	7.5	15	22.5 etc.
$10^{\circ}\Delta N =$	1.2	18.7	94.8

quantities easily measurable even without the use of an interferometer.

3. Observations.—The brass plates of the preliminary work were soon replaced by a set, larger in area but thinner, this being in the direction of the improvement of method indicated. The same unnecessarily heavy steel pendulum had, however, to be used, so that M = 1250 grams,  $h = 80^{\text{cm}}$ ,  $R = 111^{-3^{\text{cm}}}$ ,

\*The equations given for the float apply only if the float is placed at the center of gravity of the pendulum. If the float supports the axis of the pendulum, the original equations are unchanged, the effect being merely to damp the pendulum and to take the weight off the pivots.

 $\phi = 01081$  radians,  $F_{\rm R} = 42.9 \Delta N$ . The new brass plates D, d, D', were identical in size, the mass being m = 468 grams each, the diameter  $2r = 20.3^{\rm cm}$ , and the thickness  $\cdot 17^{\rm cm}$ . When all but in contact gravitational attraction should have exceeded  $\cdot 508$  dynes. The force  $F'_{\rm R}$  corresponding to the loaded pendulum is

$$F'_{\rm R} = F_{\rm R} (1 + mR/Mh) = 65.2 \Delta N$$

The double gravitational attraction should, therefore, have been at least equivalent to a difference of the displacement on the two sides of  $\cdot 0156^{\rm cm}$ , or about 31 drum parts of the micrometer. In place of this a repulsion, equivalent on the average to  $\cdot 0338^{\rm cm}$  or about 68 drum parts, was observed.

The experiments were made at some length; but as the results corroborate the more elaborate work below they need not be given here.

4. The same. Metallic contact.—The next advance consisted in placing the disks in electrical metallic contact, which was easily done by joining the pivots of the horizontal pendulum with the slide of the micrometer bearing the fixed disks, by a copper wire. Moreover, since the position of equilibrium is gradually reached in the lapse of minutes, the time of the observation is taken in minutes.

These experiments will also be omitted here as they showed no essential difference. The mean repulsion observed for the disks  $20^{\text{cm}}$  in diameter was  $2F_{\text{R}} = 65 \cdot 2 \Delta N = 65 \cdot 2 \times 013 = \cdot 85$ dyne at about  $d = 1^{\text{mm}}$  of air space.

5. Retardation due to viscosity of air.-It will next be necessary to examine the surmise, that the very gradual approach of the suspended disk to its position of equilibrium may be due to the viscosity of the interposed couche of air, in view of the small forces and small displacements involved. The case may perhaps be treated in terms of Poiseuille's law, assuming that the flow is from the center of the two nearly contiguous parallel disks radially toward the circumference. Let  $y_{a}$  be the initial distance apart of the disks, and the time t = 0 seconds, measured from the fixed toward the movable disk. Let y' be the final position of equilibrium of the movable disk, so that its excursion is  $y_{a} - \dot{y}'$ . Let a small impulsive force P act normally on the outside of the movable disk, by which it is put into the position y. The pressure generated will cause a flow radially outward in question, and if p is the pressure in the fluid at a distance r from the center, Poiseuille's law would give

$$-\frac{dV}{dt} = \frac{(2\pi r y)^2}{8\pi n} \frac{dp}{dr}$$

for the flow through a ring whose section is ydr, if  $\eta$  is the viscosity of the gas and  $\dot{V}$  the volume of fluid crossing per second. If the flow is steady so that dp/dt = 0, for all distances from the center and if the liquid is virtually incompressible, i. e.,  $\dot{V}$  independent of r, the problem may be solved without difficulty. Neither of these conditions is quite true. The second, however, inasmuch as the average pressure increment is exceedingly small relative to atmospheric pressure, may be admitted. Suppose, therefore, that at any time, y and  $\dot{V}$  are constant relatively to r, and integrate the equation. Hence the pressure excess at r is

$$p = \frac{2 \eta \dot{V}}{\eta y^2} \left( \frac{1}{r} - \frac{1}{R} \right)$$

If R is the radius of the disks, p = 0 at r = R, and the equation may be considered to hold short of r = 0. Thus the

thrust  $\int_{0}^{\dot{k}} 2 \pi r \, dr. \, p$  becomes

$$P=2 \eta R V/y^2$$

But  $V = -\pi R^2 dy/dt$ , whence on integrating Pdt

$$Pt = 2 \pi \eta R^{s} \left(\frac{1}{y} - \frac{1}{y_{o}}\right)$$

But for the horizontal pendulum the force P is proportional to y - y', which may be written

$$P = P_{\circ}(y - y')$$

so that -Pdt becomes

$$-P_{0} dt = 2 \pi \eta R^{3} dy / y^{2} (y - y')$$

This, on final integration, reduces to

$$t = \frac{2 \pi \eta R^{s}}{P_{o} y'^{2}} \left\{ \left( \frac{y}{y_{o}} - \frac{y'}{y} \right) + \log \frac{1 - y'/y_{o}}{1 - y'/y} \right\}$$

natural logarithms being in question. Since  $y - y' = \Delta N/2$ , equation for P, corresponds in case of the large disks to  $P = F'_{\rm R} = 2 \times 65.2 \Delta N/2$ . Hence,  $P_{\circ} = 2 \times 65.2$ . Furthermore, in case of this apparatus in the present experiments, the following data may be entered:

$$y' = 1/15 \text{ cm.}; y_0 = 10 \text{ cm.}; R = 10.2 \text{ cm.}; \eta = 190 \times 10^{-6}$$

The following summary contains some corresponding values of  $y = \Delta N/2$  and t computed in this way.

Am. Jour. Sci.-Fourth Series, Vol. XXXIX, No. 229.-January, 1915.

97

These values with the equation show that the position of equilibrium is reached to  $\Delta N = 10^{-4}$ , the smallest quantity easily measurable in about 25 seconds.

The fluid has been treated as incompressible, seeing that the pressure excess is a very small part of the total pressure. In endeavoring to use the gas equations directly, I have not succeeded in producing a practical form of equation.



#### FIG. 3.

6. Observations continued. Presence and absence of electrical contact.-Notwithstanding the improbability of electrical effects, it was thought necessary to test the case directly. Accordingly in fig. 3, series 1-8, experiments are recorded with the plates not in metallic contact (series 1-5), and with the plates in metallic contact (series 6-8), respectively. The behavior in both cases is virtually the same, when the inevitable shift of zero is taken into account. Observations are plotted in time series (minutes), and they are in each case continued until the motion of the plate is retrograde, whereupon the slow oscillation of the plate begins. To throw further light on the subject, a Leclanché cell was introduced in series 9 and 10 and removed in series 11. The lighting circuit of the room was placed more remote in series 12 and the system earthed in series 13 and 14, at both fixed discs.

That the differences observed are referable to the incidental shifting of the zero, is shown in series 15-18, where observations are made on one side only, with the distance between

98

discs gradually increasing, as the fixed plate moves from position 2.15 to position 2.00, i. e.,  $\cdot 15^{cm}$ . The interval of observation was 48 min.; but the interval and final reading at 2.15 differ in like degree, so that the apparent attraction indicated is merely the result of the shift of the position of equilibrium of the horizontal pendulum. Series 19 and 20 contain similar observations on the "small" side.

The present and all the following work was done in time series (min.), as shown. Observations were continued until the direction of motion was reversed and the disc reached a stage of slow vibration. Under these conditions the air gradually enters and leaves the fissure between the plates, so that errors due to the viscosity of air are out of the question.

7. Observation continued. Change of distance apart.—In the next work, the attempt was again made to vary the distances between fixed and movable plates successively; but to determine the micrometer position of contact of the plates by actually pushing them together with a weak spring.

The results of these laborious experiments, though apparently good when taken individually, were not consistent as a whole, because of the incidental flexure of the pier during the long interval of observation.

It does not seem possible, therefore, to obtain any definite results from methods which consume as much time as the present.

8. Observations. Long periods and inversion.—The unsatisfactory results obtained in the last paragraph induced me to give a final trial to the original method of alternating the sign of the repulsion, by moving each of the two fixed plates in turn near the suspended plate. The results are given in fig. 4. In series 1, 2, 3, the equilibrium position is approached from two opposed directions and for two positions on the "large" side of the micrometer. The same is the case in series 5 and 6, while in series 4, 7, 8, 9, similar observations are made on the "small" side. The mean results are (C denotes contact of plates d and D):

Fixed discs at, $\Delta x$ ,	= 2.10	2.15	•70	2.15	.75	.70	•65	cm.
Fixed and movable d	isc in							
contact, $\Delta N \times 10^3$	=	$75 \cdot$	-150	75		150		cm.
Movable disc free,								
$\Delta N  imes 10^3$	= 15	12	45	16	53	52	48	cm.
$10^{3}d$	=	31	97	30		101		cm.

Hence, there can be no further doubt that the repulsions are real, although their nature has not been made out. When the distance between the disks is larger than a millimeter, the air damping is insufficient and the free disk unavoidably oscillates. as, for instance, in case of series 1 and 4. The evidence, however, is none the less definite. In series 1 and 3, 5 and 6, 7 and 9, the equilibrium position is approached from opposite directions.

To obtain some reason for this result, one may dismiss the effect of electrical repulsion at once. The experiments to be made in the next section are for the purpose of corroborating the force equation used. Furthermore, friction at the pivots may be excluded, since the pendulum is usually in motion,



swinging about its position of equilibrium, so that friction would have operated both ways. There remains the possibility of an excess of pressure in the couche of air within a metallic fissure as compared with the surrounding air. To obtain some quantitative data, since  $F'_{\rm R} = 65.2\Delta N$ , one may note that in the successive series of measurements the average values of  $2\Delta N$  were roughly as follows:

Fig. 4<br/>Earlier $2\Delta N \times 10^3 = 40$ Max.  $F'_R = 1.3$  dynesexperiments<br/>do. $2\Delta N \times 10^3 = 13, 22, 38$ <br/> $2\Delta N \times 10^3 = 40$ Min.  $F'_R = .4$  "

As the area of the disk is 324 sq. cm., the corresponding average pressure observed per cm. is therefore here

 $p = 4 \times 10^{-3} \text{ dynes} / \text{cm}^2 = 4 \times 10^{-9} \text{ atm.},$ 

in the maximum case, or about 1/3 of this in the minimum case. The differences are to be referred to the distance apart of the plates, which was not always measured in the earlier experiments.

9. Plates electrically charged.—The endeavor was next made to overcome the repulsion of plates by aid of opposite electrical charges placed upon them. The experiments at present will necessarily be somewhat crude since the pier is liable to warp during the time in which the observations are made. Nevertheless the corroboration obtained is of great value.

The observations were made in time series when the plates were close together. For plates further apart, this is not necessary, but in the absence of other than the air damping, the suspended plate oscillates so that mean values have to be taken.

In fig. 5 I have inscribed the first observations from plates close together. In series 1 to 4, the plates are probably not far enough apart, though the contact position, C, is still beyond the equilibrium position by about  $\cdot 014^{\text{cm}}$ . It was not necessary to wait for the uncharged position of the plates as this remained pretty constant long before and after the experiments. In series 5, 6, 7, and 8, the distance apart is increased about  $\cdot 042^{\text{cm}}$ , and there is no danger of actual contact (free space  $\cdot 056^{\text{cm}}$  when charged), so that actual repulsion is in question.

ents.	1	2	3	4	5	6	7	8	9	10	11	12
erime No.	d	$\Delta N$	d'	V obs.	V' comp.	$F_{\rm R}$ obs.	$F'_{R}$ comp.	$\Delta N'$	$\overline{F_{\mathrm{R}}/F'_{\mathrm{R}}}$	x	y	f
Exp	cm		em	volts	volts	dynes	dynes			em	em	dynes
II III IV V I	·056 ·044 ·102 ·133 ·014	0.039 0.014 0.021 0.016 0.045	$^{.075}_{.051}$ $^{.112}_{.141}$ $^{.036}_{.036}$	$     \begin{array}{r}       12.5 \\       6.2 \\       12.5 \\       12.5 \\       12.5 \\       12.5 \\       12.5 \\       \end{array} $	$7.43 \\ 3.56 \\ 9.93 \\ 11.3 \\ 1.90$	$7.1 \\ 2.85 \\ 2.15 \\ 1.27 \\ 114$	$\begin{array}{c} 2.54 \\ \cdot 94 \\ 1.37 \\ 1.04 \\ 2.93 \end{array}$	$^{\cdot 110}_{\cdot 044}_{\cdot 033}_{\cdot 019}_{1\cdot 75}$	$\begin{array}{c} 2.8 \\ 3.0 \\ 1.57 \\ 1.22 \\ 39 \end{array}$	$^{0036}_{0146}$ $^{003}_{001}$ $^{001}_{85}$	$+ \cdot 020$ + $\cdot 029$ + $\cdot 096$ + $\cdot 132$ - $\cdot 84$	$4.7 \\ 1.90 \\ .46 \\ .19 \\ 110.$

TABLE	I	-Sum	mary.
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Table I shows the essential data of these and the other similar experiments in which the distance d in cm. between the plates is gradually increased.  $\Delta N$  is the difference of displacement observed, when plates were respectively charged and uncharged.  $\Delta N$  thus shows the displacement of the suspended plate in half centimeters. From  $\Delta N$  the approximate electric force (ignoring the repulsion of plates) may be computed as above,  $F'_{\rm R} = 65 \cdot 2\Delta N$ . This is given as  $F'_{\rm R}$  computed in the seventh column.

Plates were charged by aid of a storage battery to the potential shown under Vobs. (volts), in column four. From V and d, the attraction of plates  $F_{\rm R}$  may be computed, since

$$F'_{
m R} = A \, V'^{\,2} \, / \, 8 \pi d^{\,2}$$

 $A = \pi R^2$  being the area of each plate. The results are given in column six, and the F/F' in column 9.

FIG. 6.





Furthermore the potential V' may also be computed from  $F_{\rm R}$  as usual, and this is given in the fifth column.

 $F_{\rm R}$  as usual, and this is given in the fifth column. From the computed values of  $F'_{\rm R}$  since  $F'_{\rm R}$  equal to  $65.2 \times \Delta N'$ , the true value of the displacement in the absence of repulsion,  $\Delta N'$ , may be computed, the result being given in the eighth column in cm. It shows the corresponding displacement of the suspended plate in half centimeters.

The two values of  $\Delta N$  and  $\Delta N'$  now give us the displacement due to repulsion in cm.,

$$x = \left(\Delta N' - \Delta N\right) / 2$$

as shown in column 10. Again, the distance apart in cm. of the uncharged plates d' is given in the third column, being

#### d' or $d + \Delta N/2$

and found from observation directly. Finally the residual distance apart of the plates, y, if the suspended plate had taken its true displacement  $\Delta N'$  (in the absence of repulsion), is given in the eleventh column, since

$$y = \Delta N' / 2 - d'.$$

In every case, except the first, in which y is negative, the plates when charged at a distance d apart, were not under forces sufficient to put them in contact. One must observe, however, that for a distance apart y when d < y, the forces would not increase correspondingly. Only in case 5 is d = y, nearly. Thus without repulsion, the disks should have been thrown in contact when charged, in all cases. In the actual presence of repulsion, this was not the case except perhaps in the first.

The substance of these investigations is contained in column 9 where the ratios of  $F'_{\rm R}$  computed electrically and the value of  $F_{\rm R}$  computed from the given displacement  $\Delta N$  of the horizontal pendulum, are given. It is seen that the ratio

$$(F'_{\rm R}/F_{\rm R}) = (V'/V)^2$$

decreases as the charged plates are further apart (d), until at  $d > 13^{\text{om}}$ , the ratio is nearly 1:i.e., the repulsion of plates nearly vanishes when their distance apart markedly exceeds  $1^{\text{mm}}$ . Just how large d would have to be in order that  $F'_{\text{R}}/F_{\text{R}} = 1$ , I did not endeavor to find, since the suspended plate vibrates annoyingly for large distances apart. In a specially equipped laboratory and with a lighter pendulum, the sensitiveness may be indefinitely increased, particularly when the pendulum is provided with a float, while the error due to the inclination of the pier does not simultaneously increase, an obvious advantage. It seemed wise, therefore, to stop the work for the present at the point of progress reached.

Table I, however, admits of a number of preliminary estimates of the decrease of repulsion (f) with d, the distance apart of plates, for we may write,

## $f = 65.2 \times 2x = 130x$ dynes, nearly.

These values are given in column 12 of Table I and in fig. 6, with the exception of the first, which is distorted from actual contact. The second observation (2 in figure) seems to be in error for some reason not detected. The others make a compatible series. The forces found in the earlier work lay between 1.3 and 0.5 dynes, for distances of the same order, distances which were not usually the same in the two positions of the fixed disks. If we take the results in fig. 4, which are probably the best, 104 C. Barus-Repulsion of Two Metallic Disks.

 $10^{3}\Delta N = 18$  cm.,  $10^{3}d = 64$  cm., f = 1.17 dynes

the results of f and d as shown by the cross in fig. 6 fit in very well with the present data obtained from electric attraction. The repulsion therefore has throughout been found of the same order of values.

Probably the most interesting feature of these molecular atmospheres will be their bearing on the nature of voltaic contact. We may compute the pressure corresponding to the thrust f, as above, by dividing by the area A of the disks, whence p = f/324. We may then estimate the attraction of the disks per gram of air couche, at a distance h from the disk, similarly to the ordinary case of the barometric formula :

 $-dp = (p/R\tau)F(h)dh$  or  $-R\tau d(\log f)/dh = F(h),$ 

R being the gas constant,  $\tau$  the absolute temperature. Thus if one can detect the variation of f with h, the molecular attraction of the disk per gram of air should be discernible. One may anticipate its variation for different metals.

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# ART. V.—Lawsonite from the Central Coast Ranges of California; by Austin F. Rogers.

OF the new rock-forming minerals described within the last decade or two, lawsonite, a basic calcium aluminum silicate, is one of the most interesting if not important. Though usually an accessory constituent, in some cases it proves to be an essential constituent of certain rocks. The type locality of lawsonite is Tiburon Peninsula in Marin County, California, where it was found by Ransome<sup>1</sup> and by Palache<sup>2</sup> almost simultaneously. Since its discovery in 1894 it has proved to be a widely distributed mineral, for it has been observed by Franchi<sup>3</sup> in the glaucophane rocks in the Piedmont Alps, by Viola<sup>4</sup> in the diabases and gabbros of southern Italy, by Lacroix' in the glaucophane schists of Corsica and the gabbros of Corsica and New Caledonia, by Manasse<sup>6</sup> in the island of Gorgona, and by Termier' in the glaucophane schists of the department of Hautes-Alpes. In the coast ranges of California lawsonite is a fairly common constituent of the metamorphic rocks of the Franciscan series, as has been pointed out by J. P. Smith<sup>s</sup> and by Eakle<sup>®</sup>.

Lawsonite occurs in orthorhombic crystals of simple habit, which are usually tabular or prismatic. The common forms are  $m\{110\}$ ,  $c\{001\}$ ,  $b\{010\}$ , and  $d\{011\}$ , with  $mm\{110:1\overline{1}0\}$ =67° 16', and  $dd(011:0\overline{1}1)=72°53\frac{1}{2}'$ . Hillebrand and Schaller<sup>10</sup> give in addition the forms  $e\{041\}$ ,  $r\{221\}$ , and  $s\{331\}$ . The specific gravity is 3°12 and the hardness 7–8. The color is grayish-white to bluish-gray.

The optical orientation of lawsonite is a=a,  $\beta=b$ ,  $\gamma=c$ . The indices of refraction as given by Ransome' are  $n_{\gamma} = 1.684$ ,  $n_{\beta}=1.669$ ,  $n_a=1.665$ ;  $n_{\gamma}-n_a=.019$ . Basal sections are usually rhombic in outline, with first order interference colors, while the other sections are rectangular with second order interference colors. The basal sections often show polysynthetic twinning with  $m\{110\}$  as twin-plane.

Chemically, lawsonite is interesting because it corresponds to anorthite with two molecules of water added. The empirical formula is  $H_4CaAl_2Si_2O_{10}$ , as proved by the following analyses which are the only complete analyses available. The last analysis of this list (No. VI) is a new one of lawsonite from Alameda County, California, which is described beyond.

There are two characteristic kinds of occurrence of lawsonite. (1) As a secondary mineral in slightly altered or saussuritized diorites and gabbros. California, Corsica, Piedmont Alps, Gorgona, and New Caledonia. (2) As an accessory or

		I	II	III	IV Bocca	v	VI
				Tiburon, Hillebrand	Niera, Italy	Mairatale, Italy	Arroyo Mocho,
Theory		Tiburon,	Tiburon	&	Zam-	Zam-	Calif.
H4CaAl2S	Si2O10	Ransome <sup>1</sup>	Palache <sup>1</sup>	Schaller <sup>10</sup>	bonini <sup>11</sup>	bonini <sup>11</sup>	$\mathbf{Small}$
38.34	SiO <sub>2</sub>	38.10	37.32	38.45	38.37	38.21	38.10
32.44	Al <sub>o</sub> O	28.88)	95.14	31.35	32.27	31.98	32.21
	Fe <sup>°</sup> O <sup>°</sup>	0.85	35.14	0.86	0.23	$\mathbf{tr}$	nil
	FeO			0.10			$\mathbf{nil}$
	MnO			$\mathbf{tr}$			$\mathbf{nil}$
	MgO	0.53		0.12	0.18	0.22	nil
17.80	CaO	18.26	17.83	17.52	18.14	18.23	17.74
	Na <sub>2</sub> O	0.62		0.06	0.36	n. d.	
	K <sub>2</sub> Ò		· · · · ·	0.23	$\mathbf{tr}$		
	TiO			0.38			$\mathbf{nil}$
	CO						1.12
11.42	H <sub>2</sub> Ó	11.42	11.21	11.21	11.02	11.24	10.85
100.00		98.39	101.50	100.33	100.57	99.91	100.02

#### ANALYSES OF LAWSONITE

essential constituent of schists and gneisses, which usually also contain glaucophane. California, Corsica, Piedmont Alps, and Hantes-Alpes.

The opinion of J. P. Smith<sup>6</sup> that lawsonite represents the anorthite portion of plagioclase set free in the chemical readjustment incident to metamorphism is well founded. The albite portion of the plagioclase contributes to the formation of glaucophane or at times crystallizes out as albite.

Ă dimorphous (isometric) form of H<sub>4</sub>CaAl<sub>2</sub>Si<sub>2</sub>O<sub>10</sub> has been described by Cornu<sup>\*</sup> under the name hibschite. The hibschite occurs in calcareous inclusions in phonolite at Marienberg, Bohemia, and has since been found by Lacroix+ in calcareous inclusions of basalt at Ardèche in the Central Plateau, France.

With these introductory remarks, lawsonite is now described from a number of new localities in the Central Coast Ranges of California; variation in the habit is especially emphasized.

### Arroyo Mocho, Alameda County.

In a prominent outcrop of glaucophane schist alongside the road near the head of the Arroyo Mocho and about eighteen miles southeast of Livermore, Alameda County, there were found seams of lawsonite, in part as coarse fibrous masses and in part as distinct crystals in cavities. The lawsonite crystals

\* Min. petr. Mitt., vol. xxv, p. 249, 1906. † Mineralogie de la France, vol. iv, p. 705, 1910.

are about 1<sup>cm</sup> in length, 4<sup>mm</sup> in width, and 2<sup>mm</sup> thick, and in habit are prismatic in the direction of the *a*-axis. The forms are  $d\{011\}$ ,  $m\{110\}$ , and  $c\{001\}$ , as represented in figure 1. This habit is so different from that of the Tiburon crystals that it was not at first suspected to be lawsonite. There is distinct cleavage parallel to m and to c. The optical orientation is  $a=a, b=\beta, c=\gamma$ .



FIG. 1. Lawsonite from Arroyo Mocho, Alamedo County.
FIG. 2. Lawsonite from Calaveras Valley, Santa Clara County.
FIG. 3. Lawsonite from Calaveras Valley, Santa Clara County.

An analysis of this lawsonite was made by Mr. H. L. Small under the writer's direction. The results, which are the average of two, are given in column I. The lawsonite is pure except for a little calcite, which is probably an alteration product. Subtracting the carbon dioxide and an equivalent amount of lime and recalculating to 100 per cent, we have the figures of column II, while the theoretical percentages for  $H_4CaAl_2$  $Si_2O_{10}$  are given in column III.

	I	II	III
Sio,	38.10	<b>38</b> .70	38.34
Al <sub>2</sub> Õ,	32.21	32.60	32.44
CaO	17.74	17.70	17.80
MnO	nil		
MgO	$\mathbf{nil}$		
TiO,	$\mathbf{nil}$		
CO,	1.12*		
H <sub>2</sub> Ó	10.85*	11.00	11.42
Total	100.02	100.00	100.00

## Analysis of Lawsonite from Arroyo Mocho.

\* The water was determined by the Penfield tube method, while combined water and carbon dioxide were determined by loss on ignition.

#### Calaveras Valley, Santa Clara County.

Lawsonite crystals were found in seams of glaucophane-schist outcrop on the Sunol road in the northern end of Calaveras Valley. The crystals have the habit of figure 2 with the forms  $d\{011\}$ ,  $m\{110\}$ ,  $c\{001\}$ , and  $b\{010\}$ . The crystals are grayishwhite, measure from  $3^{min}$  to  $1\frac{1}{2}^{cm}$  in the direction of the *b*-axis, and greatly resemble some of the Tiburon crystals. The glaucophane-schist itself contains lawsonite, which appears to be more abundant near the seams.

Loose bowlders of glaucophane-schists from the Arroyo Hondo at the northern end of Calaveras Valley contain acicular crystals in cavities and seams. The crystals, which measure only  $2^{mm}$  in length, are elongated in the direction of the *a*-axis.

Fig. 4.



The forms present are  $c\{001\}$ ,  $m\{110\}$ ,  $b\{010\}$ , and  $d\{011\}$ , as represented in fig. 3. The optical orientation for most of the crystals is a = a,  $b = \beta$ ,  $c = \gamma$ , but some of the crystals extinguish on the (001) face in two approximate halves as indicated by fig. 4. In one part the extinction is parallel and in the other part it is about 5° to the long edge of the crystal. This possibly indicates that lawsonite is monoclinic like carpholite (H<sub>4</sub>MnAl<sub>2</sub>Si<sub>2</sub>O<sub>10</sub>), which is chemically analogous to lawsonite. According to Lévy and Lacroix\* the extinction angle of carpholite is 3° to 5°.

#### Mt. Hamilton Region, Santa Clara County.

FIG. 4. Lawsonite from Calaveras valley, Santa Clara Co. Minute lawsonite crystals from a narrow seam in a garnetiferous glaucophane-schist (from the Mt. Hamilton region in Santa Clara County (but exact locality unknown) are represented by fig. 5. The habit is tabular with the

forms  $e\{001\}$ ,  $d\{011\}$ , and  $m\{110\}$ . Optically they resemble the acicular crystals from Calaveras Valley.

#### Northeastern Santa Clara County.

Specimens of glaucophane-schist from the 3250 peak of the Mt. Hamilton topographic sheet of the United States Geological Survey, which is about ten miles northeast of Mt. Hamilton, contain acicular crystals of lawsonite in seams and cavities. The crystals are 3 or  $4^{mm}$  in length and are imperfect crystals with indistinct faces arranged in parallel position or in subradiating groups. There is a fairly good cleavage parallel to the length of the crystals. Fragments are prismatic with parallel

\* Les Minéraux des Roches, p. 164.

extinction and the elongation is parallel to the fast ray. From these tests it is evident that the crystals are prismatic in the direction of the *a*-axis. A rough water determination gave 12.97 per cent.

#### Region east of Mt. Hamilton.

Specimens of vein material in a metamorphic rock collected in the region east of Mt. Hamilton show small 3<sup>mm</sup> acicular crystals of lawsonite in a matrix of quartz. In thin sections the lawsonite appears as in fig. 8. Cross-sections are irregular or rhombic with the fast ray parallel to the long diagonal



FIG. 5. Lawsonite from Mt. Hamilton region.

FIG. 6. Lawsonite from Alameda County.

FIG. 7. Lawsonite from Colorado Creek, Santa Clara County.

while longitudinal sections are elongate, rectangular with more or less frayed ends and are in part parallel to the slow ray, in part parallel to the fast ray. Hence the crystals are prismatic in the direction of the *a*-axis with habit something like fig. 1. The optical orientation is  $a = a, b = \beta, c = \gamma$ . The double refraction  $(n_{\gamma} - n_a)$ , determining the thickness of the slide by taking the highest interference color of the quartz, is  $\cdot 022$ , which is a little higher than the value ( $\cdot 019$ ) obtained by Ransome.<sup>1</sup>

#### Southeastern Alameda County.

Bowlders of a massive lawsonite-chlorite rock were found in the extreme southeastern corner of the Tesla topographic sheet of the United States Geological Survey. The lawsonite occurs in tabular crystals of  $5^{\text{mm}}$  diameter and  $\frac{1}{2}^{\text{mm}}$  thickness. The forms are  $c\{001\}, m\{110\}, \text{ and } b\{010\}$ .

The habit is pseudo-hexagonal due to equal development of m and b, though the angle  $(110:1\overline{1}0)$  is 67°. The optical orientation is  $a = a, b = \beta, c = \gamma$ . The rock contains lawsonite and chlorite with subordinate titanite in minute granular crystals.

### Lawsonite from Colorado Creek, Santa Clara County.

This locality for lawsonite is on Colorado Creek just south of the divide between the Arroyo Mocho and Colorado Creek in the northeastern part of the Mt. Hamilton topographic sheet. At this place Mr. R. V. Anderson found a large bowlder of a chlorite-lawsonite rock. The lawsonite occurs in well-defined crystals of rhombic tabular habit (fig. 7) with the forms  $c\{001\}$ ,  $m\{110\}$ , and occasionally  $b\{010\}$ . The crystals appear almost black on account of the inclusions of dark green chlorite, but on weathered specimens the lawsonite is opaque white and stands out in bold relief. There is distinct cleavage parallel to  $b\{010\}$  and to  $m\{110\}$ . Some of the basal sections show fine polysynthetic twin-lamellæ with  $\{110\}$  as twin-plane.

In addition to lawsonite and chlorite this rock contains muscovite and titanite and also a little albite in veins. An analysis of the rock was made by Mr. H. F. Humphrey, formerly assistant in mineralogy at Stanford University, with the following results:

,		Titanite	Lawsonite	Muscovite	Chlorite
SiO,	38.12	1.02	14.41	10 <b>·9</b> 9	11.70
Al <sub>2</sub> Õ <sub>3</sub>	25.81		12.54	9.43	4.04
Fe <sub>2</sub> O <sub>3</sub>	0.13			· · · · · · ·	
FeO	9.86				9.86
MgO	6.20				6.20
CaO	7.62	0.93	6.69		
Na <sub>2</sub> O	0.20			0.20	
K <sub>2</sub> Õ	2.11			2.11	
$H_{2}O -$	0.11				
$H_{2}O +$	8.16		4.29	1.09	2.78
TiO <sub>2</sub>	1.35	1.35			
	100.27	3.36	37.93	24.02	34.88

The percentages of the mineral may be calculated from the chemical analysis. All of the titanium oxide and an equivalent amount of lime go to make the titanite. The remainder of the lime goes to the lawsonite. All the potash and soda go to the muscovite, which may be assumed to be  $H_2(K,Na)Al_3$  (SiO<sub>4</sub>)<sub>3</sub>. All the magnesia and ferrous oxide, and the remainder of the silica, alumina, and water belong to the chlorite.

Recalculating to 100 per cent, we have the following percentage composition of the chlorite:

SiO .	 	 	33.2
Al <sub>o</sub> Ó.	 	 	11.6
Fe <sup>2</sup> O <sup>*</sup>	 	 	28.3
MgO	 	 	18.6
HO.	 	 	8.0
2			
			100.0

This is close to an analysis of diabantite from Farmington, Conn., analyzed by Hawes.\* The chlorite in this rock, it \*Dana, System of Mineralogy, 6th edition, p. 659. should be emphasized, is not an ordinary alteration product but a recrystallized product of metamorphism.

This lawsonite-chlorite-muscovite rock mass probably represents an original gabbro or diabase. The fact that the chlorite is a diabantite chemically similar to that found in diabase points to the igneous origin.

A similar rock consisting of lawsonite, chlorite, muscovite, and titanite was collected by Mr. R. B. Moran at the Fillmore ranch in San Luis Obispo County. The lawsonite occurs in thin plates 1<sup>mm</sup> thick and 6 to 8<sup>mm</sup> in diameter. In a thin



FIG. 8. Lawsonite (l) in quartz (q), Mt. Hamilton region. FIG. 9. Lawsonite in slightly altered diorite, Smith Creek, Santa Clara County (l, lawsonite, h, hornblende, p, plagioclase (andesine), g, glaucophane).

rock slide the lawsonite appears principally as long rectangular sections with parallel extinction. One elongated section has the peculiar optical properties illustrated by fig. 4. Polysynthetic twin-lamellæ are present in some crystals.

Eakle<sup>°</sup> also mentions a bowlder of lawsonite chlorite rock with muscovite and titanite from North Berkeley.

### Smith Creek, Santa Clara County.

In thin sections of a hornblende diorite collected by Mr. Stephen Taber on Smith Creek, near the Smith Creek Hotel, small crystals of lawsonite were identified. This rock is made up of dark hornblende in a matrix of greenish-gray feldspar. The axial colors of the hornblende are: a = pale greenishyellow;  $\beta =$  deep green;  $\gamma =$  medium green. Absorption  $\beta > \gamma > a$ . The hornblende is bordered on the ends by a thin fringe of glaucophane in parallel position (fig. 9). The plagio-

clase is cloudy but shows albite twinning. Measurements of the extinction angle indicate that it is andesine, about Irregularly distributed through the feldspar are Ab, An,. small, elongated lawsonite crystals with parallel extinction, bright interference-colors, and elongation parallel to the fast ray. From a study of the cross-sections it is evident that the lawsonite crystals have a habit similar to fig. 3. This rock is only slightly altered and we have here the beginning of saussuritization of the feldspars. This is an excellent example of the chemical readjustment as explained by J. P. Smith.<sup>\*</sup> The soda end of the plagioclase forms glaucophane while the lime end forms lawsonite.

Slightly altered igneous rocks of this type seem to be rather common in the Mt. Hamilton region. J. P. Smith<sup>\*</sup> mentions a quartz-diorite from Oak Ridge, Santa Clara County, in which the original minerals are oligoclase, katophorite-like hornblende, and quartz. The secondary minerals are lawsonite and crossite.

### Lawsonite-glaucophane Schists.

In addition to the localities mentioned in this paper and by J. P. Smith<sup>\*</sup> in his valuable paper on the glaucophane-bearing rocks, I have studied lawsonite-bearing glaucophane-schists from the following localities:

Hubbard Ranch, Isabel Creek, Santa Clara Co. Isabel Valley, Santa Clara Co. L'Ecuyer's Ranch, Arroyo Mocho, Alameda Co. Southern end of Tesla topographic sheet, Alameda Co. Cedar Mountain, Alameda Co. Yager, Humboldt Co. (collected by Mr. W. G. Cooper).

Thelen<sup>12</sup> also mentions lawsonite as a constituent of the glaucophane schists of North Berkeley, California.

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Stanford University, California, Jan., 1914.

## ART. VI.—On the Preparation and Hydrolysis of Ethyl Hydracrylate; by W. A. DRUSHEL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.-cclxiii.]

HYDRACRYLIC acid is a well-known substance and has been prepared by several methods; its esters, however, have received but little attention. In Beilstein's Handbuch the ethyl ester alone is mentioned in connection with Klimenko's attempt to prepare paracrylic acid. Only three references are given to the ethyl ester in Richter's Lexikon and of these but one deals with the direct preparation of the ester. Apparently in no former investigation has hydracrylic ester been prepared by the esterification of hydracrylic acid, nor was the ester obtained in pure condition by any of the methods described in the literature. It seemed desirable therefore to prepare, if possible, hydracrylic ester by the direct esterification of hydracrylic acid in order to obtain the ester in pure condition for the purpose of determining its properties and supplying additional hydrolysis data for the series of esters studied in this laboratory.

Preparation of the Ester: (a) Method of Klimenko.\* Klimenko obtained what he called paracrylic acid by repeatedly evaporating hydracrylic acid with concentrated hydrochloric acid. He then heated 3 grams of this acid with an excess of absolute alcohol at 150° and obtained an ester which boiled at 185° to 190° and which he believed to be ethyl hydracrylate. Ethyl hydracrylate, however, decomposes below 185° when heated at ordinary pressure. In attempting to repeat Kli-menko's work the author was unable to prepare the so-called paracrylic acid by the method described. Baeyert did not believe that Klimenko had succeeded in preparing paracrylic acid, (C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>), but rather that Klimenko's acid was an unsaturated dibasic acid of the formula C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>. If Baeyer's observation was correct Klimenko's ester could not have been hydracrylic ester.

(b) Method of Curtius and Müller.<sup>‡</sup> These investigators obtained impure ethyl hydracrylate by converting beta-chlorpropionic ester into beta-aminopropionic ester hydrochloride and treating this with nitrous acid. The ester contained a little chlorpropionic ester as an impurity, from which it could not be freed by fractionation. The crude ester which they obtained boiled at 80° to 84° at 12<sup>mm</sup> pressure, or at 170° to 175° under ordinary pressure. The method is obviously not

\* Klimenko, Rafalowicz, Jour. Russ. Chem. Soc., xxvi, 412.
† Baeyer, Ber. Dtsch. Chem. Gesellsch., xviii, 680.
‡ Curtius and Müller, Ber. Dtsch. Chem. Gesellsch., xlx, 850; xxxvii, 1276.

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, No. 229.-JANUARY, 1915.

suitable for the preparation of the ester in sufficiently pure condition to study its properties and rate of hydrolysis.

(c) Method of Blaise and Maire.\* Blaise and Maire passed into glacial acetic acid at 0° the formaldehyde vapor obtained by the depolymerization of trioxymethylene. The saturated acetic acid solution was then allowed to warm up slowly, resulting in a polymer of formaldehyde less complex than trioxymethylene. This polymer was condensed with bromacetic ester in the presence of zinc in a mixture of equal parts of absolute alcohol and ethyl acetate. They obtained a 40 per cent yield of ethyl hydracrylate whose boiling point was given as 81° at 13<sup>mm</sup> pressure. It is to be observed that this boiling point is about the same as that given for Curtius and Müller's admittedly impure ethyl hydracrylate.

(d) Direct Esterification Method. In view of the instability of beta-oxyacids on heating in the presence of mineral acids, and of the work of Bogojawlensky and Narbut<sup>+</sup> on the use of anhydrous copper sulphate to facilitate esterification in the presence of acid catalyzers, and the more recent work of Clemmensen and Heitman<sup>‡</sup> on the use of anhydrous copper sulphate in the esterification of certain oxyacids in the absence of any catalyzing acid, it seemed reasonable to expect this procedure to be applicable for the preparation of pure ethyl hydracrylate. The work of preparing ethyl hydracrylate resolved itself into two parts, 1st, the preparation of a sufficiently large amount of pure hydracrylic acid, and 2d, the esterification of the acid.

1. The preparation of hydracrylic acid.—Of the several methods described for the preparation of hydracrylic acid the method using glycerine as a starting-out material, with certain modifications, was found to be the most expedient for preparing the pure acid in considerable quantity. The modifications of former methods which will be pointed out resulted in increasing the yield and purity of the hydracrylic acid.

A kilo of glycerine was mixed with a liter of water and oxidized in 200<sup>cm3</sup> portions by fuming nitric acid in tubes about 20<sup>mm</sup> in internal diameter kept cold by running water, according to the procedure outlined by Mulder.§ After the oxidation was complete the liquid was concentrated in 400<sup>cm3</sup> portions on the steam bath to remove any dissolved nitrous acid. On cooling some oxalic acid crystallized out. The filtrates from the several 400<sup>cm3</sup> portions were combined and treated with a little more than enough calcium carbonate to precipitate out the dissolved oxalic acid as calcium oxalate, which was removed by filtration. The filtrate was diluted with water to 3 liters

<sup>\*</sup> Blaise and Maire, C. r. d. l'Acad. des Sciences, cxlii, 215-17.

<sup>. †</sup> Bogojawlensky and Narbut, Ber. Dtsch. Chem. Gesellsch., xxxviii, 3344.

t Clemmensen and Heitman, Am. Chem. Jour., xl, 319.

<sup>§</sup> Mulder, Ber. Dtsch. Chem. Gesellsch., ix, 1902.

and heated to about 80°. The hot solution was neutralized with calcium carbonate, making use of mechanical stirring to facilitate the solution of the carbonate. The solution was allowed to stand over night for the main portion of the calcium glycerate to crystallize out. This first crop of calcium glycerate after washing with a little cold water was sufficiently pure for further use. The mother liquor, after making faintly acid to prevent darkening on heating, was concentrated on the steam bath and set aside to crystallize. After recrystallizing this second crop of calcium glycerate it was sufficiently pure, and was added to the first crop. The calcium glycerate so prepared was dissolved in hot water and treated with the theoretical amount of dissolved oxalic acid, the calcium oxalate was filtered off and the filtrate concentrated on the steam bath to a specific gravity of 1.26, containing about 61 per cent of glyceric acid. This is the most favorable concentration for converting glyceric acid into beta-iodopropionic acid by the action of phosphorus iodide.

For the preparation of beta-iodopropionic acid a modification was introduced into the method of Wislicenus\* and Erlenmeyer, + making use of solid yellow phosphorus instead of the carbon disulphide solution, whereby at last 90 per cent of the glyceric acid was converted into the iodopropionic acid. One hundred grams of iodine were placed into a 750° round-bottom flask and covered with 100 grms. of 61 per cent aqueous glyceric acid. Then 15 grms. of yellow phosphorus were added during the course of five minutes in pieces of about 1 grm. each, shaking the flask after the addition of each piece and cooling the flask by immersing it in a cold water bath from time to time. The flask was next connected with a condenser tube to serve as a reflux condenser, and the mixture cautiously warmed on a water bath to start the reaction of the phosphorus iodide with the glyceric acid. The reaction soon tends to become violent with the loss of large quantities of hydriodic acid. In order to prevent the loss of hydriodic acid as far as possible, the reaction was moderated by immersing the flask in cold water for a few minutes from time to time. After the first vigorous reaction was over the mixture was heated on the boiling water bath for half an hour, poured into a beaker, covered with a watch glass and set aside over night to crystallize. The crystals of pure beta-iodopropionic acid were then filtered off with suction, washed with a little cold water, the filtrate boiled for an hour with a reflux condenser and again set aside to allow more beta-iodopropionic acid to crystallize out. The two crops of crystals were combined and

> \* Wislicenus, Ber. Dtsch. Chem. Gesellsch., viii, 1207. † Erlenmeyer, Ann. Chem. Pharm., cxci, 284.

recrystallized from a little hot water, yielding white pearly plates of pure beta-iodopropionic acid.

To prepare the sodium salt of hydracrylic acid a modification was introduced into the method of Wislicenus\* for the conversion of beta-iodopropionic acid into hydracrylic acid by the action of freshly prepared silver oxide. Sokolow+ observed that when a water solution of beta-iodopropionic acid is boiled with freshly prepared silver oxide the iodine is quickly fixed as silver iodide and that in solution are dihydracrylic acid, C.H.,O., and an isomer of this acid besides the hydracrylic acid sought. Moldenhauert also made the observation that considerable lactic acid is formed in this procedure. In order to avoid the formation of lactic acid and the acids identified by Sokolow, Wislicenus heated his solution below 100° while fixing the iodine by means of silver oxide. The silver which combined with the hydracrylic acid formed in the reaction he removed by means of hydrogen sulphide, neutralized the acids in solution with sodium carbonate and evaporated to complete dryness. From the dry mixture of sodium salts Wislicenus extracted sodium hydracrylate with boiling 95 per cent alcohol, leaving in the residue the sodium salts of Sokolow's acids.

It was found preferable to modify this procedure by neutralizing the beta-iodopropionic acid with sodium carbonate. and then removing the iodine by acting upon a concentrated solution of sodium beta-iodopropionate with a slight excess of freshly prepared silver oxide at room temperature, making use of mechanical stirring during the process of replacing the iodine by the OH group. To remove completely the iodine from the sodium salt of 400 grms. of beta-iodopropionic acid by this procedure required about two hours, but the resulting sodium hydracrylate was apparently free from the salts of the acids formed by the older methods and identified by Sokolow and others. After the complete fixation of the iodine as indicated by no further change in the color of silver oxide when added to the solution, the precipitated silver iodide was filtered off and the filtrate evaporated to complete dryness over the steam bath. It is important that the sodium hydracrylate should be evaporated to complete dryness in order to be able to purify the salt by crystallization from 95 per cent alcohol. The dried residue of sodium hydracrylate was dissolved in boiling 95 per cent alcohol, and allowed to crystallize out on The residue of sodium salt was completely dissolved cooling. by the hot alcohol, indicating the absence of the sodium salts of Sokolow's acids. The crystallized sodium hydracrylate was treated with a little less than the theoretical amount of dilute

+ Sokolow, ibid., cl, 167.

<sup>\*</sup> Wislicenus, Ann. Chem. Pharm., clxvi, 10.

<sup>‡</sup> Moldenhauer, ibid., clxvi, 10.

(1:3) sulphuric acid in the cold. The excess of water was then evaporated off on the steam bath, the hydracrylic acid was extracted from the residue of sodium sulphate with absolute alcohol and the alcoholic solution of hydracrylic acid, free from sulphuric acid, was used in the esterification experiments to be described.

2. The esterification of hydracrylic acid.—In the preparation of one sample of hydracrylic acid a very slight excess of sulphuric acid was used in liberating the hydracrylic acid. The hydracrylic acid without purification from the trace of sulphuric acid was esterified by boiling with a large excess of absolute alcohol for twelve hours without the addition of any catalyzing acid. About two-thirds of the acid was esterified, but a relatively large proportion of the resulting ester proved to be acrylic ester. A second sample of hydracrylic acid free from sulphuric acid was esterified by boiling with a large excess of absolute alcohol in the presence of anhydrous copper sulphate prepared by the gentle ignition of crystallized copper sulphate, but not freed from the traces of sulphuric acid formed in the process of dehydration. Here again the esterification proceeded rapidly until about 70 per cent of the acid was esteri-fied, but as before, the result was a mixture of acrylic and hydracrylic esters. It seemed, therefore, necessary to avoid even very small amounts of mineral acids in the esterification of hydracrylic acid in order to prevent the formation of acrylic ester.

Wislicenus\* suggested the use of the vapor from boiling absolute alcohol as an efficient dehydrating agent in esterification. The inefficiency of absolute alcohol alone as well as that of absolute alcohol vapor passed through the reaction mixture and the superiority of anhydrous copper sulphate as a dehydrating agent are shown in the following experiment: Thirtytwo grams of hydracrylic acid free from sulphuric acid were first boiled, with a reflux condenser, with 200cm3 of absolute alcohol for three hours, giving 9.4 per cent of the theoretical yield of ester; at the end of six hours 17 per cent of the acid was esterified. Then the reaction flask was heated at 110° and absolute alcohol vapor passed through the reaction mass, giving at the end of two hours 40 per cent of ester, and after two hours more only 42 per cent of ester. The current of absolute alcohol vapor was then discontinued and about 30 grms. of anhydrous copper sulphate, free from sulphuric acid, were added and the reaction mixture gently boiled, giving after three hours 74 per cent of ester, and after three hours more 83 per cent of the acid was esterified. The ester formed was found to be hydracrylic ester free from acrylic ester.

\* Wislicenus, Ann. Chem. Pharm., clxiv, 181.

In another experiment 26.4 grms. of hydracrylic acid were gently boiled with 200<sup>cm<sup>3</sup></sup> of absolute alcohol in the presence of about 50 grms. of anhydrous copper sulphate freed from sulphuric acid, by means of absolute alcohol. At the end of three hours 66 per cent of the acid was esterified, at the end of six hours 71.4 per cent; at the end of nine hours 83 per cent of the theoretical amount of ester was formed and the boiling was discontinued. To remove the unesterified hydracrylic acid in this and in the previous experiment a little less than the theoretical amount of anhydrous sodium carbonate was added to the esterification mixture and the excess of alcohol was distilled off on the water bath. The hydracrylic ester was extracted from the residue with dry ether and the ether distilled off on a warm water bath, finally heating the water bath to boiling. From the two experiments 53 grms. of crude hydracrylic ester were obtained which on fractionation under diminished pressure yielded 45 grms. of ethyl hydracrylate boiling at 95.5° to 96° at a pressure of 20<sup>mm</sup> to 22<sup>mm</sup>. The saponification equivalent of the ester so prepared was found to be 119, and the saponification equivalent calculated from the formula  $CH_{2}OH.CH_{2}.COOC_{2}H_{5}$  is 118. When the ester was dissolved in an equal volume of water and was treated with phosphorus and iodine both beta-iodopropionic acid and betaiodopropionic ester were obtained. The ester at 20° has a density of 1.059, and like lactic ester is soluble in water in all proportions. These properties were considered sufficient to identify the ester as pure ethyl hydracrylate. The ester has a faint ethereal odor, much less pronounced than that of lactic ester. It is unusually stable in water solution, hydrolyzing very slowly in the absence of a catalyzing acid or alkali.

Hydrolysis of the Ester.—Two and a half cubic centimeters of ethyl hydracrylate were dissolved in  $250^{\text{cm}s}$  of decinormal hydrochloric acid and hydrolyzed at  $25^{\circ}$ ,  $35^{\circ}$  and  $45^{\circ}$ . The course of the reaction was followed by titrating  $25^{\text{cm}s}$  portions of the mixture at intervals as fully described in previous papers.<sup>\*</sup> The results of the velocity measurements are recorded in Table I. In Table II are recorded summary results obtained partly simultaneously with the reaction velocity measurements of ethyl hydracrylate and taken partly from the results obtained by Dean.<sup>†</sup> A striking contrast appears between the effects of alpha hydroxyl and beta hydroxyl on the velocity of hydrolysis of the esters in acid solution. This retarding effect of the beta hydroxyl on the hydrolysis velocity of the ester was predicted by Dean.<sup>‡</sup> for ethyl hydracrylate from his study of

\* This Journal, xxxv, 486, 1913.

† Dean, this Journal, xxxv, 486, 1913.

‡ Dean, loc. cit.

the hydrolysis of lactic ester, glyceric ester and the esters of the oxybutyric acids. From an examination of the velocity constants of ethyl propionate, ethyl lactate, ethyl hydracrylate and ethyl glycerate in Table II it is obvious that the effects of alpha and beta hydroxyl groups on the hydrolysis velocity are independent of each other. By comparing the constants for ethyl propionate and ethyl lactate it is seen that alpha hydroxyl here produces a slight accelerating effect at 25° which, however, falls off at the higher temperatures. The beta hydroxyl produces a very marked retardation in the hydrolysis velocity as will be seen by comparing the constants for ethyl propionate and ethyl hydracrylate. This effect does not fall off materially at the higher temperatures, as is shown by the fact that the ratio of the constants of these two esters is very nearly the same at each temperature at which velocity measurements were made. The combined effect of alpha and beta hydroxyl groups on the hydrolysis velocity is shown in the constants for ethyl glycerate. If the slight accelerating effect of alpha hydroxyl and the very marked retarding effect of beta hydroxyl are both taken into account we would expect the constants for ethyl glycerate to be but slightly larger than those of ethyl hydracrylate at 25°, the percentage of difference falling off slightly at the higher temperature. This expectation is fully borne out by the experimental results. At 25° the constants for ethyl glycerate is 13.5 per cent larger than that of ethyl hydracrylate, at 35° it is 7.9 per cent larger and at 45° the difference is but 2.5 per cent. The velocity constants in Tables I and II were all calculated from the usual titration formula for first order reactions. The temperature coefficient for ethyl hydracrylate is 2.46 for 25° to 35°, and 2.44 for 35° to 45°.

Ethyl hydracrylate was also hydrolyzed in N/80 sodium hydroxide solution at  $0^{\circ}$  and at  $25^{\circ}$ , and the course of the reaction followed by the titration method fully described in Dean's paper\* on the saponification of the esters of other oxyacids. These results are recorded in Table III, and are in accord with the results obtained for the esters of other oxyacids.

Summary: 1. Hydracrylic acid may be conveniently prepared from glycerine by introducing the following modifications into the older methods: oxidation of glycerine by fuming nitric acid and formation of the calcium salt instead of the lead salt; liberation of the glyceric acid by means of oxalic acid and conversion into beta-iodopropionic acid with iodine and solid yellow phosphorus instead of a carbon disulphide solution of phosphorus; neutralization of the beta-iodopropionic acid with sodium carbonate before removal of the iodine by

\* Dean, this Journal, xxxv, 605, 1913.

TABLE I-ETHYL HYDRACRYLATE.

Hydrolysis in Decinormal Hydrochloric Acid.

	$25^{\circ}$	$35^{\circ}$	$45^{\circ}$
Time of reaction in minutes	7240	2840	1390
Velocity constants	10⁵K	10°K	$10^{5}$ K
J	16.6	39.9	98.0
	16.6	39.8	98.6
	16.4	41.4	100.3
	16.0	40.4	97.9
	16.1	40.5	98.6
	16.6	39.3	98.9
	15.8	41.0	97.3
		· · · · ·	
Averages	16.3	40.4	98.5
Averages of duplicate series	16.2	40.9	99.0

TABLE II-OXYPROPIONIC ESTERS : SUMMARY.

Hydrolysis in Decinormal Hydrochloric Acid.

Temperature	Ethyl propionate	Ethyl lactate	Ethyl hydracrylate	Ethyl glycerate
	10⁵K	$10^{5}\mathrm{K}$	$10^{5}\mathrm{K}$	$10^{5}\mathrm{K}$
$25^{\circ}$	$\begin{cases} 71.2 \\ 71.6* \end{cases}$	76·1 74·4*	$16.3 \\ 16.2$	18.5*
$35^{\circ}$	∫ 177·1 } 179·0*	$177.5\ 179.0^*$	40·4 40·9	43.6*
45°	$\left\{ \begin{array}{c} 405.3 \\ 406.0* \end{array} \right.$	396.6 396.0*	$98.5 \\ 99.0$	101.0*

\* Determined by Dean, this Journal, xxxv, 486, 1913.

TABLE III-ALKALINE HYDROLYSIS IN N/80 SODIUM HYDROXIDE.

Ethyl Hydracrylate				Summary						
Temper-	0°	25°	T	Ethyl	Ethyl	Ethyl hydra-	Ethyl			
Time Constant	30 min. K	12 min. K	1	K	K	crylate K	cerate K			
	1.86	10.6	$0^{\circ}$	1.16*	14.6*	1.83	9.02*			
	1.63	11.0	$25^{\circ}$	5.94*	63.7*	10.2	67.3*			
	1.93	10.6								
	1.81	9.7								
	1.85	10.8								
	1.87	9.5	* ]	Taken from	m Dean's tables, xxxv, 608.					
	1.82	9.0	this	Journal, x						
Average	es 1.83	10.2								

the action of silver oxide; substitution of hydroxyl for iodine in beta-iodopropionic acid by acting on a concentrated solution of the sodium salt in the cold with silver oxide, using mechanical stirring, instead of treating the hot dilute solution of the free acid with silver oxide.

2. Hydracrylic acid free from a mineral acid may most conveniently be esterified by boiling with an excess of absolute alcohol in the presence of anhydrous copper sulphate free from sulphuric acid.

3. Hydracrylic ester boils at  $95^{\circ}$  to  $96^{\circ}$  under a pressure of  $20^{\text{mm}}$  without decomposition, but with decomposition at ordinary pressure. The ester has a density of 1.059 at  $20^{\circ}$  and is soluble in water in all proportions, but is hydrolyzed only very slowly by water in the absence of a catalyst.

4. On hydrolysis in the presence of an acid catalyst the beta hydroxyl shows a very marked retarding effect on the velocity of the reaction, while in alkaline hydrolysis the beta hydroxyl produces a distinct accelerating effect.

#### SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. The Coal Tar Chemical Industry. - A committee of the New York Section of the American Chemical Society has made a report upon the conditions and needs involved in the enlargement of the coal-tar dye industry in the United States. They have found : I. Prior to the hostilities, domestic chemical industry was utilizing and exploiting every reasonable opportunity to its fullest extent. II. Since the outbreak of hostilities domestic industry has increased its output just as fast as physical means could be provided and physical obstacles overcome. III. Since the outbreak of hostilities, domestic plants that had heretofore been shut down or partly dismantled because of disastrous foreign competition are said to have resumed operations with caution. IV. That a 30 per cent duty on some coal-tar dyes for over 30 years has not produced a real coal-tar dye industry in this country. The committee submits its conclusions as follows : A. To prevent the unfair underselling alleged to be practiced by foreigners in this country, the adoption of an effective antidumping clause. B. The so-called coal-tar intermediaries which are the basis of the coal-tar chemical industry, inclusive of explosives, medicinals and dyestuffs, should be assessed one-half of whatever the finished dyes are taxed for tariff purposes : all coaltar dyes without exception should be taxed alike, namely 30 per cent *ad valorem* and  $7\frac{1}{2}$  cents per pound specific.

Mr. BERNARD C. HESSE, chairman of the committee mentioned above, has given independently an outline sketch of the industry of the coal-tar dyes. This is exceedingly interesting, as it gives many statistics of the magnitude and complexity of the German industry, and much information in regard to its development and success. The opinion is expressed that the development of this industry in the United States is possible by the hardest kind of work, if we wish to pay the price.—Jour. Indus. and Eng. Chem., vi, 972, 1013. H. L. W.

2. The Freezing-Point of Milk.—It was observed by Beckmann twenty years ago that the freezing-point of pure cows' milk is very constant, and many investigations since that time have confirmed this result, showing the point to be between -0.55 and -0.56° C. The widely varying fat in milk, not being in solution. does not affect the freezing-point, while the casein, another variable constituent, has little or no effect, on account of its very high molecular weight and colloidal character. HENDERson and MESTON have given an account of the application of this test to the control of purity. The legal standard for milk in Queensland, Australia, provides that its freezing-point should not be higher than 0.55° C. below zero, in addition to requirements in regard to fat and other solids. This appears to be the first application of freezing-point to the public control of milk, and it has been found to give reliable results in detecting the addition of water. - Chem. News, cx, 259. H. L. W.

3. Chemical Technology and Analysis of Oils, Fats and Waxes, by Dr. J. LEWKOWITSCH. Fifth edition in three volumes. Edited by G. H. WARBURTON. Vol. I, 8vo, pp. 668. London, 1913 (Macmillan and Co.,—Theappearance of an entirely rewritten and enlarged fifth edition of this standard work is to be particularly welcomed at the present time on account of the great developments that have been made in the industry of oils and fats during the last few years. The particularly important matter is the practical transformation of the oils into more valuable fats by hydrogenation. The author remarks in his preface that whereas a decade or two ago chemical analysis pointed out the way to technical development, and purely scientific discoveries appeared to have comparatively little influence on the progress of these industries, the order is now reversed. Pure science has now stepped ahead and it is now the turn of analytical chemistry to follow in the wake of progress and to detect in the finished article the achievements of technical work.

Nearly one-half of the first volume under consideration is devoted to an elaborate description of the oils, fats, and waxes their classification, saponification, and constituents—while the remainder of the book gives a very full treatment of the physical and chemical methods used in the analysis of these substances. The book is indispensable to those who are interested in this difficult branch of analytical chemistry, and it is also of great value to chemists desiring general information in regard to these important substances. H. L. W.

4. A Laboratory Manual of Qualitative Chemical Analysis; by A. R. BLISS, JR. 8vo, pp. 244. Philadelphia, 1914 (W. B. Saunders Company).—This text-book is intended for the use of students of medicine, pharmacy and dentistry. As there are many blank pages left for the use of students in making notes, it is not as extensive in its printed contents as its size would indicate. However, it is by no means a brief treatise, and it appears to cover the intended ground in a very satisfactory manner. It gives the analytical processes in tabular form together with rather full descriptions of the tests and operations. In connection with each element its important compounds are mentioned, particularly those included in the U. S. Pharmacopæia. The book pays practically no attention to chemical equations, although the formulas of the compounds are given. H. L. W.

5. Absorption and Resonance of Helium.-The recent experimental investigation of the infra-red lines of helium by F. PASCHEN has brought to light a number of interesting and important facts. The assemblage of apparatus used comprised thermopiles, interferometers, absorption screens, etc., which do not require special notice in this place. On the other hand, the method which Paschen has perfected for purifying helium merits attention. The successful study of the phenomena of absorption and resonance exhibited by helium required an unusually high degree of purity since the slightest traces of impurities, especially of hydrogen, decrease the absorption. The ordinary methods of purification do not suffice. Helium which has been allowed to remain for a long time in contact with charcoal cooled by liquid air is not pure enough. Paschen's process consists in introducing into the quartz vacuum-tube small quantities of pure oxygen derived electrolytically. At the same time the tube is excited with a "constant" current. The oxygen soon vanishes and with it all other impurities. By repeated additions of oxygen a degree of purity of helium is attained which corresponds to a maximum of absorption. The gas maintains its extreme purity, for a relatively long time, when produced in quartz tubes provided with aluminium electrodes which have been heated red-hot in vacuo. When the absorption begins to decrease, the tube can be brought back to experimental perfection by the introduction of a little more pure oxygen. The author says that a tube, which had been filled with helium at a pressure of about 5<sup>mm</sup>, was purified once a week with oxygen during a period of six months. The quantity of helium and the radiating and absorbing powers of this gas at a given current strength remained constant during the interval of time just stated. It is thus clear that Paschen's process makes it possible to rapidly establish with helium exactly reproducible conditions to a degree heretofore unknown with Geissler tubes. The author is as yet unable to account for the

complete disappearance of the oxygen which has a relatively large mass after numerous resuscitations of a given tube.

A recapitulation of the more important facts brought out by Paschen's investigations will now be given. The spectrum of helium consists of two series whose respective fundamental lines, at 10830 Å and 20582 Å, comprise by far the greatest proportion of the total radiation. Pure helium gas in the positive column of the glow discharge or in other parts of a Geissler tube absorbs the energy of the two infra-red lines at current densities as low as  $10^{-7}$  amperes per cm<sup>2</sup>. For such currents the intensity of emission of the infra-red lines and of the visible lines is barely noticeable. In this connection, it is especially worthy of note that a current must be sent through the gas in order to start absorption. In this respect helium differs from the vapors of sodium and mercury. It is shown by curves that, as the electric current is increased in strength, the line absorption increases very rapidly at first and then gradually rises asymptotically towards a superior limit. The lines in the visible spectrum first exert measurable absorption when the current is about 10,000 times as great as is required to produce observable absorption by the two fundamental lines. The line at 10830 Å possesses the majority of the energy of the entire spectrum. With a column of gas 30<sup>cm</sup> long the line absorption attains the value 95 per cent. The detailed investigation of the question concerning what becomes of the energy absorbed, brought out a most interesting and important fact relative to the resonance radiation of the strongest line 10830 Å. It was found that a resonator is present in the helium atom having the property of again radiating into space all of the energy which it had absorbed. This discovery affords the first concrete example of the type of electric resonator introduced by Planck in his remarkable theory of radiation. On the contrary, the second fundamental line, at  $\lambda 20582$ , has not as yet shown a detectable amount of resonance radiation, in spite of the fact that it exerts strong absorption. Finally, Paschen investigated the temperature of a black body which would radiate  $\lambda\,10830$  with the same intensity as does helium gas. In this sense, a lower limit for the "temperature of the monochromatic radiation" of helium is obtained. The values found were 7890° and 9580° C. absolute, according to the current sent through the Geissler tube.-Ann. d. Physik, vol. xlv, p. 625, October, 1914. H. S. U.

6. Intermittent Vision.—In a paper communicated, in the year 1913, to the Royal Society by Mallock, in order to account for the intermittences seen when observing a revolving disc of black and white sectors, at the instant when a slight mechanical shock is given to the head or body, the hypothesis is advanced that a slight mechanical shock of any kind produces a periodic but rapidly extinguished paralysis of the perception of light, and that the nerves on which seeing depends cannot bear more than a certain amount of mechanical acceleration without loss of sensibility. This phenomenon has been recently subjected to experimental test by SILVANUS P. THOMPSON and the results obtained show that the hypothesis of a momentary paralysis of the sense of vision is unnecessary.

The sector disc making from two to six revolutions per second presents a uniform gray tint. At the instant when the intermittence is produced, either by stamping the foot or tapping the head, the most prominent effect observed by Thompson was the enhanced brightness of stationary white sectors and not the momentary appearance of stationary gray or black sectors. "A momentary paralysis, if it occurred, should produce momentary blackness of the entire disc, which is not what happens." To subject the matter to further test, the author arranged a revolving sector disc, driven at constant angular velocity by a small electric motor, in such a manner that it could be observed either directly from a distance of a few feet or by reflection in a small plane mirror held in the hand or clamped elastically between two rubber stoppers supported by a rigid stand. When a slight mechanical shock was given to the mirror so as to alter momentarily and by a small amount the apparent position of the revolving disc, an intermittence was produced of the same kind as was observed when a shock was given to the head or body. The sectors appeared to stand still, and the brightness of the white sectors was temporarily increased. "This intermittence, if such it can be called, occurs equally whether the observer taps the mirror or whether some other person taps it." "The phenomenon is in this case independent of any mechanical acceleration of the nerves or nerve-structures, and is not due to any temporary paralysis of vision."

"The explanation appears to be that when the moving images of the white sectors on the retina are suddenly shifted by a minute displacement, they fall on some of the rods and cones which are relatively unfatigued, and which, for the instant, are therefore of greater sensitiveness." The writer of this notice desires to call attention to the fact that the phenomenon in question can be observed while walking heavily on the pavement and watching the spokes of the wheels of passing automobiles. (Yellow wheels can be seen better than red or black ones, of course.)—*Proc. Roy. Soc.*, vol. xc (A), p. 448. H. S. U.

7. Bausteine zur Flugbahn- und Kreisel-Theorie; by AUGUST DÄHNE. Pp. 44, with 5 figures. Berlin, 1914 (R. Eisenschmidt). —The text of this monograph is divided into two parts, the first and second of which deal respectively with the theory of the rotation of rigid bodies and the motion of projectiles. In the first part the author attempts to show that some of the current explanations of gyroscopic phenomena are incorrect. In particular he criticizes adversely both Poinsot's theory of the composition of simultaneous infinitesimal rotations and Poggendorff's elementary explanation of the starting of precession. On page 17 Dähne comes to the conclusion "that the deviation of a rotating body must take place not only when an attempt is made to alter the

direction of its axis of rotation but also when this axis is displaced parallel to itself by imparting momentum to the rotating system by means of a foreign body." The fact that the latter phenomenon is not observed with gyroscopic apparatus is explained on the ground of frictional resistance at the axle bearings. The second part of the text (pages 24-44) relates to practical ballistics and the author's interpretation of air resistance. Since the arguments advanced are not formulated mathematically but are rather long and controversial, it is difficult to find out just how far the contentions of Dähne are correct without making a very exhaustive and time consuming study of the text. Nevertheless, the consequences of the author's "theory," as applied to the recorded behavior of large projectiles, agree qualitatively and without exception with the results of observation. Furthermore, it is only fair to state that the monograph contains much food for thought and hence it should be useful in suggesting lines of further investigation. H. S. U.

8. Text Book on Wireless Telegraphy; by RUPERT STANLEY. Pp. xii, 344, with 202 figures. London, 1914 (Longmans, Green and Co.).-This book is intended to meet the needs not only of students who have had no preliminary practice with wireless apparatus, and who are taking up the subject for the first time, but also of experts in ordinary manipulation who do not fully understand the underlying theory of the appliances employed and the phenomena involved. "The electron theory has been used ; on it has been based all theoretical considerations, the author believing that this theory, modern, simple, direct, and well established, will present fewer difficulties to the student than the vague fluid theories which it has replaced." That the field is covered in a thorough manner may be seen from the following list of the headings of the several chapters, namely :--"The Earth, the Atmosphere and the Ether. Matter and Electrons. Magnetism and Magnetic Strains in the Ether. Electricity and Electric Strain in the Ether. Electrical Measurements and Calculations. Capacity and Induction Effects. Induction Coils, Alternators, and Transformers. Oscillatory Discharges. Historic Development of Radio-telegraphy. How Ether Waves are propagated and received. Coupling of Circuits. Transmitter Circuits for Spark Systems. Transmitting Apparatus. Aerials, Insulators and Earth Connections. Receiver Circuits. Detectors. Receiv-ing Circuit Apparatus. Undamped Wave Systems. Miscellaneous Apparatus. Measurements in Radio-telegraphy."

The author's explanations are full and clear, the diagrams and half-tone figures are excellent, and the book contains much useful, up to date information. Most of the chapters end with a list of questions and numerical exercises (171 in all) to be solved by the student. Four appendices on codes and signals precede the index. From the practical standpoint the text is quite accurate. There exist, however, a few minor slips such as "Wein" for Wien, and "... X rays, discovered by Sir. Wm. Crookes."

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9. Principles of Electrical Measurements; by ARTHUR WHIT-MORE SMITH. Pp. xiv, 243, with 99 figures. New York, 1914 (McGraw-Hill Book Co.) .- " This book is written for the instruction of those who are beginning their course in Electrical Engineering, or who desire a more complete understanding of this branch of Physics than is afforded in most elementary manuals, ....." Hence the material is so presented as to meet the requirements both of the class room and of the laboratory. In addition to covering a good deal of ground the book has several other admirable features. For example, the practical and theoretical definitions of electric and magnetic units are clearly stated and emphasized by italics. The subject is developed progressively not only as regards the successive chapters but also with respect to the material in each chapter. Thus it is shown in the first chapter how to measure current, electromotive force, resistance, and power, by ammeter and voltmeter methods. In the seventh chapter considerable use is made of Kirchhoff's second law. The sections dealing with B and H are unusually clear and thorough. A few problems are distributed through the text, the diagrams and typography are excellent, and the volume closes with a subject index, therefore, as implied, the book is very well adapted to meet the needs for which it was written.

H. S. U.

10. Geometry of Four Dimensions; by HENRY PARKER MANNING. Pp. ix, 348, with 3 plates. New York, 1914 (The Macmillan Co.).-The chief object of this book is to meet the difficulties of the subject as far as possible. In order to accomplish this purpose the author has used synthetic processes exclusively. One advantage of the synthetic method is that it concentrates our attention on the figures themselves and thus takes us directly to the heart of the difficulty and keeps it before us until the difficulty has been thoroughly mastered. Taken as a whole, the text is an extension of ordinary Euclidean geometry to four dimensions. It follows, therefore, that no knowledge of higher mathematics is necessary for a full understanding of the contents of the volume. The author has wisely given the pages a familiar appearance by following the elementary text-books and by building up a structure which rests on the foundations laid in the schools. The theorems in the first five chapters are rigorously demonstrated without the introduction of the axiom of parallels. In other words, these chapters pertain to "Pangeometry," (Lobachevsky). The three remaining chapters relate to figures with parallel elements, to measurement of volume and hypervolume in hyperspace, and to the regular polyhedroids. "In the chapter on the hypersphere, its geometry, being elliptic, is stated as such, and a group of theorems is given from the non-Euclidean geometry; and in the last chapter the non-Euclidean properties of the hypersphere are used quite freely." "Although these portions of the book may be omitted, the student will find it an advantage to make himself familiar with the Hyperbolic and

Elliptic geometries." A list of technical terms precedes the index. The serious reader will be well repaid, for the time spent in studying the text, by his gain in power of intuition and imagination.

11. Experiments; by PHILIP E. EDELMAN. Pp. 256, 135 figures. Minneapolis, 1914 (Philip E. Edelman).-A correct idea of the scope of this volume may be obtained from the following quotations taken from the title page, namely :- "Book 1. Selected, grouped and graded experiments which may be repeated in a simple manner, including some of the most brilliant demonstrations in science, physics, chemistry, electricity, wireless communi-cation and mechanics." "Book 2. The principles of original experimenting in science, invention, and the industries together with chapters on industrial testing and commercial experiments." Since the book contains a very heterogeneous mixture of all kinds of "stunts" and experiments it is in a class by itself. The numerous half-tones and striking cover attract attention at once. On the other hand, the diagrammatic text-figures are, in general, too small and poorly lettered. The word coherer is consistently spelled "coheror." One is somewhat surprised to have the frontispiece and chapter 33 given to the experimental mill of the Washburn-Crosby Company of Minneapolis. The text is not adapted to class-room work; nevertheless, it may stimulate independent experimentation on the part of those who have not the opportunity of attending systematic courses in technical schools and colleges.

H. S. U.

### II. GEOLOGY AND MINERALOGY.

1. The Transportation of Debris by running Water; by GROVE KARL GILBERT. Based on experiments made with the assistance of EDWARD CHARLES MURPHY. Pp. 263, with 83 tables, 3 plates, 89 figures. Professional Paper 86, U. S. Geol. Surv., Washington, D. C., 1914.

In engineering and in geology many problems arise the accurate solution of which requires a knowledge of the power of a stream to sweep material along its bottom. From the geologic point of view: how much is the capacity of a stream to transport sediment increased by a given increase in slope, or in volume, or in breadth, or in depth, or in fineness of sediment? To turn the problem around, in an ancient alluvial deposit, what kind of a stream transported and deposited the material? What was its length, slope, volume, and velocity? From the engineering point of view : in a modern stream how much material and of what sizes can be poured into it without overloading it and thereby destroying arable lands, or what changes in transporting power will be induced by straightening and deepening the channel?

Up to the present the little experimental work which has been done to develop a knowledge of these subjects has been accom-
plished chiefly in Germany. In California the problems occasioned by the overloading of certain rivers with waste from placer mines had become of great economic importance and justified on that basis a thorough study. Thirty-five to forty years ago G. K. Gilbert began to make effective studies in the west on the work of streams in shaping the face of the land, and in their manner of transporting material. These studies, with those made by Powell and Dutton, became the foundation of the modern science of physiography. It was fitting that the same veteran investigator should continue work in this field by taking up this problem of the transportation of debris by running water. His former studies were based upon the results accomplished by nature ; these are based upon experiments made by man. The latter work shows the same thoroughness, perception, and judicial qualities as the former.

An abstract, pages 10 to 12, gives a summary of the results, so that but little need be said here in that line. The results of the experiments are more directly applicable to flume transportation, since this approximates more to the conditions of the experiments. As Gilbert notes, the principles discovered in the laboratory are necessarily involved in the work of rivers, but the formulas are not directly applicable, since they depend upon complex conditions which are essentially different in nature. Under some circumstances they may be used to compare the work of one stream with that of another stream of the same type. It appears, however, that the results should be of great value geologically as a basis for the further study and interpretation of field observations on river action. J. B.

2. The Mississippian Brachiopoda of the Mississippi Valley Basin ; by STUART WELLER. Illinois Geol. Surv., Mon. I, 1914, 2 vols., text and plates, pp. 1-508, pls. i-lxxxiii, text figs. 1-36.-In this excellent monograph Professor Weller brings together all that is known regarding the great wealth of Lower Carboniferous or Mississippian brachiopods found in Illinois and the adjoining states. The maximum thickness of the strata of this period is here about 1700 feet. Of species there are 310 (85 new), distributed in 63 genera (4 new). The genera with more than 10 species are Spirifer (46), Productus (23), Chonetes (12), Dielasma (11), and Syringothyris (11). The new genus Echinoconchus is largely if not wholly synonymous with Pustula, defined earlier in the year by Ivor Thomas. Of lingulids, there are 2 genera and 8 species, and of neotrematids there are also 2 genera, with 13 species. The strophomenids are represented by 5 genera (19 species), productids 7(49), orthids 2(13), pentamerids 1(3), rhynchonellids 10(35), centronellids 3(4), terebratulids 7(24), atrypids 1(1), spiriferids 13(101), retziids 4(10), meristellids 3(7), athyrids 3(23).

The author states that "it is not improbable that the sedimentation was continuous from the preceding Upper Devonian into the Kinderhook," and yet in this work we do not find a single species

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, NO. 229.—JANUARY, 1915. 9 common to the two periods, although before the book appeared it was believed that at least two Devonian forms continued to live into Kinderhook times. Many genera are, however, common to the two periods, and this is especially true for the Upper Devonian and the Kinderhook. The following Devonian genera practically die out in the Kinderhook: Leptæna, Productella, Centronella, Atrypa, and Nucleospira.

The work is illustrated by a wealth of photographs in halftone, and should make the work of future workers easier and more secure. The State of Illinois is to be congratulated on publishing this fine paleontologic monograph, and the thanks of all invertebrate paleontologists are due Professor Weller for this helpful addition to their working libraries. c. s.

3. The Anticosti Island faunas; by W. H. TWENHOFEL. Geol. Surv. Canada, Museum Bulletin No. 3, 1914, pp. 39, 1 pl.-There is no more interesting Paleozoic locality, nor one with a richer fauna, than the island of Anticosti in the Gulf of St. Lawrence. The fauna was first made known by Richardson, Logan, and Billings, and in 1910 the section was modernized by Schuchert and Twenhofel. The sequence begins in the earliest Richmond and continues unbroken into the Silurian (Rochester). In this paper the author lists the fauna according to formations, so far as developed, and describes the new genera (Paleofavosites Strophoprion, Virgiana, Protozeuga, Lissatrypa) and a few of the more striking new and old species. Among these may be noted the oldest Chonetes (C. primigenius), found in the Richmond series; Anabaia anticostiana Clarke, which is the same as Rhynchonella eva Billings, and both are synonymous with R. decemplicata Sowerby, one of the common Silurian shells of Europe; and Protozeuga anticostiana, the oldest known terebratulid, also occurring in the Richmond along with spire-bearing Hyattidina charletona, n. sp. Triplecia ortoni is found to be closely related to the European T. insularis Davidson.

It is now evident that the Silurian fauna had its origin in Charleton and Ellis Bay time of the Richmond series of the Cincinnati system, and that the North Atlantic is the realm in which originated the Tabulata, Tetracoralla, and the spire- and loop-bearing brachiopods.

4. The British Carboniferous Producti. I. Genera Pustula and Overtonia; by IVOR THOMAS. Mem. Geol. Surv. Great Britain, Palæontology, vol. I, part iv, pp. 197-366, pls. xvii-xx, text figs. 1-10, 1914.—In this work the Producti are reinvestigated by Doctor Thomas, at great length from their historical, morphological and evolutionary aspects. The author is a very careful and detailed worker and correctly regards *Productus* as a polyphyletic genus requiring division into several genera. The genus sensu stricto is based upon *P. productus* (Martin), a form that is costate throughout all stages of growth and has but few spines. The following are new genera : Avonia, having for its genotype *P. youngianus* Davidson, and including forms that are spinose in the early stages but develop costæ at a later period ; Pustula, genotype P. pustulosus Phillips, with decidedly spinose forms ; Buxtonia, genotype P. scabriculus Martin, which is costate and spinose in the young and adult stages and only spinose in old age: Overtonia, genotype P. fimbriatus Sowerby, which is based upon internal peculiarities of the dorsal valve. The new generic names other than Pustula are taken from place names, and no one but an Englishman will discern their significance ; authors nowadays often resort to this easy method of coining new generic name, a practice that is making of our binomial nomenclature a senseless jargon. About one-half of the work is devoted to the description of species of Pustula, and Overtonia fimbriata (Sowerby). c. s.

5. Palaeontologische Zeitschrift, Bd. 1, Heft 3. September, 1911.—The third number of this periodical arrived in New Haven November 25, 1914. It contains, besides the proceedings, constitution, list of officers and members of the society, book reviews, etc., the following papers: (1) On the phylogeny of the shell of turtles and on the relationship of the soft-shelled turtles (*Dermochelys coriacea*), by J. Versluys; (2) On the Clymenias and goniatites, by D. Sobolew; (3) A large Pterygotus [tail piece only], and (4) Lodanella mira, an Edriocrinid, by O. Jaekel, both from the Lower Devonian of the Rhine; (5) Progress and results of the Berlin expedition to Tendaguru, East Africa, by E. Hennig [about \$58,000 has been spent in the field]; (6) On the significance of our new (German) laws regarding excavations in relation to paleontological discoveries, by O. Jaekel.

The Zeitschrift will be continued, but while the war lasts can not be sent to foreign countries. c. s.

6. Topographic and Geologic Survey Commission of Penn-sylvania, Report No. 10, 1913. Pp. 81, plates I-XXXII. The Broad-Top Coalfield; by JAMES H. GARDNER. Map in separate case.-The fact that the coals of the isolated Broad-Top area differ in character from the anthracite deposits further east, although both districts lie within the belt of Appalachian folding, has frequently been noted. The explanation given by Mr. Gardner is that the metamorphism at Broad-Top was the less intense because in the anthracite basins the bituminous beds were at greater depth during the period of folding. The decrease in fuel ratios from 12.04 to 1.0 with decrease in degree of metamorphism for points in Penusylvania is clearly indicated in Plate XXVII. The interpretation of the structure of this field possesses interesting features aside from its economic aspects. In the absence of geologic information, mining in this field has been marked by many failures, which have given rise to the belief that the coal is nearly exhausted. In the author's opinion the field is capable of an annual increase in production for many years to come.

H. E. G.

7. Geological Survey of New Jersey, HENRY B. KÜMMEL, State Geologist. Bulletin 12, Annual Administrative Report of the State Geologist for the year 1913. Pp. 51. 1914.—Papers of general interest in preparation for publication include résumé of the geology of New Jersey by J. V. Lewis, and the State Geologist, H. B. Kümmel; report on Triassic reptilian footprints by C. H. Hitchcock; studies on the stability of the New Jersey Coast by D. W. Johnson, and a laboratory study of minerals found in the traps by J. V. Lewis. Bulletin 12 contains a paper on "Recent storm effects on the New Jersey shore line" by D. W. Johnson and Warren S. Smith, in which the conclusion is reached that, contrary to general belief, vigorous wave erosion is not an indication of coastal subsidence. H. E. G.

8. Iowa Geological Survey, Volume XXIV, Annual report, 1913 with accompanying papers: Pp. 792, plates I-LXVI, figures 65. 1914.—Two papers of large local interest are included in the Annual Report for 1913: Road and concrete materials of Iowa, by S. W. BEYER and H. F. WRIGHT (pp. 33-686), and Analyses of Iowa coals, by A. W. HIXSON (pp. 687-763). There is also an account of mineral production in Iowa in 1911-1912 by the State Geologist, GEORGE F. KAY. The Iowa Survey, which has on its rolls eighteen geologists who devote a portion of their time to work within the state, is actively engaged on problems of areal geology, ground waters, Pleistocene geology, stratigraphy of the Mississippian and Devonian rocks, and topographic mapping.

H. E. G.

9. Wisconsin Geological and Natural History Survey, Bulletin No. XXVII, Scientific series No. 9, 1914. The Inland Lakes of Wisconsin; by Edward A. BIRGE, Director, and CHANCEY JUDAY, Biologist. The Hydrography and Morphometry of the Lakes; by CHANCEY JUDAY. Pp. 137, maps I-XXIX, figures 8.-Following a chapter on the origin, extinction, and shore modification of lakes, based on a study by N. M. Fenneman (previously published in Bulletin VIII, 1910, of the Wisconsin Survey), Mr. Juday discusses the physical characteristics of ten groups of lakes. Surveys, including shape of the bottom, topographic features of the shores, measurements of volume, etc., have been completed for sixty lakes. Measurements of area and depth are given for one hundred and eighty-seven additional lakes, forty-five in the southeast, seventy-nine in the northeast, and sixty-three in the northwest parts of the state. The lake basins described are glacial in origin,-kettle holes, blocked valleys, or morainal depressions. H. E. G.

10. College Physiography; by R. S. TARR and L. MARTIN. Pp. XXII, 837, with 503 figures and 10 plates. New York, 1914 (The Macmillan Company).—The general principles of physiography have been so clearly presented in the books by Davis and by Salisbury that this new book is of interest chiefly because of what might be called its secondary features. There is now a considerable body of principles not included in the older texts, but we do not find them here as the title "College Physiography" would lead us to suppose. The illustrations, the bibliography, and the descriptive matter are therefore the only new points of interest. The bibliography includes a nearly complete list of the chief physiographic papers in English, as well as a number of foreign papers. Its usefulness would have been increased by bracketed references in the text. In its present form and for the college student it is little more than a long list of references of very unequal value. However, from the teacher's standpoint it is useful to have the list in printed form.

The chief contribution of the authors consists of much new and highly useful descriptive matter. To point out a few illustrations: The positions of the magnetic poles and related subjects, the variations of Alaskan glaciers, and the nature of sea ice. The general character of the book would have been enhanced by less rather than more reference to the influence of physiographic features upon man. The relationships pointed out are nowhere full enough to be either clear or convincing, and are very unequal in value. They should have been organized about a body of distinct principles and really analyzed, not left as mere suggestions, loose in application and doubtful in character.

11. Deposits of the Useful Minerals and Rocks, by BEYSCHLAG, VOGT, and KRUSCH. Translated from the original German text by S. J. TRUSCOTT. In three vols., Vol. I; 8°; pp. 514; figs. 219: 1914 (Macmillan and Co.).-It is a very excellent thing that this great work should have been translated into English and thus made accessible to a much wider circle of those who, either from theoretical or practical reasons, or both, are interested in all that pertains to ore deposits. This first volume deals with the subject of ore-deposits in general, then takes up magmatic segregations, contact-deposits, and passes on to lodes, irregular cavity-fillings, and metasomatic deposits, under which tin and quicksilver are considered, at which point the present volume closes. A special feature is the great number of illustrative examples cited, usually with maps and diagrams, so that a very comprehensive view of the best known ore occurrences is obtained. Under several headings the student will find in condensed form the substance of the notable papers published by Vogt in the "Zeitschrift für praktische Geologie" on the origin of certain classes of ore deposits, especially by magmatic segregation, on the concentration of the metallic elements, etc., etc.

The subject of classification is thoroughly discussed, a good historical review being presented; the one furnished by the authors is that primarily of mode of occurrence, the chief groups being: I, Magmatic segregations; II, Contact-deposits; III, Cavity-fillings and metasomatic deposits; IV, Ore-beds. The secondary divisions under these are chiefly of a chemical nature; thus under II, we find: a Oxide ores, Iron group, and b, Sulphide ores, Leadzinc and copper group. Of course by this method III is a very great division with 19 sub-divisions and comprises a large proportion of all the important deposits. The work of translation has been well done, the corresponding technical terms in English having been carefully considered, while the phraseology is idiomatic and free from foreign constructions. It is handsomely printed and bound and is a work that should be in every technical library and in the hands of all who are interested in ore-deposits. L. V. P.

12. Practical Instruction in the Search for, and the Determination of, the Useful Minerals, including the Rare Ores; by ALEXANDER MCLEOD. Pp. ix, 114. New York (John Wiley & Sons).—It is not often that so practical a study as that of prospecting for useful minerals is discussed by one who has had many years' experience in active work. That is the case, however, with the little volume in hand; and the directions given, and the tables for the determination of mineral species and other matter, should prove useful to those needing such help.

13. The Origin of Thaumasite; by FREDERICK I. ALLEN. (Communication to the Editor.)—This rare mineral, with the remarkable composition represented by the formula CaSiO<sub>3</sub>. CaCO<sub>3</sub>.CaSO<sub>4</sub>.15H<sub>2</sub>O, was found at Burger's Quarry, West Paterson, N. J., and was identified and studied by Penfield and Pratt in 1896.\* Recently I have obtained from this same quarry handsome specimens of pale blue, transparent anhydrite, CaSO<sub>4</sub>, associated with amethystine quartz. The crystals are simple and in fan-shaped aggregates. They are lath-shaped, much compressed parallel to c (001) and greatly extended parallel to a (100); the forms observed are the three pinacoids, a, b, c, (100), (010), (001). The composition-plane of the fan-shaped aggregates is c.

Among the specimens of anhydrite were a number that were partially changed to thaumasite, and these showed every gradation of change from the blue, transparent mineral to the white, opaque product. There is no doubt, therefore, that the thaumasite is an alteration product of anhydrite. The thaumasite has in many cases disappeared from the places of its formation, leaving cavities in the quartz in the form of the original anhydrite crystals. Specimens showing these rectangular cavities have been collected in large numbers, but it has not been known heretofore what mineral these pseudomorphs represented. Dr. W. M. Bradley of the Sheffield Scientific School has kindly given me his assistance in confirming the identity of the minerals.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. National Academy of Sciences.—The autumn meeting of the National Academy was held in Chicago on Dec. 7, 8, 9. The sessions were carried on in the buildings of the University of Chicago and the support and hospitality extended by the President and the members of the Scientific staff of the University contributed very largely to the success of the meeting. Two public lectures were delivered by Professor W. W. Campbell,

\* This Journal [4], i, 229.

Director of the Lick Observatory; the subject of these was "Stellar Evolution, and the Formation of the Earth."

The following is a list of papers presented :

W. W. CAMPBELL : On the radial velocities of nebulæ.

HEBER D. CURTIS: Preliminary note on nebular proper motions. R. A. MILLIKAN: The coefficient of slip in gases and its relation to the nature of the impact between a molecule of a gas and the surface of a solid or liquid.

W. D. HARKINS and E. C. HUMPHREY : The capillary and electrical forces at the interface between two liquids.

HERBERT N. McCoy: The solubilities of radium compounds as indicated by the solubilities of analogous compounds of calcium, strontium, and barium.

L. A. BAUER: Present status of the general magnetic survey of the globe. CHARLES J. CHAMBERLAIN : A phylogenetic study of cycads.

C. M. CHILD : A dynamic conception of the organic individual. S. W. WILLISTON : The American land vertebrate fauna and its relations. A. J. CARLSON : Some new observations on the physiology of the stomach in man.

LEONARD E. DICKSON: Recent progress in the theories of modular and formal invariants.

**HENRY** S. WHITE: The synthesis of triad systems  $\Delta_t$  in t elements in particular for t = 31.

E. J. WILCZYNSKI: Conjugate systems of space curves with equal Laplace-Darboux invariants.

ELIAKIM H. MOORE: On the integration by successive approximations of the ordinary differential equation of the first order in general analysis. EDWIN B. FROST: An interesting stellar system. GEORGE E. HALE: The direction of rotation of solar storms.

A. A. MICHELSON : Behavior of metals and other substances near the rup-

ture point. C. W. BALKE and GEORGE W. SEARS : The atomic weight of tantalum. E. W. WASHBURN : Our systematic knowledge of the properties and behavior of solutions of non-electrolytes.

T. C. CHAMBERLIN: The fundamental segmentation of the earth.

WILLIAM TRELEASE : Phoradendron.

CHARLES E. ALLEN: Development of the male germ cells of polytrichum. C. T. KNIPP: Experimental data on the stability of positive and negative

ions. S. W. PARR: The development of an acid-resisting alloy for a bomb

W. L. TOWER : Experimental production of a new ordinal character.

G. A. MILLER : The  $\phi$ -subgroup of a group of finite order.

E. E. BARNARD: Explanation of certain phenomena of the tail of comet Morehouse (III, 1908).

PHILIP Fox : The rotation period of the sun.

J. C. KAPTEYN and W. S. ADAMS: On the relations between the proper motions and the radial velocities of the stars of the spectral types, F. G. K. and M.

S. B. NICHOLSON : Discovery of a ninth satellite of Jupiter.

FRANK R. LILLIE : The fertilizing power of sperm dilutions.

GILBERT AMES BLISS: A generalization of a theorem of Gauss concerning geodesic triangles.

F. R. MOULTON: An extension of the process of successive approximations for the solution of differential equations.

JULIUS STIEGLITZ : Molecular rearrangements of triphenylmethyl derivatives.

WILLIAM CROCKER and J. F. GROVES : Methods of determining the lifeduration of seeds.

EDWIN O. JORDAN : Variation in bacteria.

SHIRO TASHIRO : On the nature of nerve impulse.

2. A Study of Foods; by RUTH A. WARDALL and EDNA NOBLE WHITE. Pp. vii, 174. Boston, 1914 (Ginn & Co.).—The introduction of the domestic arts into educational institutions in this country has stimulated the preparation of suitable textbooks to meet the various aims of the modern home economics movement. This little book is not a work on the chemistry of foods or the physiology of digestion, but a guide to the study of the behavior of different classes of familiar products in the processes incident to the preparation of foods. Each exercise in the cooking laboratory is intended to elucidate underlying scientific principles. It is by such instruction that the preserving of fruit or the baking of bread, for example, will be changed from a haphazard empirical procedure to a controllable process based upon rational operations. Directions for understanding food values and the cost of the ration are also included, along with well selected lists of references for collateral reading. Instruction along the lines indicated in this volume will help to make intelligence replace mystery in the household arts. L. B. M.

3. The Source, Chemistry and Use of Food Products; by E. II. S. BAILEY. Pp. xiv, +517. Philadelphia, 1914 (P. Blakiston's Son & Co.).—This is not a laboratory manual nor a systematic work on the chemistry of foods, but deals in a readable way with the sources and manufacture of most of the common food products. In this respect it fills a need; for the growing interest everywhere in matters pertaining to nutrition has created a demand for a guide to the general character of the materials and processes concerned in the preparation of the dietary in American homes. Whether it be in respect to bread, macaroni, grape juice, koumiss, mincemeat, cheese, paprika, poultry, tamarinds, tapioca, nuts or olive oil—to select a few instances at random—the reader will find the salient facts presented in a lucid manner in Professor Bailey's illustrated volume. L. B. M.

4. Food Industries. An Elementary Text-book on the Production and Manufacture of Staple Foods; by HERMANN T. VULTÉ and SADIE B. VANDERBILT. Pp. viii, 309. Easton, 1914 (The Chemical Publishing Co.).—This book deals with the technique of the processes concerned in food manufacture rather than with the chemistry and nutritive value of the nutrients. It therefore includes such topics as milling, baking processes, the starch and sugar industries, the activities of the packing house, the canning industries, milk and its by-products, the manufacture of condiments and spices, and the preservation of foods. Historical considerations are introduced in connection with many of the descriptive features. The volume is not adapted to the training of food experts or technical chemists, but may serve to emphasize the great changes that modern life has brought about in the production of the foods of the twentieth century.

L. B. M.

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#### CONTENTS.

	Page
ART. I.—The Ternary System CaO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> ; by G. A. RANKIN. With Optical Study by FRED. E. WRIGHT	1
II.—New Meteoric Iron from Sams Valley, Oregon; by W. M. FOOTE	80
III.—New Longirostral Mastodon, Tetrabelodon lulli. Pre- liminary Notice ; by E. H. BARBOUR	87
IVRepulsion of Two Metallic Disks, nearly in Contact; by C. BARUS	93
V.—Lawsonite from the Central Coast Ranges of California ; by A. F. ROGERS	105
VI.—Preparation and Hydrolysis of Ethyl Hydracrylate; by W. A. DRUSHEL	113

#### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics-Coal Tar Chemical Industry, B. C. HESSE, 121.— Freezing-Point of Milk, HENDERSON and MESTON: Chemical Technology and Analysis of Oils, Fats and Waxes, J. LEWKOWITSCH, 122.—Laboratory Manual of Qualitative Chemical Analysis, A. R. BLISS, JR.: Absorption and Resonance of Helium, F. PASCHEN, 123.—Intermittent Vision, S. P. THOMPSON: Bausteine zur Flugbahn- und Kreisel-Theorie, A. DÄHNE, 125.—Text Book on Wireless Telegraphy, R. STANLEY, 126.—Principles of Electrical Measurements, A. W. SMITH: Geometry of Four Dimensions, H. P. MANNING, 127.—Experiments, P. E. EDELMAN, 128.
- Geology and Mineralogy Transportation of Debris by running Water, G. K.
  GILBERT, 128. Mississippian Brachiopoda of the Mississippi Valley Basin,
  S. WELLER, 129. Anticosti Island faunas, W. H. TWENHOFEL: British Carboniferous Producti, I. Genera Postula and Overtonia, I. THOMAS, 130. Palaeontologische Zeitschrift: Topographic and Geologic Survey Commission of Pennsylvania, 131. Geological Survey of New Jersey: Iowa Geological Survey: Wisconsin Geological and Natural History Survey: College Physiography, R. S. TARR and L. MARTIN, 132. Deposits of the Useful Minerals and Rocks, 133. Practical Instruction in the Search for and Determination of the Useful Minerals, A. MCLEOD: Origin of Thaumasite, F. I. ALLEN, 134.
- Miscellaneous Seientific Intelligence-National Academy of Sciences, 135.-Study of Foods, R A. WARDALL and E. N. WHITE: Source, Chemistry and Use of Food Products, E. H. S. BAILEY: Food Industries, H. T. VULTÉ and S. B. VANDERBILT, 136.

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## AMERICAN JOURNAL OF SCIENCE

#### [FOURTH SERIES.]

ART. VII.—Notes on the Physiography and Glacial Geology of the Northern Catskill Mountains; by JOHN L. RICH, University of Illinois.

CONTENTS.

INTRODUCTION. PHYSIOGRAPHY. General Statement. Drainage. Detailed Physiographic Features. GLACIAL GEOLOGY Direction of Ice Movement as Indicated by Striæ. Moraines. Along headwaters of West Branch of Delaware River. Moraines in Schoharie Valley. Moraines along the East Branch of the Delaware. Local Glaciation. The Grand Gorge Lake. Grand Gorge Delta. Platter Kill deltas. Deltas on the Manor Kill. Deltas along Batavia Kill. Delta at Windham. Apparent absence of deltas on the upper Schoharie Creek and its tributaries. Lake clays. Lower lake levels in Schoharie Valley. Drift-filled Gorges and Hanging Valleys. SUMMARY.

THE following paper is an attempt to assemble, in as nearly complete form as possible, the results of somewhat scattered observations on the physiography and glacial geology of the northern Catskill Mountains and the adjoining plateau. These observations have been made at intervals, mostly in vacation time, during the past eight years.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 230.—February, 1915. 10

#### Physiography.

#### General Statement.

The region described is that portion of the Allegheny Plateau of Eastern United States lying in eastern New York in the angle between the Mohawk Valley lowland on the north and the Hudson River lowland on the east, and extending southward to include the northern Catskill Mountains.



FIG. 1.

FIG. 1. Key map.

The region is underlain by sedimentary rocks of varying character which, though everywhere nearly horizontal, dip at low angles toward the south and southwest. The more resistant beds, such as the Lower Devonian limestones, the Hamilton shales and sandstones, and the Catskill sandstones and conglomerates, are each marked by cuestas<sup>\*</sup> presenting steep

\*Grabau, A. W. (Geology and Paleontology of the Schoharie Valley, N. Y. State Museum Bull. 92, 1906, pp. 333-348) describes some of the features here mentioned.

escarpments toward the lowlands on the north and east and gentle dip slopes or platforms toward the south and southwest.

The physiography of the region has been complicated somewhat by at least two cycles of erosion. During the first, the northern part of the area was reduced to a plain of advanced old age (a peneplain), while the southern partthe Catskills,—being underlain by more resistant rocks, was carried only to the stage of late maturity with a relief of 1500 to 2000 feet. During the second cycle the streams, intrenching themselves to a depth of about 1000 feet, have dissected the peneplain to the stage of late youth, while in the Catskills they have excavated steep-sided valleys in the bottoms of the broad, late mature valleys of the previous cycle. This con-  $\infty$ dition, however, is not found in the extreme upper courses of the streams. Here the features characteristic of the preceding cycle still persist (fig. 2, right center), either because trenching has not vet progressed so far or because new cycle has brought about so sught a lowering of the profile of equilibrium of these headwater streams that widening has practically kept pace with downcutting.

A subsequent glaciation does not seem to have modified materially the broader features of the physiography.

The cuestas already mentioned constitute the most conspicuous elements of the topography. From northeast to southwest each rises higher than the preceding and represents the outcrop of younger rocks. The most northerly of these, the *Helderberg Cuesta*, is



ment stretches from Utsayantha southeastward to and beyond the point so labelled. At the foot of the escarpment to the east is the line formed by the mountain summits and, in the foreground to the right, the late mature character of the topography. The Central Escarp end of the northeastern branch of the Catskil The vanishing by Schoharie Creek. From photograph renched. 2000 foot plateau (or peneplain) deeply trenched Escarpment appears in the background to the left. determined by the outcrop of the heavy Lower Devonian limestones. It is best developed at the extreme northeastern end of the plateau about 12 miles west of Albany (fig. 1). On the west it dies out as a conspicuous feature soon after crossing Schoharie Creek. On the south it becomes gradually lower and more broken until finally, after a course of 20 or 25 miles, it merges into the Hudson River lowland.

The *Hamilton Cuesta*, as it may be called from the Hamilton shales and sandstones to whose resistance it is due, is very pronounced and may be traced continuously from the western border of the Hudson River lowland, where its inface parallels the Helderberg Escarpment and practically constitutes its upper member, across Schoharie Valley and westward to an undetermined distance beyond Otsego Lake (fig. 1).

The Catskill Escarpment, representing the inface of the highest of the three cuestas, rises abruptly out of the Hudson Valley to a height of over 4000 feet and marks the eastward termination of the flat-lying resistant rocks which constitute the mountains. It is practically a unit as far north as the headwaters of Schoharie Creek (at Overlook Mountain), but beyond this it splits into two distinct branches. The first, constituting the main escarpment, continues northward parallel to the Hudson Valley for about seven miles, then turns northwestward, in which direction it extends in nearly a straight line for some 20 miles before dying out. The second branch, probably representing rocks somewhat higher in the series, turns northwestward from Overlook Mountain and, as a strong but maturely dissected escarpment, which we may call the Central Escarpment,\* continues thence northwest in a line bowing slightly southward, to a point at the headwaters of Delaware River near Stamford, where it splits. The higher member turns southwestward, gradually decreases in height and finally dies out, while the lower member continues northwestward about five miles farther, to Potter Hill, then turns at right angles, and extending southwesterly, forms the divide between the waters of the Delaware and the Susquehanna.

All these larger topographic features appear to be expressions of rock character and structure, each escarpment representing a more resistant horizon, and trending in general in the direction of the strike.

The roughly rectangular arrangement of the escarpments appears to be due to the relation of this region to the old land from which, in Paleozoic times, it received its sediments. The region, as already indicated, lies in the angle between the

<sup>\*</sup> Guyot, A., this Journal (3), vol. xix, pp. 429-451. On p. 432 this escarpment is mentioned as "the central chain of all the Catskills," while the northern escarpment is spoken of as the "northeast border chain."

Hudson on the east and the Mohawk on the north, each of which marks in a general way the trend, though probably not the location, of the boundaries of the old land on the east and north. The escarpments are accordingly the infaces of cuestas,\* the one set facing northward to the Adirondack Old Land; the other eastward to that beyond the Hudson.

The splitting of the northern part of the Catskill escarpment is due, presumably, to original differences in rock resistance resulting, no doubt, from original differences in the constitution of the marginal portions of the great Catskill Delta.<sup>+</sup> The weakening, and final dying out of the Catskill escarpments to the west, particularly of the northern branch, is doubtless to be explained in the same way—the rocks responsible for them becoming finer, and less resistant farther out from the source of supply, and consequently less able to maintain the escarpments.

#### Drainage.

The drainage of the region accords closely with its structure. In their broader relations the subsequent Hudson and Mohawk lowlands separating the region from its old-land are strictly in accord with the structural features.

Of the streams draining the plateau the Susquehanna and the Delaware on the west flow in consequent courses down the dip toward the axis of the Paleozoic bay in which the rocks of the plateau accumulated. Esopus Creek—evidently obsequent —drains eastward directly into the Hudson; whereas Schoharie Creek—in its extreme upper course consequent, flowing down the dip of the rocks; in its middle course subsequent, following the base of the Central Escarpment; and in its lower course obsequent—flows northward into the Mohawk. Catskill Creek, in a subsequent valley, flows southeastward parallel to the base of the Catskill Escarpment. Fox Creek and Cobleskill Creeks, both subsequent streams, follow the base of the Hamilton Escarpment, while finally Bozen Kill parallels the base of the Helderberg Scarp.

The courses of all these, except possibly Esopus Creek, seem to accord perfectly with the structure. Why this obsequent stream should have been able to gnaw so far back into the escarpment while those at the headwaters of Schoharie Creek worked back only a short distance is puzzling. Again it may be that the reason lies in the structure. The pattern of Esopus Creek within the mountains is dendritic and perfectly symmetrical. In this respect it differs radically from that of

\* Grabau, A. W., loc. cit.

† Barrell, J., this Journal (4), xxxvi, 429-472, 1913: xxvii, 87-109, 225-253, 1914. almost any other stream in the region. most of which have a unilateral pattern. A perfectly symmetrical dendritic drainage pattern in stratified rocks means to the physiographer that those rocks are *horizontal*. Inclined rocks, even where the dip is gentle, give the unsymmetrical patterns. If the rocks here are horizontal as the drainage pattern indicates,\* an obsequent stream would have a much better chance of development than along other parts of the escarpment where the rocks dip inward. Under these conditions the obsequent Esopus with its short, steep course might very readily work its way back into the escarpment as far as it has done, while other streams less favored accomplished little.

#### Detailed Physiographic Features.

For a comprehensive view of the essential physiographic features of the northwestern Catskills, one could do no better than to climb to the summit of Mt. Utsayantha, at the northwestern end of Central Escarpment, near Stamford, where, from the observation tower at an elevation of 3270 feet, an extended view may be secured. A panorama from southwest round through south to east taken from this point (fig. 2) includes most of the essential physiographic elements. To the south, marking the summit of the higher mountains at 3000 to 3500 feet, is a remarkably even skyline sloping gradually westward. This terminates abruptly to the northeast (southeast of the observer) in the long, nearly straight line of the Central Escarpment. At the foot of this escarpment, and to the east-southeast from the observer at elevations of 1800 to 2000 feet, is the plateau of the upper Schoharie bounded on the east by the northeastern branch of the Catskill Escarpment (figs 3, 4). The view directly to the east is perhaps the most interesting: Immediately beyond the mountain top in the foreground is the steep front slope of the Central Escarpment; in the middle distance is the gently rolling plateau of Schoharie Valley, deeply trenched in the middle by the youthful gorge-like valley cut during the later cycle by Schoharie Creek; and on the skyline in the distance, the northern end of the Catskill escarpment sinks down to the north into the plateau. The appearance of this comparatively smooth plateau wrapping round the vanishing end of the escarpment and extending bay-like up the upper

<sup>\*</sup> It has been necessary to rely mainly upon the drainage pattern and other physiographic evidence in questions involving dip in this part of the Catskills. In various stratigraphic reports dips are recorded, but they are so out of harmony with each other that they seem to have little value for the determination of the general dip of the region. They seem to express only the crossbedding which is so pronounced in these rocks.

Schoharie is striking and not unlike that of a body of water drowning a late mature mountainous landscape. To the north and west, the westward continuation of this plateau presents an almost unbroken skyline. To the southwest one looks down the valley of the West Branch of the Delaware River bordered on the northwest by the plateau and on the southeast



FIG. 3. Looking north down Schoharie Valley from a point 3/4 mile west of Prattsville. Note even skyline of 2000 foot plateau and sharp trench of Schoharie Creek. From a photograph.

FIG. 4.



FIG. 4. Looking southwest from base of Reed Hill, one mile north of Gilboa village. In foreground is Schoharie Creek, in middle distance, the eventopped 2000 foot plateau and on skyline the peaks of the Central Escarpment. Note the pronounced bench at about 1300 feet half way between Schoharie Creek and the plateau level. From a photograph.

by the gradually diminishing southwestward arm of the Central Scarp.

The even skyline of the higher Catskills to the south is striking when seen from such a point of view as Utsayantha, and perhaps even more striking is its gradual and uniform descent toward the southwest. This even skyline should not be taken as proof of a former peneplain at this level, although even this may lie below the level of some of the earliest, e.g. Jurassic, erosion planes.\* It seems more likely, since it corresponds very closely with the stratification, that it is mainly structural. Furthermore, such an even skyline is to be expected, irrespective of former peneplanation, in the late mature development of a region of homogeneous rocks.+

Certain features of the 2000 foot plateau which borders the Catskills on the north lend support to the view that it is a structural feature rather than an erosional plain, but other features pointing toward the latter hypothesis seem more conclusive. Of the features which might be interpreted as indicating a structural origin the following may be mentioned:-

(1) The plateau either extends flat or, locally, rises gradually toward the north from the base of the Catskills to the crest of the Hamilton Escarpment, then drops down 400 to 500 feet to another platform lying at elevations between 1200 and 1500 feet and developed on the Devonian limestones. This in turn breaks down into a local erosion level at about 700-800 feet which borders the vouthful trench of the Mohawk River. The close accord of at least the higher of these steps with the outcrops of resistant members of the rock series leads one to believe that structural control has at least been strong.

(2) In several places, notably near Gilboa and Grand Gorge, the flat-topped hills marking the 1800-2000 foot level are capped by resistant beds of sandstone which, it might be urged. are entirely sufficient to account for the flat-topped plateau in that vicinity.

Opposed to the structural hypothesis is the fact that according to the profiles on the Geological Map of New York State, 1901, the 2000 foot upland bevels the gently dipping beds, and consequently cannot be determined throughout by resistant strata, however pronounced this feature may be locally. Furthermore, certain features of the valleys in the plateau and in the Catskills to the south indicate rejuvenation at a relatively late period and therefore lend support to the peneplain hypothesis. In the Catskills, for instance, the valleys of Town Brook (Hobart sheet, U. S. G. S.) and Batavia Kill (Gilboa and Durham sheets) are broad and open (i.e. late mature) in their upper parts within the mountains, while farther down stream, below the 2000 foot level, they take on the characteristics of youth: the sides become steep, and the valleys narrower. Batavia Kill may be taken as an example. Above Windham (1500 feet) the valley has every characteristic of late maturity : there is considerable relief, but the valley is broad and open, with steepest slopes near the divides. Followed down stream, despite the fact that it is leaving the highest mountains, the

\*Compare Barrell, this Journal (4), xxxvii, p. 104. †Shaler, N. S., Bull. Geol. Soc. Amer., x, 263–276, 1899.

valley becomes narrower and steeper-sided until, where it enters the Schoharie, it is a veritable canyon, only 3/4 mile wide at the top, with walls 700 feet in height, and is trenched sharply into the 2000 foot plateau.

A second feature indicating that the plateau is the product of an earlier erosion cycle is well illustrated in the southeastern part of the Cooperstown sheet. The drainage here is what might be described as *unilateral*—all tributaries come in from the north, while the south walls of the main valleys are practically unbroken.

This lack of symmetry, it is to be presumed, is a result of the adjustment of the streams to gently dipping rocks. This adjustment must have taken place in a cycle previous to the rather sharp dissection which produced the present topography, for there is no evidence of any considerable down-dip migration of the master streams, or of other adjustments, since this dissection began.

The plateau appears, therefore, to represent an old age plain or, as some would call it, a peneplain produced during an earlier cycle of erosion and sharply dissected by the streams during the present cycle.

Grabau\* correlates this 2000-foot plateau with the Cretaceous peneplain. Davis† suggests that the Cretaceous peneplain level in the Catskills lay at about 2500 feet—too high for our 2000-foot plateau, and too low for the general summit level of the mountains. Since the precise dating of these physiographic features must wait upon more detailed investigations outside of the area under discussion, no attempt is here made to assign a date to the 2000-foot peneplain, or to correlate it with others, further than to state that it apparently continues westward across southern New York.

What may prove to be evidence of a later period of halted downcutting is found within the Schoharie Valley trench. A rock bench is revealed by postglacial gorge cutting at North Blenheim and Mine Kill at elevations of about 940 feet at the former place and about 1050 at the latter. One and one half miles below North Blenheim also, on the east side of the valley, is a similar rock bench between 900 and 960 feet above sealevel. This may correlate with one of the platforms in the Mohawk Valley—possibly that at 700–800 feet.

Several pronounced passes or gulfs cut the Catskill escarpments. Three of them cutting through the strong Central Escarpment are especially noteworthy. Among the simplest is that through the northeastern escarpment at East Windham. This seems to be a normal stream valley beheaded by the recession of the escarpment, and subsequently smoothed out

\* Grabau, A. W., loc. cit.

+ Bull. Geol. Soc. Amer., ii, 566.

somewhat by glacial erosion. (As indicated on a following page, it was an important channel of ice movement.)

Two minor passes through the Central Escarpment near Stamford seem, like that at East Windham, to be due to valleys beheaded by recession of the scarp.

Of the three deep passes or "Cloves" through the Central Escarpment, Grand Gorge is one of the most significant. It is a double pass. The higher pass at 1900 feet seems to represent a mature beheaded valley like those just mentioned, though somewhat sharper. Just east of this is the deep, rocky "Grand Gorge" cut down to 1560 feet, and in every way a true gorge with naked rock ledges rising almost perpendicularly

FIG. 5.



FIG. 5. Sketch of Grand Gorge to show the double character of the pass.

on either side. The gorge gives every evidence of having been stream cut at a relatively recent date. The only stream which could have done the work must have been glacial. It is difficult to understand why this glacial stream did not utilize the pre-existing 1900-foot pass, unless it started marginal to an ice lobe which, pushing through the pass, may have closed it effectively until the marginal channel became permanently established (fig. 5). The "gorge" was later utilized as the outlet of the glacial Grand Gorge Lake, to be described on a later page.

Deep Notch, 15 miles to the southeast (Phoenicia quadrangle), and Stony Clove, 14 miles farther southeast, are both deep (1400 feet), exceedingly narrow, steep-sided clefts through the range, and, as has been suggested by Darton,\* are very likely

\* Darton, N. H., N. Y. State Museum, Report 47, 1894, p. 565.

due, like Grand Gorge, to cutting by glacial streams. The movement of the glaciers round the mountains produced conditions which would naturally lead to the formation of some such notches, for, as will be shown on a subsequent page, two great glacial lobes were pushing into this region from nearly opposite directions :—one, moving down the Hudson Valley and pushing into the upper Schoharie Valley from the east,\* would effectively block drainage in that direction; while the other moving up Schoharie Valley from the north must have closed that outlet and forced the water to find a passage to the south across the range.

#### GLACIAL GEOLOGY.

#### Direction of ice movement as indicated by strice.

Observations of striæ are not very numerous, but they are sufficient to indicate certain broader features of the glacial movement (fig. 6). On the hill just north of Hobart, striæ point nearly due south. At the head of Trout Brook also the striæ point south. On the hill one mile west of Stamford village the direction is a little east of south. These localities, all on the 2000 ft. plateau to the west of the termination of the Central Escarpment at Potter Hill, accord closely with each other and agree in indicating a general north-south movement of the ice here.

On the north and east sides of the Central Escarpment, however, in the drainage basin of Schoharie Creek, the striæ indicate that a lobe of ice lay over Schoharie Valley and that it spread out fan-like north of the Catskills, and even pushed over some of the higher passes through the escarpment. Thus, where the road crosses the divide a mile northwest of Mayham Pond at 2100 feet, striæ point almost due southwest. At an elevation of nearly 3000 feet in a pass through the Central Escarpment three quarters of a mile north of McGregor Mountain the direction is also about southwest-varying somewhat with the topography from southwest to about S. 40 W. On the hill north of Grand Gorge Station at 1800 feet, the striæ point S. about 25° W. and a mile farther north, across the railroad, the direction is nearly the same. (It is remarkable that the direction of the striæ near the Grand Gorge Station does not seem to be influenced by the Grand Gorge gap. They point, not toward the gap, but toward the eastern slope of Irish Mountain, as if at the time the striæ were made the ice was overriding the whole range.) Across Schoharie Creek at 1800 feet on the extreme south point of Darling Hill (2 miles northnortheast of Gilboa, Gilboa sheet) the striæ point about 20

\*Ramsay, A. C., Quart. Jour. Geol. Soc., London, xv, 208-09, 1859.



FIG. 6. Outline map showing glacial striæ, deltas, and the more important geographical features mentioned in the text. Deltas are indicated by the small black triangles.

FIG. 6.

degrees east of south—parallel to the general direction of Schoharie Valley at that point. Farther down the Creek, along the road near the base of the hill one-half mile south of Fultonham, striæ were observed pointing south, parallel to the river valley.

Farther east observations are few. Along the road a little over half a mile south of Medusa (Durham sheet), the striæ point about S. 40 W., conforming closely to the direction of the local drumlins and pointing toward the gap in the range near Mt. Pisgah. In the gap through the Catskill Scarp at East Windham the striæ point about 25 degrees west of southparallel in a general way to the valley in which they lie. At the cross roads just below Union Society they point about S. 35 W., roughly toward the gap south of Hensonville. This is rather surprising inasmuch as the moraines farther down the valley, near and beyond Windham, indicate that ice moved down the valley of Batavia Kill rather than at right angles across it as the striæ at Union Society seem to show. The moraines may, however, represent either a later phase of the movement, when it was dominated by topography, or merely a lateral lobe protruded down the valley.

The evidence of the striæ indicates that three major lobes of ice invaded this region. One moved south over the plateau west of Potter Hill, another moved up Schoharie Valley, and spread out fan-like from the deep trench of Schoharie Creek; and a third, an off-shoot of the Hudson Valley lobe, pushed into the mountains through the low passes at and northeast of East Windham, and near Kaaterskill. As will be shown in the description of the moraines, the southward moving lobe west of Potter Hill was probably the earliest; the meeting of the other two lobes in the neighborhood of Prattsville has given rise to interesting complications.

It is probable that within the mountains local glaciers assumed considerable importance, but more detailed studies are necessary before their full extent can be stated.

#### MORAINES.

#### Along the Headwaters of the West Branch of the Delaware.

Our observations cover only the upper part of the Delaware system. A mile below South Kortright (Hobart Sheet), at the mouth of Rose Brook, is a strong hummocky mass of gravelly moraine. Its relationships, however, whether made by a glacier coming down the valley of Rose Brook, or by one pushing up from the north, have not been determined. Just south of South Kortright in the valley of the Delaware is a strong moraine clearly pointing down the valley. Along the south side of the valley for a couple of miles up stream from South Kortright there is a considerable moraine in which several distinct marginal channels are developed. Moraines and channels both indicate ice movement down the valley. A little over half way between South Kortright and Hobart is another prominent morainic mass. At Hobart is a complex mass of moraine, apparently built up largely by ice moving down the valley from the direction of Stamford.

Along the lower course of Town Brook, which enters the Delaware from the east at Hobart, is an interesting group of morainic loops. Between the village and the first road turning south across Town Brook is a very perfect loop, convex down valley and clearly built by a glacier moving west down the Town Brook valley. Two other similar though less pronounced loops, both convex down valley, are found within the next two miles up the brook. This arrangement of the moraines is surprising, particularly in view of the south-point-The loops were at first ing striæ just north of Hobart. thought to be the work of a local glacier in the Town Brook valley, but the discovery of the striæ indicating ice movements southwestward into the valley through the pass between Utsayantha and McGregor Mt. led to the alternative and apparently more reasonable hypothesis that the moraines were produced by a tongue of ice from the Schoharie lobe pushing over this pass and down the valley of Town Broōk.

In the valley of the Delaware River between Hobart and Stamford are many morainic loops, all convex down stream. Such loops are especially conspicuous about one mile above Hobart. Stamford is the center of strong morainic accumulations \* formed, apparently, at the ends of ice tongues which pushed from the Schoharie lobe through the gaps between Utsayantha and Bald Hill and between the latter and Mine The moraine is very hummocky, yet presents many Hill. distinct loops convex toward the west. It extends continuously from a point one mile below the village, where one of the outer loops encloses a small filled lake basin, to the pass between Ball Hill and Utsayantha. In the northern branch of the valley, strong morainic loops, fronted on the west by an outwash plain, hold in Utsayantha Lake. From this lake to Mine Hill Pond, the valley is greatly choked by moraines, some of the loops of which enclose small peat bogs. These loops, like the others, indicate that the ice pushed through the gap from the east.

A small tongue of ice from the Schoharie lobe pushed a short distance throught the gap between Mine Hill and Potter

\* Chamberlin, T. C., 3d Ann. Rept. U. S. Geol. Survey, pp. 367-8.

Hill and just below where the road crosses the stream, about a mile above the Stamford reservoir, built up an exceedingly perfect morainic loop which now encloses a small swamp, once a lake. A couple of miles west of this, along the upper two miles of the valley of Lamb Brook are strong morainic loops evidently built up at the end of an ice lobe which pushed from the north through the gap in the escarpment at the head of the valley.

The exact correlation of these various moraines must wait upon more detailed investigations, but it seems evident that the great Schoharie lobe lay banked against the Central Escarpment, sending tongues of ice through the gaps and over the lower passes opposite which the moraines are now found.

All the moraines thus far described: namely, those in the lower course of Town Brook between Hobart and Stamford; above the Stamford reservoir; and at the head of Lamb Brook, are believed to be nearly contemporary, and to mark approximately the margin of the Schoharie lobe at the time of their formation. The north-south striæ north of Hobart are believed to be somewhat older.

Moraines in Schoharie Valley.—The morainic system in Schoharie Valley is complex because here, between Gilboa and Prattsville, was the meeting place of two opposing ice currents, one from the north, moving up the valley; the other from the south and east, moving down-valley. Two lines of evidence lead to the above conclusion: in the first place, the shape of the morainic loops indicates ice movement in the directions mentioned; secondly, there are two types of material composing the moraines. Those to the north, formed, according to this hypothesis, by ice moving up the valley from the north, are yellow or bluish and carry a large percentage of northern bowlders-gneisses, limestones, etc., foreign to the region. The moraines formed by the ice moving down the valley from the south, on the other hand, are composed almost exclusively of local material-red and gray sandstones and red shales.

Between Gilboa and Prattsville seems to be the meeting place of these two morainic systems. At Devasego Falls, one and one-half miles below the latter village, is a strong morainic loop convex down stream. The moraine, in fact, by turning the stream out of its normal course, produced the falls. The down-stream side of the morainic loop is plainly not an ice contact feature and presents many of the characteristics of a delta front. It is composed of irregularly stratified sand and clay, while the up-stream side is till. Nearly the whole loop, which must have been built under the waters of Grand Gorge Lake (to be described later) is overlain by *red* lake clay from one or two to six or eight feet thick. Both till and lake clay are composed of red local materials. Foreign rocks are found only rarely.

For a couple of miles below this loop the valley is nearly free from drift. On the hill slope, however, near where the stream swings against the west side of its valley, opposite Mt. Royal, is a fairly distinct morainic mass, convex down stream, and composed of local materials. Rather careful examination here failed to show more than a very few foreign stones. A hundred yards farther down stream is the great morainic mass, 200 feet thick above river level, which chokes the valley for several miles to the north. Here the drift is entirely distinct from that only a few hundred feet up stream, and is typical northern till. Foreign stones—limestones, gneisses, schists, etc., constitute a large percentage.

A rough section of this thick till mass as exposed in the stream-cut bluff opposite Manorkill Falls is reproduced below. The base of the section is about 15 feet above mean river level. All figures are approximate only.

Тор				
Yellowish blue, coarse bowldery till, less compact than				
that at base of bluff. Large percentage of north-				
ern material clear to top		50	feet	t
Yellow sand		6	66	
Partly covered—probably blue till		75	46	
Homogeneous pebbly blue till (crumpled)	5	to 10	) ((	
Homogeneous pebbly blue till		15	66	
At base, blue northern till, irregularly mixed with				
clay and very fine sand. Percentage of foreign				
pebbles very large-probably 50 per cent		20	66	

Another rough section of the same mass was taken along the gully (of the main tributary) just south of Gilboa village.

At top, yellowish blue, northern till, relatively little	
local material, large bowlders, and only a moder-	
ate proportion of clay. Bowlders mostly of north-	
ern origin. Not particularly compact	60-70 feet
Unstratified, dark, slate-blue clay with many small	
pebbles, with but few large bowlders—the clay	
very free from grit.	40-50 "
Drab to slate-blue stratified clays-layers extremely	
thin; no pebbles, and no grit	variable
Below this comes more of the blue bowlder clay,	
then occasional small outcrops of the stratified	
clay—some apparently included in the till. Still	
lower, just above first road crossing, is an expo-	
sure of crumpled stratified clay carrying occa-	
sional thin layers of red sand.	

The two sections agree in three particulars—the compact, blue, pebbly till below; the zone of stratified materials near the center; and the less compact, yellowish blue, bowldery till above.

The upper member of this series is puzzling. It differs greatly both in color and in texture from the blue till and the clay below. Is it possibly the product of a later glacial epoch? Or does it represent the results of ice moving from the *south* overriding the previously deposited blue till? These are questions which must be left unanswered. Of possible significance in this connection is the fact that the surface of the deep valleyfilling from Manorkill Falls at least four miles northward is remarkably smooth and nearly level, and stands at an elevation of about 1300 feet (fig. 4). It has occurred to me that this flat may be either a surface smoothed by overriding ice or a wavedetermined level in an old lake bottom. The surface of the flat is covered locally by lake clay to a depth of several feet.

An extremely significant section was revealed in 1909 in the stream bed just below the lowest houses along Fly Brook about one mile northwest of Prattsville. Excavations for a railroad abutment were in progress. At the road a pit about six feet deep showed coarse bowldery red till made up entirely of local materials—in this respect resembling the till which covers the surface all the way up the valley of Fly Brook, and also that in the Devasego morainic loop. Another pit in the bottom of the valley on the west side of the stream showed some six feet of local red stream gravel and red bowldery till underlain by a pebbly blue clay containing a few pebbles, mostly scratched limestones and other rocks foreign to the region. This blue clay is unquestionably the same as the drift which makes up the bulk of the moraine near Gilboa, and contrasts strikingly with the overlying local red till.

This section makes it certain that ice from the north has at one time pushed at least as far south as this, depositing the blue clay, and that subsequently ice moving from the south down Schoharie Creek or down Fly Brook (or both) has deposited the red bowldery till. Whether this indicates two distinct glacial epochs or merely fluctuations of ice front during a single epoch is another unsettled question.

Above the Prattsville loop, in the valley of Batavia Kill, there is a remarkable series of moraines, all of them apparently convex *down* valley (toward the west). At Red Falls, Ashland, East Ashland, Windham, and half way between Union Society and East Windham, the moraines are especially strong. They appear to have been developed in connection with ice that moved from the Hudson Valley lobe across the Catskill Escarpment, mainly through the gap at East Windham and

AM. JOUR. Sci. – Fourth Series, Vol. XXXIX, No. 230. – February, 1915. 11 others further northeast. That these northern gaps were important channels of ice movement is indicated by the fine development of west-facing moraines opposite them in the valleys of the Manor Kill and the Platter Kill. The moraines in these valleys are even more strongly developed than those along Batavia Kill.

The writer's observations in the upper valley of the Schoharie and its tributary, the East Kill, are very meager. They warrant the statement, however, that these valleys are not so choked by moraine as the others just mentioned. It is possible that they were occupied in part, at least, by local glaciers moving outward from the mountains, but this is a question which must await further investigation.

Moraines along the East Branch of the Delaware.—There is an extensive series of moraines along the East Branch, extending from near Grand Gorge at least to Arena and probably farther. They are especially well developed for several miles on either side of Roxbury, and again between Margaretville and Arena. Observations are not sufficiently detailed to warrant any further statement concerning these moraines except that on the east side of the valley just above Roxbury there are distinct loops convex down valley (southward).

A well-developed delta at about 1560 feet at the mouth of Montgomery Hollow at Hubbell Corners and another reported by von Engeln\* at the mouth of Pleasant Valley Brook just opposite, indicate the presence of a standing water body at about that level. The size of the first-mentioned delta indicates that most likely the lake existed at the time of the formation of the moraines in Montgomery Hollow (described in the following section). It seems too large to have been formed by the ordinary drainage of the Hollow.

The existence of such a lake in the valley of a south-flowing river is difficult to explain unless local glaciers descending one of the mountain valleys blocked the main valley farther down. This is a problem which should repay investigation.

A flat-topped terrace between Margaretville and Arena, called to my attention by O. D. von Engeln, may indicate another temporary lake due to a similar cause.

#### Local Glaciation.

Various scattered observations indicate the former presence of local glaciers in the mountains. Some of the evidences, however, like that just cited in connection with the traces of local water bodies along East Branch, are indirect and inconclusive. Features which have come under my observation are

\* Private correspondence.

here recorded in the hope that they may be of assistance to future investigators.

What appears to be the clearest case of local glaciation is that at the head of Fly Brook, described by the writer in 1906.\* A subsequent examination of this locality served only to confirm the results of the first visit.

In Montgomery Hollow, over the mountain immediately west of the Fly Brook locality, are three strong morainic loops pointing westward down the valley. These may represent the work of local glaciers, or they may have been formed by a



Fig. 7. Sketch showing relations in the gap at head of Montgomery Hollow.

tongue of ice from the Schoharie lobe pushing through the gap from the valley of Fly Brook previous to the formation of the local glacier in that valley.

The notch between the valley of Fly Brook and Montgomery Hollow presents several interesting features whose explanation has not yet been worked out. The conditions are sketched in figure 7. The eastern end of the pass is banked with moraine. At the divide within the pass, on the south side of the road, and higher than the moraine, is a sharply cut gorge leading eastward, separated from the main notch by a rock island. Just west of the divide is a deep rock gorge opening westward and overshadowed on the north by sheer cliffs some 200 feet high. Evidently the pass was occupied at different times by glacial outflow streams. The determination of the exact relationship of these outflow channels may throw light on the question of the origin of the Montgomery Hollow moraines whether local or not.

\* Jour. Geol., xiv, 113-121, 1906.

#### 156 J. L. Rich-Physiography and Glacial Geology

In the summer of 1913 the writer tramped from Arkville up Dry Brook, past Furlough Lake, then down into the valley of the Beaver Kill, visiting Balsam Lake, Beecher Lake, and Alder Lake; thence over the mountain to Arena. During this trip several features were observed which seem to point to local glaciation. Some of them, however, lack the merit of conclusiveness.

Two miles up Dry Brook from Arkville, a distinct morainic loop over 100 feet high chokes the valley. This is tied onto the hill on the western side in such a way as to indicate that it was formed by a glacier moving down the valley. One mile above Dry Brook village is a considerable mass of moraine also

FIG. 8.

FIG. 8. Cirque-like form above Alder Lake. Similar features are found at the head of most of the valleys in the vicinity.

swinging down the hillside on the east side of the valley in a manner indicating ice movement *northward* down the valley. If the direction of these moraine loops has been interpreted correctly, they unquestionably indicate local glaciation, since the topographic relations are such as to preclude the possibility of their having been formed by lobes of a southward-moving continental glacier.

Furlough Lake is a small pond held up by a morainic dam, which the writer could not interpret otherwise than as convex down valley, indicating its formation by a local glacier moving northward.

On the south side of Mill Brook Ridge is a series of lakes of which three, Balsam, Beecher, and Alder, were visited.

Each is held in by a morainic dam and lies below steep-sided mountain hollows, which strikingly resemble cirques. At the head of the valley above Balsam Lake are forms which on the contour map look exceedingly like cirques. Unfortunately time did not permit their examination. The head of the valley above Beecher Lake as seen from the lower end of the lake appears "hanging" and decidedly cirque-like. Above Alder Lake the same conditions are even more conspicuous (fig. 8). A profile of Alder Creek (fig. 9) brings out the steplike character of the upper part of the valley. Following down the valley along the road, one at first descends rapidly on a



FIG. 9. Profile through Alder Lake to top of Mill Brook Ridge. Shows pronounced steps in valley bottom.

steep grade, then crosses a nearly flat area through which the stream has cut a deep gorge in drift, after which another relatively steep descent is encountered; then comes the hollow in which the lake lies, and finally the steep descent at its foot. These steps in the valley bottom appear to be drift rather than rock. Above the lake they are characterized by smooth topography as if they had been overridden by ice. The loop which forms the lake, however, is hummocky, at least in part.

About a mile below Beecher Lake the hill, or broad ridge, which the road follows after leaving the stream is apparently composed of drift—at least no bed rock appeared in cuts along the road. Its surface, however, is smooth and non-hummocky, and suggests that it may have been overridden by ice. The till here, as exposed in the road cuts, has a yellowish, weathered look which gave the impression that it is older than the latest glacial period. This is merely an impression, but one, nevertheless, which is believed to be not without foundation.

The topography and the appearance of the drift left the impression that moraines of an earlier epoch have been overridden, and that subsequently a final late stand of the ice has

157

produced the morainic loops behind which the present lakes are impounded. Whether the ungraded valley heads above the lakes are, as they appear, true cirques formed by local glaciers, the writer is not prepared to venture an assertion. There is, of course, the alternative hypothesis that all these features were produced by ice tongues from the continental glacier spilling over the lower parts of Mill Brook Ridge. With this hypothesis conditions at Furlough Lake and the moraines along Dry Brook do not seem to accord. The region certainly promises to repay detailed investigation.

A little less than two miles below Grant Mills at the junction of the two valleys is a distinct morainic ridge convex down valley (toward the west). Another occurs a little over a mile farther down. Both these morainic loops may possibly be the products of local glaciers in the valley of Mill Brook.

#### The Grand Gorge Lake.

Since Schoharie Creek flows northward, the glaciers, when they lay over the lower Schoharie, ponded its waters and compelled them to find an outlet to the south. One of these outlets, first recognized by Darton,\* was through the gap in the Central Escarpment at Grand Gorge at an elevation of 1561 feet. Grand Gorge Lake, as we may call the water body outletting here, lay within the narrow youthful valley of the Schoharie, well below the level of the 2000 foot peneplain.

In a number of the valleys tributary to the lake, prominent deltas are found, while in others they seem to be lacking. In the following paragraphs each of the deltas is briefly described and its significance suggested.

Grand Gorge Delta.—A finely developed delta of considerable size is found at an elevation of 1620 feet, 3/4 of a mile north-northwest of Grand Gorge village. It is composed of rather fine gravel almost exclusively local. A careful search failed to reveal a single foreign fragment, though some large igneous bowlders lie near the bottom of a cut made through the delta by a post-glacial stream.

The comparatively large size of this delta presents an interesting problem. It is developed at the debouchment of a very small stream only two miles in length and without tributaries, while Bear Kill, a much larger stream, has no delta, or if one is present it fails to show on the topographic map and has escaped notice. If present it is, at best, inconspicuous as compared with the one under consideration, though the latter lies at the mouth of the much smaller stream. The only explanation of this condition which comes to mind is that the delta

\* Bull. Geol. Soc. Amer., vii, 1895, 505-7.

gravels were supplied by glacial waters escaping from an ice tongue pushing over the divide from the north. No channel leading down to the delta has been identified with certainty, but the stream valley up to the first road seems abnormally wide and flat, and may have carried a good-sized glacial stream for a short time. A morainic mass in front of the delta appears to be convex down stream (eastward), an arrangement in harmony with the above explanation of the delta gravels.

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FIG. 10. Front of Platter Kill delta. Note the sharp wave-cut terrace about 30 feet below top. From a photograph.

#### FIG. 11.



FIG. 11. The Platter Kill delta as it appears from the hill to the west. From a photograph.

On the hillside south of Grand Gorge village, at about the level of the delta, bared rock ledges may indicate the results of wave action.

The Platter Kill Deltas.—The largest of the deltas corresponding in height to the Grand Gorge outlet lies at an elevation of 1620 feet in the valley of Platter Kill about  $2\frac{1}{2}$  miles northeast of Gilboa village. It is nearly half a mile in length and stands about 100 feet high at the front (figs. 10 and 11). Along most of the front typical landslide topography has developed, but in one part it is absent and there the delta front is beautifully wave-cut at a level some 30 feet below the top, indicating a short stand of the lake waters at the lower level.

This delta, also, seems much too large for the small stream, only  $3\frac{1}{2}$  miles long, in whose valley it occurs. The explanation of its abnormal size is doubtless that during at least a part of the history of Grand Gorge Lake a good-sized glacier tongue pushed through the pass round the end of the Catskill Escarpment at Broom Center, discharging its debris-laden

#### FIG. 12.



FIG. 12. The delta north of Conesville. Cattle grazing on top of delta serve as scale. From a photograph.

waters down the Platter Kill Valley into the lake. Such an interpretation is strongly confirmed by the topographic map which shows what appears to be an extensive series of morainic loops in the upper part of the valley. This interpretation, if correct, will be of assistance in the final correlation of the positions of the ice front during the life of Grand Gorge Lake.

Deltas on Manor Kill.—On a small branch of Manor Kill, one mile north of Conesville, is a large, well-defined delta at an elevation between 1600 and 1620 feet (fig. 12). This also was probably augmented by the outwash from glacial tongues pushing over the divide from the northeast.

At the village of Manorkill a pronounced flat-topped bench at a little over 1600 feet is clearly brought out on the contour
map. This was not visited, but it seems reasonably safe to assume that it, too, is a delta.

Deltas along Batavia Kill.—One half mile north of Ashland village, in West Hollow, is a beautiful delta standing at about 1600 feet. The stream has destroyed a considerable part of it by cutting through the middle, but remnants are preserved on either side. It has a distinct lobate front of fine gravel and sand. The top is generally fairly level, though one part near the front rises slightly higher than the part behind. The up-stream part of the mass appears to be morainic.

Just east of the village of East Ashland, at the mouth of the first valley coming in from the north, is a flat-topped deposit of fine gravel and sand between 1580 and 1600 feet, which is interpreted as a delta built into Grand Gorge Lake. The material constituting the terrace was beautifully exposed in 1913 in a cut near the junction of roads. A moraine on the north side of this deposit seems to cross the north-south valley as if formed by an ice tongue coming down the Batavia Kill from the direction of Windham. The delta, if such it be, seems to be later than the moraine. A part of the flat-topped gravel mass is, for some unexplained reason, partially isolated from the remainder.

The Delta at Windham.—One of the finest of the deltas built into Grand Gorge Lake is found at Windham at an elevation between 1580 and 1600 feet. On the south side of the valley the flat-topped terrace extends conspicuously for fully a mile. On the north side, just north of the road in the western end of the town, the terrace is well developed. The fine gravel composing it is well shown in several cuts.

The eastern end of this delta is open and morainic, and seems to be an ice-contact front. Its nature is well brought out in the photograph (fig. 13) which shows the irregular morainic and slump topography in the foreground and the flat-topped delta terrace clinging to the opposite hillside, but finally wedging out up stream. Just at the right of the picture the stream enters a narrow valley which it has cut through the main part of the delta. These relations are taken to mean that, at the time the delta was building, a lobe of ice pushing through the gap at East Windham, or possibly originating locally in the high mountains at the head of Batavia Kill, extended down to this point. It is difficult to see how, if this were not the case, the flat-topped delta could have been produced without the lower, open depression behind becoming filled.

The heights of the delta tops thus far described bear an interesting relation to each other. The one opposite Grand Gorge and that on the Platter Kill have, as nearly as can be determined from the topographic maps, elevations of 1620 feet. That at Conesville lies between 1600 and 1620. At Manorkill, a little farther east, what appears to be a delta lies just a little over 1600 feet. At Ashland, East Ashland, and Windham, the elevations are between 1580 and 1600 feet.

It has occurred to the writer that this progressive decrease in elevation toward the east may be due to the lower deltas having been developed at a somewhat later time than the higher ones, when the lake level had been lowered slightly by the downcutting of the outlet channel through the Grand Gorge





FIG. 13. Eastern end of delta at Windham. Foreground seems never to have been filled by delta gravel. From a photograph.

gap. Lack of synchronism in the building of the deltas might well be due to the gradual eastward recession of the ice tongues pushing out from the Hudson River lobe as that gradually melted away. Such an explanation harmonizes well with evidence of lowering of the lake level furnished by the wave-cut front of the Platter Kill delta.

If differential tilting of the land has affected this water plane, its effects cannot be determined without fuller investigations than it has been my privilege to make. Such an explanation is opposed by the fact that the delta just north of Grand Gorge Station and the Platter Kill delta lie at approximately the same level in spite of the fact that they are so situated with respect to each other that they ought to show the maximum discordance.

Apparent Absence of Deltas on the Upper Schoharie Creek and its Tributaries.—All of the deltas thus far mentioned, with the exception of that at Manorkill, have been visited. The writer has not, however, had an opportunity to visit the region to the south, except for one hurried trip down Schoharie Creek from Tannersville to Prattsville. A tentative interpretation of the evidence offered by the maps seems legitimate, inasmuch as each of the deltas thus far described is very clearly represented on the maps and might have been located with a considerable degree of certainty from a map study alone without field investigation. It would seem, therefore, that if similar deltas occur on the other streams it should be possible to detect them from the maps.

By a careful study of the maps no sign of any topographic feature resembling a delta could be found at the elevation of the Grand Gorge channel along any of these southern streams, except at Jewett Center (Phoenicia quadrangle) where East Kill empties into Schoharie Creek. Here a bulging spur on either side of the stream looks suspicious. In the valley of Schoharie Creek below Hunter, along West Kill, and along Little West Kill, the contour maps do not give the slightest indication of the presence of deltas; in spite of the fact that these are good-sized streams flowing in valleys wide enough to have preserved at least some remnants of the deltas had they once been present. Mine Kill and other tributaries to the northwest show no deltas conspicuous enough to be detected on the maps.

Two possible explanations of the lack of pronounced deltas in the southern arms of the glacial Grand Gorge Lake present themselves: which is correct must be left to future investigators to determine. One is that while deltas were building in the northern arms of the lake, local glaciers, flowing northward from the higher Catskills to the south, filled the southern valleys and prevented delta building. The second is that the conspicuous size of the deltas described is due to their having been built by streams issuing from ice tongues heavily laden with sediment and, consequently, able to build up large deltas within a space of time so short that normal non-glacier-fed streams, like those coming from the southeast may have been if local glaciers were unimportant, could do little in the way of delta building.

If the latter is the true explanation, the delta at Jewett Center, if it proves to be a delta, is significant, since its stream, East Kill, is so situated that it would doubtless be fed to some. extent by an ice tongue pushing south from the gap at East Windham through the low passes south of Hensonville.

Lake Clays.—Glacial lake clays are conspicuously developed in many places within the area covered by Grand Gorge Lake. They have been noted at Grand Gorge, near Gilboa, between Gilboa and North Blenheim, and on the morainic loop at Devasego Falls, 1 1/2 miles north of Prattsville. At the latter place the clays are thick, very pure, and, in places at least, beautifully stratified.

## 164 J. L. Rich—Physiography and Glacial Geology

Lower Lake Levels in Schoharie Valley.—An examination of the divide on the west side of Schoharie Valley shows that the first possible lower outlet for the waters of the lake is the narrow, 300-foot-deep gorge 1 1/2 miles directly south of Braymanville Schoharie sheet), with bottom elevation of about 1320 feet, whereas the first possible outlet on the east side of the valley is the 1200 foot divide at the head of Catskill Creek. This, however, according to Fairchild\* shows no evidence of having carried a glacial stream of any considerable size. The other, as represented on the map, bears the earmarks of a glacial channel of considerable importance.

The writer has not examined this possible outlet, and does not desire to discuss it further than to call attention to the statement on a preceding page, made before this possible outlet had been located, namely, that the thick drift mass near Gilboa village presents a remarkably flat top at about 1300 feet, which gives the impression of having been wave-determined. It may be that future work will show a correlation between these features.

#### Drift-filled Gorges and Hanging Valleys.

Several drift-filled gorges and hanging valleys found in different parts of the area deserve a brief description.

Just below the main road crossing Mine Kill half way between Gilboa and North Blenheim (Gilboa quadrangle) is an interesting waterfall where the stream cascades over the wall of a pre-existing drift-filled gorge. The old gorge runs under drift just south of the falls and, so far as could be determined, does not appear again farther up stream. Below the falls the stream follows the old gorge to Schoharie Creek, having only partially cleared it of drift. Whether this drift-filled gorge is interglacial or dates back to preglacial times is a problem for the future investigator. This gorge, cut in rock across the prominent bench in Schoharie Valley already mentioned, proves that the bench, in part at least, is rock—not entirely drift, as the conditions just above Gilboa might lead one to suppose.

Mill Creek enters the village of North Blenheim through a gorge in the rock platform which here extends part way across Schoharie Valley at an elevation of about 940 feet, a little over 100 feet above the river level. (See sketch, fig. 14.) This gorge is entirely postglacial; the older one doubtless lying to the south under drift.

West Kill flows across the platform in a partially excavated drift-choked gorge. In the down-stream section this is partly filled with stratified sandy clay, sometimes locally crumpled, in which are embedded large iceberg (?) bowlders. A little farther

\* Fairchild, H. L., New York State Museum Bull., 160, pp. 26-7, 1912.

up stream the old gorge is entirely filled with till and blue bowldery clay, the latter apparently water-laid. For a little distance above this the stream is entirely out of its old gorge, and has cut a hundred-foot-deep postglacial gorge.

A little farther up it again occupies its older gorge. This older gorge, like that of Mine Kill, may, so far as the evidence at hand shows, be either interglacial or preglacial.

Of the hanging valleys, those of Platter Kill, Manor Kill, and Huntersfield Creek, are most conspicuous. It may



FIG. 14. Sketch showing relations at mouths of Mill Creek and West Kill at North Blenheim.

be, however, that none of them are truly hanging in the sense of having their rock floors out of harmony with that of Schoharie Creek. All may be merely the result of a diversion of the streams from their former courses by the deposition of drift. Of these Manor Kill and Huntersfield Creek present features most typical of true hanging valleys, but in each there is room for a buried gorge to the southeast of the present stream course.

In the Delaware drainage system (Hobart quadrangle) Pleasant Valley Brook\* and Montgomery Hollow, both entering the Delaware at Hubbell Corners, are cutting on rock near their lower ends and are probably hanging 100 feet or so above the rock bottom of the main valley.

A number of small valleys on the north side of the West Branch of the Delaware between South Kortright and Delhi (Delhi quadrangle) are distinctly hanging, but neighboring

\* Von Engeln, private communication.

larger valleys are not—a condition which is believed to point to relatively more rapid deepening of the main valley by normal stream erosion or to meandering, rather than to any effects of glaciation, as the cause of the hanging valleys.

#### SUMMARY

In a broad way the physiography of the Catskill region is dominated by structural features. The region seems to present clear evidence of at least two distinct erosion cycles and probably of one or two other partial cycles. During the earliest recognized cycle the extensive plateau north of the Catskills seems to have been nearly peneplained while the more resistant rocks of the mountains were reduced only to advance maturity.

The region in the latest phases of its glacial history was affected by two lobes of the continental glacier: the one, a branch of the Mohawk Valley lobe, pushed up Schoharie Valley from the north; the other, tributary to the Hudson River lobe, pushed down Schoharie Valley from the east and northeast. The meeting of these two lobes has given rise to a complex series of moraines in the middle Schoharie Valley.

Local glaciers within the mountains seem to have been important, but further investigations are necessary before their full importance can be judged.

A glacier-dammed lake in Schoharie Valley outflowed through the Central Escarpment of the Catskills at Grand Gorge. Into this lake an extended series of deltas were built. Since the majority of these deltas seem to have been built by ice-fed streams emerging from minor tongues of ice protruding from the major lobes, their detailed investigation should be of prime importance in connection with the correlation of the different positions of the ice front.

No certain evidence bearing on the question of the multiplicity of glacial epochs has been found.

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Jaggar, Jr.-Outbreak of Mauna Loa, Hawaii, 1914. 167

## ART. VIII.—The Outbreak of Mauna Loa, Hawaii, 1914; by T. A. JAGGAR, JR.

THE scientific staff of the Hawaiian Volcano Observatory has been awaiting an eruption of Mauna Loa since 1911. On Oct. 1 of that year the writer recorded this expectation and the statistical data on which it was based, as follows :\*-"" It is fair to expect that Mauna Loa will renew activity with a lava pool at the Mokuaweoweo center, and without flows at first, before Feb. 1, 1915. After lakings and fountains, with intervals of retirement of the lava, one outflow is expectable in the course of the five years following the outbreak (average duration since 1868). As the last flow in 1907 was to the south, the next, by the law of alternation which has held since 1868. should be on the north side of the mountain. These N. flows have not commonly been accompanied by strong earthquakes. As the flows on each side, N. and S., have been progressively higher since 1868 and there is no sign of collapse like that which led to the 1868 crisis, the new flow on the north side may be expected at a higher level than the Dewey crater of 1899. Thus the flow may be looked for near the high crater of 1843 N.E., or near the vent of 1859 on the N.W. slope."

In accordance with such precedent the great lava fountains appeared in the summit crater on Thanksgiving eve, Nov. 25, 1914, about 3.45 P. M. Hawaiian Standard Time. This date brings to a close an interval of repose which in length is within two months of equalling the maximum recorded interval of the last half century, namely the eight years from 1888 to 1895 inclusive. At that time as at present, the long repose period followed one of the southern outflows. The summit outbreak of April, 1896, inaugurated an active epoch which culminated in the northern outflow of July 4, 1899.

The four seismographs of the Whitney Laboratory of Seismology of the Massachusetts Institute of Teehnology, in charge of Mr. H. O. Wood, in the basement of the observatory, have abundantly recorded a seismic prelude to this eruption, fiftysix earthquakes, all but one local, being registered in the twentyone days preceding the outbreak. Moreover, throughout the year there have been strong recurrent seismic spasms, sometimes accompanied by strongly felt shocks, especially in the region of the Mauna Loa longitudinal axis. The seismic activity of the above-mentioned twenty-one days was greater than any similar period of the last three years. On Nov. 25 in the early afternoon there were eight or more shocks, beginning shortly after noon with a continuous shaking, having several

\* Report of the Hawaiian Volcano Observatory, Jan.-March, 1912, Mass. Inst. Tech., Boston. maxima, extending over several minutes. No shocks were registered after the mid-afternoon. These shocks attracted no attention except instrumentally, showing that the statements that the outbreaks of Mauna Loa are frequently unheralded by shocks of earthquake are loose assertions, and refer only to earthquakes of perceptible magnitude. The action of the instruments about noon on Nov. 25 was so peculiar that Mr. Wood called my attention to it and mentioned the probability that an outbreak of Mauna Loa was the cause.

Kilauea cannot be said to have shown the slightest instantaneous sympathy with the Mauna Loa revival. Throughout 1914 Kilauea has gradually increased in the activity of a rising lava column, following upon marked dormancy in 1913. As a whole the lava column of Kilauea rose gradually from 1906 to 1910, its revival taking place just before the culminating outflow of Mauna Loa in 1907. In the winters of 1910 and 1912 the Kilauea lava column rose to within sixty feet of the rim of the Halemauman cone, but did not overflow. Since 1912 the lava has gradually receded, and even now, while brilliant, is very low, 460 feet below the rim. There were thus three years of rise, two years of high level, and three years of subsidence in Kilauea, with minor semi-annual and monthly fluctua-And this term of eight years checks closely with the tions. repose period of Mauna Loa. If the lava of Kilauea disappears in 1915, and during the term of the active epoch of Mauna Loa remains dormant, we may well suspect a sympathy of alternation between the two volcanoes.

During the week of Nov. 15, 1914, Mr. Conant of Kona, with Charles Ka as guide, went to the summit crater of Mauna Loa, Mokuaweoweo, and found conditions as usual, the 1907 cone on the floor of the crater just as it has been in the last eight years, with a few sulphurous cracks vaporing on the floor near the cone. Therefore, in the week before the outbreak there was no significant visible change. At the observatory, notes have been kept for months past on the appearance of Mauna Loa, not a trace of vapor being seen above Mokuaweoweo. From time to time since 1912 high thin vapor columns have been recorded rising several hundred feet above three old conelets on the northeast rift line of the mountain, the highest of many such cones which appear in profile from the observatory, and about in the position where the next flow might be expected. This locality has not been vaporing of late, nor has it been especially active this year.

On the afternoon of Nov. 25, 1914, Wednesday, shortly before four o'clock, the observatory was enveloped in a drizzling mist, but at Pahala on the southern flank of Mauna Loa the summit was clearly seen and a column of white vapor suddenly rose from the north side of the summit; then four other Jaggar, Jr.-Outbreak of Mauna Loa, Hawaii, 1914. 169

columns rose in rapid succession beside it and next south of it, occupying apparently an arc of the mountain top, about equal to the diameter of the main Mokuaweoweo basin. There was no noise and no earthquake.

When darkness came the fume columns were brilliantly lighted from below, and then there was some good seeing from the observatory on Kilauea. The slender vapor stems over Mauna Loa reflected bright yellow light from what must have been immense fountains of lava below, and they made collectively a wide trunk for a spreading mushroom of vapor above. The night was moonlit, and a photograph was made by the



writer from the gravel flats east of Kilauea, near Keanakakoi crater, looking westward across Halemaumau at Mauna Loa. This was made with Zeiss Tessar F 6.3, Wratten Panchromatic plate, exposed twenty-five minutes during the hour following midnight. It shows the Kilauea fume cloud below on the right, blown toward the left with the trade-wind. Right over it is the great "pino" or pine-tree of smoke rising above Mauna Loa, and the profile of both domes are shown in the volcanic glare. The Mauna Loa column, twenty-two miles away, rises in still air from its high base (13,675 feet, 4168 meters) and spreads above into a diffuse table of fume. In the sky on the left is a glare made by the track of the moon. Kilauea was very active and made a bright reddish glow on its fume cloud, but the Mauna Loa column appeared almost silvery in

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 230.—February, 1915. 12 its whiteness by contrast. The writer would judge the color to have been the yellow resembling a coal-gas flame. The Mauna Loa column was made up of from four to six thin wavy strands, apparently separate fume jets above separate fountains, almost stationary at the great distance of observation. One strand to the right (north) maintained its distance from the others, leaving a dark belt of sky between it and them.

This first night was unquestionably the most brilliant and up to the present (Dec. 7) represented the maximum fountain activity. On the night of Nov. 27 the summit was clearly seen from Puu Lehua on the N. W. slope by the writer, when the brightest column rose from the south side of the band and there was a secondary smoky strand on the north side with a dark zone in between, and the color was orange.

Fortunately, in view of the stormy weather which followed. an ascent was made by two good observers, Messrs, Leslie Forrest and L. C. Palmer, from Pahala on the evening of Nov. 27 and they spent the night on the edge of Mokuaweoweo southeast near the Wilkes station. I am indebted to these gentlemen for the following description and the accompanying plan. They reached the rim in the early evening, watched the fountains off and on all night, and returned down the mountain next morning. The activity was confined to the main central basin of Mokuaweoweo, where an elongate area of new lava overspread the middle part of the floor in a N.E.-S. W. direction and seemed to overlap the northern lunate platform of the Alexander map. Mr. Palmer did not see the remnant of that platform at all. This new lava was an elongate fountaining pool at the south and apparently overflows on the floor at the west and north. There were eight main fountains mostly playing continuously, the southernmost a tremendous sheet fountain estimated 150 feet wide apparently playing above a north-south crack which determined its elongate character. As seen from the east it varied in width (length) like a flickering flame on a ragged flat lamp-wick, but played continuously to heights estimated between 300 and 400 feet. The height was estimated by comparison with the west wall behind it. The other fountains were lower, 40 to 50 feet high, the southern ones having in part the character of shore jets working in grottoes. Several mounds had been built up by spatter, and some of the fountains were concealed behind these mounds, or possibly within them. At  $F^2$  (see diagram) was a spasmodic fountain which erupted at varying intervals, sometimes ten minutes, sometimes an hour or more, resembling a fiery flower pot, and shooting up to heights estimated at 200 feet. The new lava flows glowed from time to time, especially between 2 and 4 A. M. Nov. 28, when there was general recrudescence.

There was white vapor on the south lunate platform and all around the northern end of the lava field. In the greater fountains the lava jets reached the curved upper limits of their trajectories still red and blackened in their downward course.

The following is the text of Mr. Palmer's description of sketch-map:--"If the southern platform is 550 feet down (Alexander), the lake of lava must have been about 600 feet



Outline of Mokuaweoweo, November 27-28, 1914. (From the J. M. Alexander map of 1885.) Scale  $1\frac{1}{4}$  inch to 1 mile. x = glowed a little. L = new lava, mostly flows. EE' = edge of distinct

x = glowed a little. L = new lava, mostly flows. EE' = edge of distinct pool. F' = large fountain. F = fountains. S = steam (white vapor). M = mounds. F<sup>2</sup> = irregular fountain. Sketched by L. C. Palmer.

below the top of the mountain. Circles are fountains (F). M are mounds with fountains back of them or else cones with fire coming through them. (Mr. Palmer identified no definite flames.) I could not tell at night, and by morning there did not seem to be any lava coming over them at all. F' is a large fountain varying in width, as it sometimes included a small fountain to the south—about 150 feet was the average width, but that is only a guess. The great fountain played continuously about half the height of the west wall of the crater, sometimes higher, particularly between 2 and 4 A. M., when it must have reached a height 2/3 or 3/4 that of the west cliff.

 $F^*$  is a fountain which sent up a single column of lava at irregular intervals, not as high as F'. S is steam or vapor. Most of the night there was black crust over most of the lava area, but towards morning between 2 and 4 it disappeared, particularly in the northern part, where the surface was all red for a while, but by daylight it looked black again. Between the lake and the east wall (x), the lava was the same level as the lake but black, except that a little fire showed at x."

The next night, Nov. 28, the writer's party reached the summit area, but was driven back by a severe sleet storm. In camp at a distance of about three miles from Mokuaweoweo west, distinct rumbling could be heard from the crater at intervals, resembling the rumbling heard at Kilauea during activity a few feet back from the edge of Halemaumau. Messrs. Palmer and Forrest on the previous night described the noises of the fountains as heard at about one mile distance on the east rim as rumbling and plashing, but not very loud or different from the sounds usually heard at Kilauea.

Stormy weather followed and covered the summit area and the floor of the crater with ice and snow. A second party, consisting of Charles Ka, Hawaiian guide, and an assistant, was sent up by the writer Dec. 3, 1914, to recover abandoned camp equipment. They reported four fountains in the southern part of the creater, the northernmost the largest, the whole four corresponding in position with the large fountain F' of Nov. 27. Such dwindling corresponds with the appearance from below. Ka saw the mounds, and identified the cone of 1907 as still in place in the western part of the crater. He described the entire eastern half of the crater and the eastern plateau as plastered with heavy ice. He saw very little smoke.

Dec. 6 from the observatory at Kilauea at 10 P. M. the summit of Mauna Loa was clear with only a single slender vapor column rising and spreading at a height of perhaps 7000 feet above the summit into a thin illumined balloon of fume. The color of the light was orange. This morning, Dec. 7, Mauna Loa was capped with snow, and a thin faint column or fume could be seen widening above into very tenuous blue films in the upper atmosphere. The smoke has the same quality as that from Kilauea, brown in transmitted light and blue in reflected light. It is undoubtedly sulphurous but as yet its odor has not been perceived by anyone.

# ART. IX. — Carboniferous Plant Tissue; by ERWIN H. BARBOUR.

UNUSUAL amounts of actual plant tissue of Carboniferous age were found in 1912 one mile south of Peru, Nebraska, while exploring the newly discovered Eurypterid beds.\* Only the most resistant tissue could have endured through such a lapse



FIG. 1. Photomicrograph of Carboniferous Plant Tissue, Peru, Nebraska. Magnified 110 diameters.

of time. When freshly cleaved, the Eurypterid shales reveal innumerable bits and patches of tissue, mostly bright red in color. The tissue has surprising substance, pliability, and strength, and can be collected easily by stripping from the shale and dropping into phials of water or alcohol. When

\* Barbour, E. H., this Journal, vol. xxxviii, p. 507, December, 1914.

dry it curls like thin shavings, but upon immersion in water straightens out nicely. It is readily handled in the laboratory, for it can be dehydrated, stained, cleared of coal particles, and imbedded and sliced for examination.

We have about one hundred permanent mounts in our collection. The tissue varies from fragments to pieces 10 millimeters wide by 75 long. Most of it, under transmitted light, is a bright transparent yellow, ranging to orange, red, brown, and blackish, according to the amount of iron and ulmate. All mounts show cell structure well, and photomicrographs are readily obtainable.

Apparently these pieces of tissue are the resistant cuticular layers of certain leaves. Two or three distinct kinds have already been noted. The cells are sub-parallel to parallel in arrangement, and are interspersed by numerous stomatous openings. The still greater number of small circular openings probably represent truncated epidermal hairs.

As far as examined, the bulk of the material, especially the larger pieces, seem referable to Cordaites. Such tissue has had occasional mention in Europe and America, but the Nebraska material seems unique in amount and excellence of preservation. As many as fifteen to twenty pieces to the square foot have been noted.

This problem has been assigned to a Fellow in the Department of Geology, the University of Nebraska, for careful study and publication. The material is a part of the geological collections of Hon. Charles H. Morrill.

University of Nebraska, Lincoln, Nebraska.

## ART. X. — Crystallization — Differentiation in Silicate Liquids ; by N. L. BOWEN.

## Introduction.

EVER since Darwin pointed out the possible importance of the sinking of crystals in a fluid magma, this process has received some attention from geologists when considering the causes that have brought about the observed variety of igneous Though having a few ardent advocates like Schweig, rocks. the process has met on the whole with little favor. The question is not infrequently dismissed with the statement that there is no evidence that crystals sink in magmas. This summary rejection of the process is quite inconclusive. Such a statement, to have any weight, should be accompanied by a fair discussion of the kind of evidence that would be expected and a convincing proof that such evidence is absent. The importance of the process must be judged by the extent to which observed results agree with the results to be expected if such a process were operative. Examined in this way it soon becomes apparent that the subject cannot be dismissed in a sentence, for many igneous bodies showing density stratification forbid it. In the writer's opinion the sinking of crystals will not only escape summary rejection as a result of such examination, but will be accepted as of very fundamental importance. In this paper discussion will be avoided of the whole question of the extent to which observed field-facts indicate the importance of the sinking of crystals in magmas. The purpose of the paper is principally to describe a few experiments which illustrate the operation of the process in mineral solutions from which crystals are forming and to apply the results to one or two occurrences.

In a recent paper on "The Ternary System : Diopside-Forsterite-Silica," the writer discussed the results which would follow from the sinking of crystals in some of the liquids of the system." These liquids are rather more fluid than most *artificial anhydrous* melts, and among such melts should be rather favorable for the sinking of crystals. It was determined, therefore, to hold a small crucible of one of these melts at a temperature at which it should consist of liquid and crystals and to observe what effects of this kind could be obtained. The advantages of using artificial melts which had formerly been completely investigated are many. It was known at what temperature the mixture should be held to obtain the desired effect. No com-

\* This Journal (4), xxxviii, 258, 1914.

plication due to a chemical action, such as oxidation of ferrous iron, could ensue, as might be the case if a natural rock were used. The results obtained should therefore be capable of straightforward, unequivocal interpretation. That crystals would sink in such a liquid when they are heavier than it seems an obvious necessity. Nevertheless, in the case of many natural occurrences where the conditions are equally favorable the process has been questioned. For this reason the experimental results will be described.

#### The Sinking of Olivine.

A homogeneous mixture of the composition of a pyroxene, diopside 56 per cent, MgSiO<sub>3</sub> 44 per cent, was first used. A quantity of this mixture was placed in a small platinum crucible 2.5<sup>cm</sup> deep and 1.5<sup>cm</sup> in diameter, and the crucible was suspended in a platinum-resistance furnace. The temperature was measured by a Pt: Pt-Rh thermoelement whose junction was nearly in contact with the surface of the melt. After raising the temperature until the charge was entirely liquid and filled the crucible to a depth of about 1.5cm, the temperature was lowered slowly to 1430°. At approximately 1460° olivine (forsterite) begins to crystallize out. This continues until the temperature 1430° is reached, when the cooling was checked and the temperature maintained at this value for varying periods of time. The charge should consist of olivine crystals 4 per cent, liquid 96 per cent. Sinking of crystals should result in this case merely in their accumulation towards the bottom, the liquid remaining of uniform composition whether crowded with crystals near the bottom or quite free from them near the top. When the temperature had been maintained for the desired length of time the crucible was quickly removed from the furnace and cooled in water in order to prevent further crystallization.

When this was successfully accomplished it was found that the accumulation of crystals towards the bottom of the crucible was marked, the effect becoming more evident when the time allowed for the sinking of crystals was increased. The effect was plainly visible with the naked eye, even after the brief period of 15 minutes. The glass at the top of the crucible was clear and transparent; with increasing depth it assumed an increasing milky appearance, and at the bottom it was an opaque white. The milky, opaque appearance was caused by the dispersal of light due to continued reflection from the faces of the small olivine crystals, and it increased in intensity with the increasing abundance of olivine crystals towards the bottom. The individual olivine crystals were plainly recognizable with the aid of a hand-lens.

176

When the time allowed was 45 minutes, about one-half the depth of the crucible was a clear glass; the lower half milky, to opaque at the bottom. After 80 minutes the upper  $13 \cdot 5^{\text{mm}}$  layer was entirely free from olivine crystals, all having collected in a  $1 \cdot 5^{\text{mm}}$  layer at the bottom. In all cases the liquid portion was of uniform composition from top to bottom, as shown by the uniform refractive index of the glass.

The charges are traversed by innumerable cracks as a result of the quick cooling which must be resorted to. It is, there fore, very difficult to cut a single section from the top to the bottom of the crucible to show the increasing proportion of the olivine crystals. One charge which was held only 15 minutes was broken out of the crucible in 6 approximately equal layers. A piece from each of the 2d, 4th, and 6th or bottom layers was selected and sections were ground. Photomicrographs of these sections are shown in fig. 1, which indicates at the same time their positions in the crucible. The very marked effect obtained in only 15 minutes is plain. The manner in which the crystals are packed together at the very bottom is clearly shown. The crystals in this bottom layer are noticeably smaller than those higher up, owing to the fact that they sank only a very short distance before coming to rest on the bottom, and had therefore less opportunity for growth than those which sank a considerable distance. The lowest of the three sections of fig. 1 is shown in greater magnification in fig. 1a. Close to the middle portion of the right-hand edge, three clusters of crystals are shown, each collected about a bubble. These groups of crystals have weighted the bubble so that it did not escape from the liquid, and the crystals were likewise buoyed up by the bubble. The minimum of motion resulting has left the crystals smaller than their neighbors and comparable with those near the bottom.

Fig. 2 shows, in a single section from the lower part of the crucible, the more rapid passage from the portion without crystals to that rich in crystals when the time allowed was 45 minutes.

These trials were repeated a number of times and always with the same result. Other mixtures from which forsterite is the first mineral to crystallize gave similar results.

## The Sinking of Pyroxene.

In order to observe the effects of increasing viscosity, mixtures which contain an excess of silica over pyroxene composition (metasilicate ratio) were also used. In the case of the mixtures of pyroxene composition, from which olivine first crystallizes, it was usually possible to cool the crucible quickly

N. L. Bowen-Crystallization-

Fig. 1.



FIG. 1. Olivine (forsterite) crystals in glass showing position of sections in the crucible.  $\times$  10.

enough to prevent further crystallization. Occasionally, however, rims of amphibole formed about the olivine crystals. In the mixtures with an excess of silica, from which pyroxene first crystallizes, this tendency towards the formation of amphibole during cooling was still more marked, indeed very difficult to prevent in spite of the greater viscosity of the

FIG. 1a.

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FIG. 1*a*. Same as lowest section of fig. 1. For sterite crystals in glass.  $\times$  25.

liquid. This must be attributed to a greater power of the pyroxene crystals to induce crystallization of amphibole. In order to overcome this difficulty it was necessary to use very much flattened crucibles which exposed a large cooling surface. These were made by folding thin platinum foil into the desired shape and had about the same depth  $(2\cdot 5^{\text{cm}})$  as had the ordinary crucibles.

A mixture of 92 per cent of the pyroxene, diopside 56 per cent,  $MgSiO_{a}$  44 per cent, with 8 per cent  $SiO_{a}$  was placed in one of these crucibles and after raising the temperature to about 1500° it was lowered slowly to 1420° and held at that temperature for varying periods. At this temperature the mixture should consist of about 95 per cent liquid and 5 per cent of a pyroxene much richer in magnesia than is the liquid. Quite



Fig. 2.

FIG. 2. Forsterite crystals in glass, showing rapid passage from lower portion rich in forsterite to upper portion free from forsterite.  $\times$  25.

definite sinking of pyroxene crystals was observed. After 3/4 hr. about  $1/2^{cm}$  from the surface of the liquid was free from crystals as a result of their sinking towards the bottom. In 2 1/2 hrs. all the crystals had collected on the bottom, about  $1.7^{cm}$  of the liquid above them being entirely free from crystals. The pyroxene crystals so produced were stout prisms  $0.5^{mm}$  long, remarkably large for crystals obtained in small crucibles without a special flux.

## Differentiation in Silicate Liquids.

In spite of the fact that the charges were very much cracked by the sudden chilling, it was possible in some cases to make a vertical section by grinding down the whole charge. One of these is shown in fig. 3. The black border of irregular width

FIG. 3.



FIG. 3. Vertical section of clucible showing pyroxene crystals in glass.  $\times$  5.

bounding the sides and bottom is the remnant of the platinum crucible left after grinding. The surface of the liquid is marked by a line of amphibole crystals (principally spherulites) which formed at the surface during cooling in spite of the fact that this was very rapidly accomplished. The surface of the

#### N. L. Bowen—Crystallization—

liquid was inclined to the horizontal because the crucible became pinched very thin at one side and the liquid rose by capillarity at that side. Below the line of amphibole marking the surface the glass is entirely free from crystals for a considerable distance. Pyroxene crystals then appear sparingly and they increase in abundance downward. In the lower part the crystals occur for the most part in clusters, though individual crystals are quite frequently discernible. The effect shown in fig. 3 was obtained in 45 minutes.

#### The Floating of Tridymite.

Examples of crystals separating from silicate liquids heavier than themselves are probably rare in nature. Orthoclase may, perhaps, be lighter than some of the more basic magmas from which it may form, such as essexitic magma. Sodalite is possibly lighter than some of the magmas from which it crystallizes. The importance of the rising of crystals in a magma is, however, probably small. In order to illustrate its possibility in certain artificial melts, mixtures of the same general type as those showing sinking of olivine and pyroxene crystals were By adding a still greater proportion of silica, mixtures used. from which tridymite is the first mineral to crystallize are obtained. On account of its very low density tridymite is to be expected to rise in such a liquid. A mixture of 85 per cent of the pyroxene, diopside 75 per cent, MgSiO, 25 per cent, with 15 per cent SiO, was held at 1±30°, at which temperature it consists of 98 per cent liquid and 2 per cent tridymite. On account of the increased viscosity of this more siliceous melt the rising of tridymite must be expected to take place slowly. After 3 hours no definite effect was discernible but after 54 hours a little more than 1<sup>cm</sup> from the bottom of the crucible was entirely free from tridymite crystals, all having risen into the upper  $5-6^{mm}$  of the liquid. The crystals were of subhexagonal, tabular form, about 0.2<sup>mm</sup> in diameter and 0.06<sup>mm</sup> thick.

In fig. 4 a section near, the top of the melt is shown. The tridymite crystals are fairly abundant in this portion, though they constitute only about 2 per cent of the charge, the whole lower portion being entirely free from them. There is also a crowding together of the crystals at the top of the section which corresponds with the top of the liquid. The crystals in the uppermost part are distinctly smaller than those lower down owing to the fact that they rose through only a short distance before coming to rest at the surface and had therefore less opportunity for growth. The relation is of the same nature as that shown by the olivine crystals at the bottom in fig. 1.

182

## The Effect of Convection Currents.

The cooling of a body of magma at its upper margin must be considered to cause a greater density of the liquid near the top and, therefore, to exert a tendency towards the establishment of convection currents. We are acquainted with convec-

### FIG. 4.



FIG. 4. Section from top of melt showing tridymite crystals in glass.  $\times$  25.

tion currents largely in their very vigorous form as set up in a beaker of water when placed over a flame. Very little of a quantitative nature is known relative to convection currents. It appears, however, that a marked gradient of temperature, a high coefficient of thermal expansion of the liquid and a low viscosity should favor vigorous convection. When a beaker of water is placed over a flame it is exposed to a very high temperature gradient such as cannot reasonably be supposed to exist in any considerable magma body except, perhaps, quite close to its margin. The thermal expansion of water is very considerable. Between 4° C. and 100° C. it expands more than 4 per cent of its volume. Diabase glass (undercooled liquid) expands only a little more, about 6 per cent, in a range of more than 1100°, its kilogram volume being 362 at 25° and 384 at 1150°.\* The viscosity of water must also be considered very much less than that of magmas. Each individual factor affecting convection is decidedly in favor of the familiar case of a beaker of water placed over a flame. It is not to be expected that the vigor of convection in a body of magma would even remotely approach that established in the beaker.

Vigorous convection, by causing a general stirring of the liquid, might seriously interfere with the sinking of crystals. It has been shown above that convection of such a character is scarcely to be expected in natural magmas. In spite of this expectation it was considered desirable to conduct the experimental attempts to obtain the sinking of crystals under condi tions which favored the existence of convection currents. With this end in view the temperature distribution within the furnace was carefully explored with two thermoelements free from contamination. They agreed in placing the maximum temperature a little below the middle of the vertical cylindrical tube of the furnace as might be expected. From this point the temperature falls off both upward and downward at first slowly and then more rapidly. By holding the crucible above the position of maximum temperature, in the region where the temperature increases downward, the bottom of the crucible could be maintained at a slightly higher temperature than the top, a condition favoring the establishment of convection currents. It was under such conditions that the results already described were obtained. The crucible was held in a position where the temperature gradient had been found to be rather steep, about 4° per cm. The gradient cannot be supposed as great in the contents of the crucible itself but it must have been considerable. In spite of such currents as may have been set up the definite results already described were obtained. In a magma body a gradient of 1° per cm. is probably extreme except in the region near the margin for a brief period prior to crystallization in that region. A gradient of 1° in several meters is probably more common in the main mass of a body of magina. The tendency towards convection must be small, and would probably not interfere with the sinking of crystals any more effectively than it did in the crucible containing the artificial melt.

\* Day, Sosman and Hostetter : Determination of Mineral and Rock Densities at High Temperatures, this Journal, (4), xxxvii, 27 and 35, 1914.

### The Viscosity of the Melts.

If the effect of convection currents in delaying the sinking of crystals in the crucible may be considered negligible it is possible to obtain a rough idea of the order of magnitude of the viscosity of the silicate melts. It must be thoroughly emphasized that the figures so obtained and stated below cannot be considered as having any exact significance. They merely form a basis for the rough comparison of the viscosity of these silicate melts with that of liquids of everyday experience. The rate of sinking of small spheres in a liquid is given by the equation

$$V = \frac{2}{9} \frac{gr.^2 d - d'}{v}$$

where V is the terminal velocity; r, the radius of the sphere and d its density; v, the viscosity of the liquid and d' its dens-The rate of sinking of forsterite crystals from the less ity. siliceous melts was approximately 1 cm. per hr., since the surface indicating the upper limit of crystals moved downward at approximately that rate. The crystals lying near this limiting surface have an average diameter somewhat less than 0.1mm. The difference in density between forsterite and the liquid at the temperature of the experiment is not known, but since forsterite does not invert before melting it is probably not far from the difference at room temperature, approximately 0.4. These values would indicate an absolute viscosity of about 8. It is to be noted, however, that the crystals were growing while sinking, and though they grew very quickly at first and were nearly their final size throughout the greater portion of the time it is probable that a viscosity 1/2 as great as that given above would be a fair estimate of its actual value. The viscosity indicated is, therefore, about 4, or approximately 400 times that of water and somewhat less than 1/2 of that of glycerine at room temperature. In so far as the sinking of crystals was interfered with by convection currents this value is to be considered too high and, therefore, a maximum estimate, but the fact that the surface marking the upper level of crystals moves downward as a fairly definite plane indicates that the effects of convection currents in keeping the crystals evenly distributed is negligible.

For the more siliceous type of mixtures from which pyroxene crystals settled out the viscosity is considerably greater. The difference in density between the crystals and liquid is approximately the same. Crystals of pyroxene of average dimension  $0.5^{\text{mm}}$  sink in these liquids only about as fast (1<sup>cm</sup> per hr.) as did crystals of forsterite  $0.1^{\text{mm}}$  in diameter in the less siliceous mixtures. In another case crystals  $0.3^{\text{mm}}$  in diameter sank about

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 230.—February, 1915.

 $1/3^{cm}$  per hr. These examples agree in placing the absolute viscosity of the mixtures at roughly 25 times that of the less siliceous mixtures or at about 100.

The still more siliceous mixture which exhibited the floating of tridymite crystals shows a further increase of viscosity. The difference in density between tridymite and the liquid is approximately the same as that between forsterite and the liquid from which it settled, but of the opposite sign. Crystals of tridymite and of forsterite of the same size should rise in the one case or sink in the other at approximately the same rate in liquids of the same viscosity. But crystals of tridymite rise in the artificial melt at about 1/50 the rate at which forsterite crystals of the same size sink. The viscosity of the liquid is therefore approximately 50 times as great, or in absolute units about 200.

The liquid \* of composition, pyroxene 98 per cent, SiO, 2 per cent, has a viscosity of about 4 at 1430°, pyroxene 91 per cent, SiO, 9 per cent at the same temperature, a viscosity of about 100, and pyroxene 86.5 per cent, SiO<sub>2</sub> 13.5 per cent, a viscosity of about 200. All of these are rough estimates and tend to be rather too large than too small.

### Differentiation.

When the crystallization of the liquid is completed in those artificial preparations in which olivine crystals sank, the upper part consists of pyroxene and free silica and the lower part of pyroxene and olivine. It is sometimes suggested that the sinking (or rising) of minerals in the magma has been a factor in producing differentiation in cases where the differentiates consist of the same minerals in varying proportions. Thus Ussing thinks the process likely for his nephelite-sodalite-eudialyte syenites, which are rich in sodalite in the upper layers and rich in eudialyte and other heavy minerals in the lower layers; but he denies its general importance.<sup>+</sup> The result of the sinking of crystals is, however, not necessarily of such a simple character. A partially different assemblage of minerals may result, as shown in the comparatively simple artificial mixtures described above, and the likelihood of such phenomena is greater in more complex systems.

## The Sinking of Crystals in the Palisade Diabase Magma.

J. V. Lewis describes an olivine-rich layer in the Palisade diabase as the olivine-diabase ledge. It occurs 40-50 feet

<sup>\*</sup> The composition of the liquid is obtained by correcting the total composition of the original mixture by the amount necessary on account of the separation from it of the small proportion of crystals. † Geology of the Country around Julianehaab, Greenland, p. 347.

above the base of the Palisade sill, and is remarkably rich in olivine. He interprets it as due to an accumulation in this layer of sunken olivine crystals. It is to be noted, moreover, that the main body of the diabase, from which the olivine crystals have sunk, contains free silica (quartz), therein presenting an analogy to the upper portion of the artificial mixtures in the experimental work. The observed result appears to be exactly that to be expected if the process pictured by Lewis was operative. It may seem that this occurrence of free silica in the main portion of the sill is merely a superficial analogy with the case of the artificial mixtures, but a little consideration should dispel this idea. In the artificial mixtures the olivine would have been redissolved had it not settled to the bottom and become very concentrated there. In the upper layers, as in all the layers, its resolution would have resulted in the formation of the more siliceous pyroxene by reaction with the liquid. The failure of this reaction in the upper layers on account of the removal of the olivine leaves the liquid with an excess of silica. Now in the Palisade diabase there are quickly chilled marginal phases from which the olivine did not settle out. The olivine crystals are partially redissolved, having reacted with the liquid to form pyroxene. The failure of this reaction in the main mass of the diabase on account of the removal of olivine must, as in the artificial mixture, leave the liquid with an excess of silica. The similarity of the two cases is of a fundamental nature and lies in the fact that the olivine would have been partly redissolved. It is clear that the formation of at least some of the quartz of the main mass of the diabase is to be attributed to the process of differentiation by the movement of crystals under the influence of gravity. It is not necessary to assume solution of the surrounding quartzites or arkoses, a process of which Lewis finds no evidence.<sup>±</sup>

It is likely that the rate of sinking of olivine crystals was many times greater in the diabase liquid than in the artificial melts here treated. The rate of sinking of a crystal increases with its size, with the fluidity of the liquid and with the difference in density between crystal and liquid. Palisade diabase glass has a density at room temperature of 2.763. The liquid inwhich forsterite crystals sank in the experimental work has a density as glass at room temperature of 2.82, considerably greater than that of diabase glass. The artificial liquid is very closely related to diopside in composition and therefore may be assumed to expand at nearly the same rate as diopside liquid. Now

<sup>†</sup>J. V. Lewis: Petrography of the Newark Igneous Rocks of New Jersey, Ann. Rept. State Geologist N. J., 1907, p. 127.

‡ Loc. cit., p. 132.

diopside glass expands at nearly the same rate as diabase glass, so that at high temperatures the ratio of densities is nearly the same as at low temperatures.<sup>\*</sup> It is, therefore, safe to state that the liquid in the experimental case, closely similar to diopside liquid, would still be considerably heavier than diabase liquid at high temperatures, especially since the diabase liquid must be considered somewhat lighter in its natural state owing to the presence of volatile constituents. Nothing is known of the change of density of forsterite with temperature, but it is known that magnesia-iron olivine would be heavier than pure magnesian olivine at any temperature. With the crystals heavier and the liquid lighter in the natural case as compared with the experimental case, the rate of sinking should be greater from this cause.

The liquid from which the forsterite crystals sank in the experimental example had the composition of a lime-magnesian pyroxene with a little excess silica. Diabase may be considered to be made up of this same material with plagioclase material and certain ferruginous material added. The plagioclase material would undoubtedly render it more viscous, but the ferruginous material would compensate this effect. It is probable, therefore, that even anhydrous diabase liquid is as fluid as the liquid in the experimental example. Day, Sosman and Hostetter describe diabase liquid as rising by capillarity in the walls of a porous alundum crucible "like water in filter paper."<sup>+</sup>

With the addition of water and other volatile constituents the viscosity of diabase liquid may be considered probably as small as that of the artifical pyroxene melt even though the temperature was considerably lower. Morey has demonstrated the remarkable effect of water in lessening the viscosity of silicate liquids.<sup>‡</sup>

If the viscosity of the liquid and the density difference between the olivine crystals and liquid are considered comparable in the natural case with the same factors in the experimental case, a moderate assumption, the larger olivine crystals  $(0.7^{mm} \text{ diam.})$  in the olivine-diabase ledge would have settled at the rate of about 1 meter per hour. The thickness of the sill is from 200–300 meters. If the time occupied in cooling through the interval of crystallization of olivine, partly alone and partly in company with other minerals, were as much as 200–300 hours, it would suffice for the collection of the olivine

\* Unpublished data furnished by Dr. Sosman.

† Determination of Mineral and Rock Densities at High Temperatures, this Journal (4), xxxvii, 34, 1914.

<sup>‡</sup> New Crystalline Silicates of Potassium and Sodium, their preparation and general properties, Jour. Am. Chem. Soc., xxxvi, 226, 1914.

crystals in a layer near the bottom.\* This does not seem to be an unreasonable expectation as to the rate of cooling of such a body of magma in its interior portions. Towards the border it would no doubt cool much faster, and this fact is clearly expressed in the contact phase which bears olivine. Near the contact the cooling was too fast to allow time for the sinkingout of the olivine crystals, which are therefore retained. There is no reason for appealing to the Soret action, an accumulation of certain constituents towards the cold border while the magma is still entirely liquid.<sup>+</sup> Neither is there any reason to accept an explanation involving a diffusion of material towards the cold border during crystallization, Harker's preferred explanation of such phenomena.<sup>‡</sup> It is a plain case of restriction of differentiation at the contact on account of quick cooling and continuance of gravitative differentiation by sinking of crystals in the more slowly cooled part removed from the contact. This is substantially the process advocated by Daly to explain 'basic contacts's in general, though he considers immiscible liquid portions as the probable units of gravitative differentiation. To this phase of Daly's explanation many objections can be raised, but of the truth of the general idea the Palisade sill furnishes an excellent example.

In stating that the accumulation of olivine crystals might have been accomplished in a period of 200-300 hours the influence of convection currents has not been mentioned. The deduction was, however, made on the basis of experimental work in which the opportunity for convection was favorable and possibly comparable with that in the main interior portion of the sill, though this is a question difficult to decide. That convection has played no important part seems, however, to be shown by the sill itself. It was cooled both at the top and at the bottom surfaces, the temperature therefore rising inward from both to a layer near the center. In the lower half the temperature gradient was in the proper direction to eliminate convection currents, whereas in the upper half they were favored. It might be considered therefore that sinking of crystals was free to take place in the lower half, but seriously interfered with or prevented in the upper half. Thus would

\*In assigning a viscosity to the diabase magma comparable with that of the artificial melt from which olivine settled (4, or about 400 times that of water) Becker's estimate of the viscosity of Hawaiian basalt has been exceeded 8 times. If the Palisade diabase magma had a viscosity as low as 50 times. If the Falisade diabase magina had a viscosity as low as so times that of water, and this is quite possible, the collection of olivine crystals might have taken place in from 25-40 hours.
†J. V. Lewis, Petrography of the Newark Igneous Rocks of New Jersey, Ann. Rep't State Geologist of N. J., 1907, p. 131.
†The Natural History of Igneous Rocks, pp. 317-320.
§ Igneous Rocks and their Origin, pp. 243-242.

arise an arrangement in which the upper half showed little differentiation and the lower half marked differentiation. The sill, however, has no such dual character. It is a unit, the bottom portion representing, in a general way, an accumulation of the heavy crystals from the whole body and the top portion the lighter residuum.\*

### The Sinking of Crystals as a General Factor.

The Palisade sill clearly illustrates, as Lewis concludes, the importance that the sinking of crystals may have in differentia-There are many other more or less similar occurrences, tion. among them the Duluth gabbro laccolith, + the Preston gabbro laccolith<sup>‡</sup> and the Sudbury sheet, which illustrate its general importance. Harker has recently expressed his belief that the sinking of crystals may be of importance in deep-seated magma basins, but for differentiation in place he appeals to diffusion towards a cooling boundary. In the face of so many examples of differentiation in place through sinking of crystals it seems wholly inadvisable to follow Harker in making this distinction.

The sinking of crystals may possibly be considered of greater importance in basic than in intermediate and acid rocks on account of greater viscosity of the latter. There is, however, little very convincing evidence that acid rocks are really much more viscous than basic rocks so long as they are kept confined and retain their volatile constituents. Where they occur in very large, deep-seated bodies whose cooling must be a very slow process, a viscosity even several hundred times as great as that of diabase magma could not prevent some differentiation through the sinking of crystals. There is little reason to believe that these bodies of magma usually have such great viscosity. It is certain, therefore, that we cannot avoid assigning a general importance to the sinking of crystals in the differentiation of igneous rocks.

## Summary.

Experiments with artificial melts were undertaken in order to observe whether sinking or floating of crystals could be obtained. The sinking of olivine and pyroxene and the floating

<sup>\*</sup> Lewis, loc. cit. p. 132.
† W, S. Bayley, Jour. Geology, vol. ii, p. 814, 1894.
‡ G. F. Loughlin, Bull. 492, U. S. Geol. Survey, 1912, p. 78.
§ A. P. Coleman, Rep't Bureau of Mines, Ontario, vol. xiv, pt. 3, 1905.
¶ Daly has listed a large number of examples of gravitative differentiation.
Igneous Rocks and Their Origin, pp. 220-236.
¶ Compte Rendu, XUe Session, 1913, p.

<sup>¶</sup> Congrès Geologique International, Compte Rendu, XIIe Session, 1913, p. 208.

of tridymite were quite readily obtained in various mixtures of the system: diopside, forsterite, silica.

With the rate of sinking of the crystals as a basis rough estimates were made of the viscosity of the melts, and they show, as might be anticipated, a progressive increase of viscosity with increase of silica.

The importance is discussed of the sinking of olivine crystals in the Palisade diabase sill to which J. V. Lewis has called attention. Contact chilling may, by restriction of the process of sinking of crystals, bring about the formation of a basic contact phase.

The fact is pointed out that the sinking of crystals cannot safely be considered negligible even in acid magmas when they occur in large bodies.

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## ART. XI.—Note on Bottom Currents in Lake Ontario;\* by E. M. KINDLE.

THE observations which are presented in this paper relate to data which were obtained as an incidental result of the study of certain phenomena associated with sedimentation. They were made while using specially devised apparatus for the making of ripple-mark molds under water. It was not foreseen that bottom currents would be met with in connection with the investigation of the problems of sedimentation which were undertaken. The writer was, therefore, not provided with instruments for precise measurement of the velocity of the subsurface currents encountered. For the opportunity to observe these and other factors in the general problem of sedimentation in Lake Ontario, the writer is indebted to the very liberal policy of Mr. R. W. Brock, former Deputy Minister of the Department of Mines and Director of the Geological Survey of Canada, in initiating work in this important and little developed field of investigation.

The surface currents of Lake Ontario, in connection with those of the other Great Lakes, were made the subject of an elaborate investigation<sup>†</sup> some years ago by tabulating of the drift records of several hundred bottles thrown overboard at numerous and widely distributed points. Harrington's investigation of the lake currents relates almost entirely to the "body currents" or those connected with the general outflow or set of the water toward the outlet and their modifications by surface currents due to the prevailing winds. The extremely slow movements of these currents, varying from four to twelve miles per day, which Harrington was able to demonstrate and chart, renders them of comparatively slight importance as geologic agents. They could be effective in transporting only sediments in which the minute size of the particles made them nearly intangible elements of the products of sedimentation. Wholly independent of these gentle surface and outflow currents, there are in Lake Ontario subsurface and bottom currents which are at times effective and powerful agents for the transportation of sediments. Their erratic appearance and behavior is the result apparently of the varying wind and barometric pressures which produce them. Their subsurface operation and irregular periods of activity render them difficult of investigation but extremely important when considered as factors in the sorting and transportation of sediments. Their movement along the

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 $\dagger\,{\rm Currents}$  of the Great Lakes, U. S. Weather Bureau, Bull. B., 1894, by Mark W. Harrington.

bottom makes them competent to sort or transport recent sediments which would be unaffected by surface currents. The bottom currents must differ chiefly in their activities as agents of sedimentation from the persistent operations of tidal and river currents in transporting materials, through lacking the systematic cumulative effect which the latter produce. The activities and results on sedimentation of the work of such currents must vary with the atmospheric conditions which produce They represent in Lake Ontario, and doubtless in other them. large bodies of inland waters, important factors in sedimentation concerning which we have but little recorded information. The great strength sometimes displayed by these currents as compared with surface and wind currents is illustrated by the case of a yacht which overturned in a bay on the south shore of Lake Ontario near Charlotte, N. Y. and shifted cargo so that the stern sank very low while the bow remained just out of water.\* This capsized yacht was observed to drift slowly directly toward the wind during a heavy storm. The only systematic observations which have been made regarding these currents in Lake Ontario relate to the waters of the lake near Toronto, where Mr. L. J. Clarket undertook to ascertain the direction of local currents with reference to the location of sewers passing into the lake and the position of an intake pipe for the city water supply. In all of Clarke's observations, the currents were found to be correlated with the winds but their directions were often very different from those of the winds producing them. He says:-"Thus northeast, east and southeast winds pretty generally produce currents flowing southwest, while south, southwest and west winds give northeasterly currents and north and northwest winds give rise to variable currents. On seven occasions when the wind was from the north and northwest, the resulting currents were two northeast, three southwest and two southeast. Also a southwest wind would produce a northeast current south of the island and a northwest one west of the island. The phenomenon of the current being in a contrary direction to the wind was more marked in Humber Bay than to the south of the island, although on one occasion, on the seventeenth of July, we put out near Victoria Park, first, a thirty-foot float; second, a surface float without flag or drag, a mere tin can with an iron rod, four feet in length, attached; and third, an empty tin can. The wind was fresh from the east. The first and second floats went dead against the wind, while the empty can was driven along before the wind on the top of the waves. Close in shore we sometimes observed the current in an opposite direction to that farther out."

\*L. J. Clarke, Currents in Lake Ontario, Trans. Can. Inst., vol. ii, pp. 156, 1890.

+ Ibid. vol. ii, pp. 154-157, 1890 and vol. iii, pp. 275-281, 1891.

## 194 Kindle-Note on Bottom Currents in Lake Ontario.

The writer's observations on bottom currents were made on the south side of Prince Edward Island in Wellington Bay, near the town of Wellington.\* Wellington Bay is a roughly crescent-shaped indentation on the south shore of Prince Edward Island with a maximum width of about eight miles. The water deepens very gradually, the fifty-foot contour generally lying nearly two miles from shore. The current observations were made in this bay about one and one-third miles southwest of the old pier at Wellington in thirty feet of water, while using apparatus for taking ripple-mark moulds under water. On the date of the observations (July 9th) the surface of the lake and the air were absolutely calm until nearly noon, when very light air currents became perceptible. The quiet atmospheric conditions which prevailed are worthy of note because the writer's observations were made under the conditions of a dead calm, the reverse of those described by Clarke, who attributed the currents observed to the influence of winds blowing at the time. On putting overboard the heavily weighted metal ripple-mark mould, the presence of a strong undercurrent manifested itself by immediately pulling below the surface the wooden float attached to the end of the line used in hauling up the apparatus. The float, which was of pine wood  $2' \times 2\frac{1}{2}'' \times \frac{1}{3}''$ , was pulled down 12' or 15' below the surface by the strong tension of the current on the line and kept at that depth from 9.30 to 10.30 A.M. During the next half hour the current slackened, the float approaching the surface. From 11 to 11.15 the float remained on the surface, showing a current trending as before but much weaker, with a direction of N. 60° W. (Mag). After 11.15 the current strengthened somewhat and shifted to due west (Mag.) At 12, when observations ceased, the current was strengthening and running at right angles (west) to the very light breeze which sprung up just at noon. Summing up these details we may say that this current had a maximum velocity of probably four and one half miles an hour, which it maintained under the atmospheric conditions of a dead calm when the surface of the lake was as smooth as a sheet of ice. Both the velocity and direction of the currents were greatly altered while the atmospheric conditions remained unchanged at that locality, thus showing that they bore no relation to local air currents. This current where observed traversed a sandy bottom and it could not fail when running at the maximum strength noted to move constantly a film of sand grains across the bottom, thus making it an important factor in spreading sediments widely over the lake.

The bottom currents are well known to the deep water fishermen of the lake, who call them tides. The writer was told by

\* In making these observations the writer was assisted by Mr. E. J. Whitaker.

fishermen who set their nets in water 150 to 250 feet deep on the fishing grounds sixteen to twenty miles south of Presque Isle, that their floats are at times pulled down below the surface by the bottom currents so that they are sometimes unable to locate and haul up their nets for several days. They endeavour to avoid setting nets on sand bottom, stating that the currents when running are apt to make rope-like masses of them when set on sandy bottom. Hard or rocky bottom is chosen for setting nets for this reason. The deep water nets are anchored near the bottom by weights of from 75 to 100 pounds. The nets carry in addition about  $\frac{1}{4}$  lb. of lead for each 10' of net. Notwithstanding these heavy anchors and distributed lead weights it is said that nets are sometimes moved some distance by bottom currents during heavy storms. In such cases the nets, which are generally several hundred feet in length, are apt to be pulled into a horseshoe shape, the end anchors being found near together. It is evident that currents which would greatly disturb and sometimes ruin fishing nets or cause them to drag heavy anchors would be very effective distributors of fine and possibly of rather coarse sediments.

It is not alone as carriers of rock-making materials, however, that these bottom currents possess interest and invite investigation. They are important factors in the ecology of lake life. In those areas where they appear with most regularity and vigor they will doubtless be found to greatly stimulate the abundance of molluscan and vegetable life as well as the fish life which feeds upon it. It is not improbable that the areas which deep water fishermen have found to furnish the best fishing ground will be found to lie in zones where strong bottom currents are more prevalent than elsewhere. The writer found, while examining the bottom of Lake Ontario at the head of the St. Lawrence with the aid of a diving suit, that the strong bottom outflow current into the St. Lawrence exercises a very marked influence over the distribution of the Unios and other large bivalves. These large shells could be readily seen through the windows of the diving helmet in twenty-five or thirty feet of water. In descending from the shallow inshore water on the east shore of Wolf Island opposite Cape Vincent into the channel, one passes from an imperceptible current into the strong steady bottom outflow current of the head of the St. Lawrence. On the still-water zone shell fish are very scarce but on the current-swept bottom they are abundant, ten or twelve large bivalves being sometimes observed in the space of one square foot. Although familiar with a large part of the shores of Lake Ontario and Lake Erie, the writer has nowhere else seen the large fresh water molluscs in numbers which

would compare with the assemblage observed in the bottom current zone off Wolf Island.

The presence in the deep waters of the great lakes of the marine molluscan genus *Mysis*, and the marine fish *Triglopsis thompsoni*, has led some naturalists to infer a long period after the lakes had been separated from the sea by elevation, during which fresh water is assumed to "occupy entirely the upper stratum, while the heavier sea water remained at the bottom."\* The activity at frequent intervals of powerful currents in the lower levels of the lake which has been pointed out, would, however, make such a separation of fresh and salt water for any considerable period very improbable. The readjustment of such creatures from a salt to a fresh water environment has more probably been due to a long period of brackish water conditions, during which the whole body of the lake water slowly approached freshness.

Geological Survey, Ottawa, Canada.

\*Dr. William Stimpson, On the deep-water fauna of Lake Michigan, Am. Nat., vol. iv, p. 404, 1871.
Minnig-Separation and Estimation of Aluminium. 197

# ART. XII.—The Separation and Estimation of Aluminium Associated with Iron, by the Action of Acetyl Chloride in Acetone; by H. D. MINNIG.

# [Contributions from the Kent Chemical Laboratory of Yale Univ.-cclxiv.]

WATER becomes so modified as a solvent for barium chloride when hydrogen chloride is dissolved in it to saturation that this salt, which is easily soluble in pure water, dissolves in the saturated aqueous hydrochloric acid only in the proportion of 1 to about 20,000 parts. The addition of ethyl ether to the concentrated aqueous hydrochloric acid thus produced so diminishes the solvent action of the mixture upon barium chloride that the salt will then dissolve in the proportion of 1 to about 120,000 parts. Barium chloride may, therefore, be separated with accuracy from the ether-hydrochloric acid solution of the chlorides of calcium and magnesium which remain soluble in high degree, as was shown in a former paper from this laboratory.\*

Aluminium chloride, as was subsequently shown, + may be similarly precipitated by thorough saturation of the cooled aqueous solution after addition of an equal volume of ether, and effectively separated from iron; and by the same procedure aluminium may be separated from beryllium, zinc, copper, mercury and bismuth.<sup>±</sup>

Instead of charging the water solution with gaseous hydrogen chloride that reagent may be produced by the action of acetyl chloride upon the water, and this reaction has been tested more recently § in its application to the precipitation of barium chloride-inconvenient violence of reaction being moderated by acetone, which mixes in all proportions with both acetyl chloride and water and by itself exerts no appreciable solvent action upon hydrous barium chloride.

The present paper is the account of results obtained in applying the acetone-acetyl chloride mixture to the precipitation of aluminium as chloride and the separation of that element from iron. In preliminary experiments it was found that the hydrous aluminium chloride, AlCl., 6H, O, may be precipitated completely by the [4:1] acetone-acetyl chloride mixture and, after careful drying, may be converted directly to the oxide by ignition. In the quantitative experiments recorded below the aluminium chloride, prepared by saturating a strong solution of the commercial salt with gaseous hydrogen chloride and washing with concentrated hydrochloric acid until free

<sup>\*</sup> Mar., this Journal (3), xliii, 521, 1892.

Gooch and Havens, this Journal (4), ii, 416, 1896.
 Havens, this Journal (4), iv, 111, 1897; vi, 45, 1898.
 Gooch and Boynton, this Journal (4), xxxi, 212, 1911.

from iron, was dissolved in water and the solution was standardized by precipitating the aluminium hydroxide, igniting and weighing the oxide. The acetone-acetyl chloride mixture was made up in the proportion of four of acetone to one of acetyl chloride. In each experiment a portion of the standard solution was measured from a pipette into a small beaker and evaporated on the steam-bath to the smallest possible volume. To the concentrated solution, cooled by immersing the beaker in running water at a temperature of about 15° or in ice water, the acetone-acetyl chloride mixture was added drop by drop, with stirring, to the amount of 15<sup>cm<sup>3</sup></sup> to 20<sup>cm<sup>3</sup></sup>. The precipitate was transferred to a perforated crucible, washed with the precipitating mixture, dried for ten or fifteen minutes high above a low Bunsen flame, which was gradually increased to its fullest heat. Covering the precipitate with red mercuric oxide (to prevent mechanical loss during the ignition) and igniting under a good draft-hood was tried in a few cases, but without advantage over the simpler method. The results of experiments made with the pure aluminium chloride are given in Table I.

#### TABLE I.

Solution of	$Al_2O_3$		
AlCl <sub>3</sub> .6H <sub>2</sub> O	by	$Al_2O_3$	
taken	standard	found	Error
$\mathrm{cm}^3$	grm.	grm.	grm.
5	0.0213	0.0213	0.0000
5	0.0213	0.0215	-0.0001
5	0.0213	0.0213	0.0000
5	0.0213	0.0214	+0.0001
5	0.0213	0.0212	+0.0005
10	0.0426	0.0426	0.0000

In Table II are given the results obtained by similar procedure in the precipitation of the aluminium chloride from solutions containing also known amounts of ferric chloride.

TABLE II.

Solution of AlCl <sub>3</sub> .6H <sub>2</sub> O taken cm <sup>3</sup>	${ m Al_2O_3}\ { m by}\ { m standard}\ { m grm.}$	Fe <sub>2</sub> O <sub>3</sub> present as chloride grm.	Al <sub>2</sub> O <sub>3</sub> found grm.	Error grm.
5	0.0513	0.0293	0.0212	+0.0002
5	0.0213	0.0293	0.0211	-0.0005
5	0.0213	0.0593	0.0213	0.0000
5	0.0213	0.0293	0.0212	-0.0001
5	0.0213	0.0293	0.0213	0.0000
5	0.0513	0.0593	0.0214	+0.0001
10	0.0426	0.0593	0.0426	0.0000
10	0.0426	0.0286	0.0425	-0.0001

In the experiments of Table II the iron was precipitated by NH<sub>4</sub>OH after cautiously diluting the filtrate with water and then determined gravimetrically as the oxide. The error of the results ranged from +0.0004 grm. to +0.0013 grm. in terms of ferric oxide. On investigation this was found to be due to ferric phosphate derived from the phosphorous compounds used in the preparation of the acetyl chloride.

Since the precipitation of the aluminium was quantitative and rapid, and iron could be determined easily other than as the oxide, larger quantities of aluminium were used with measured quantities of ferric chloride without determining the iron in the filtrate. With the use of larger quantities of the acetone-acetyl chloride solution, necessary for the increased amount of the salts, the aluminium chloride precipitate also began to include phosphate appreciably, as is shown in Table III.

TABLE III.

Solution of AlCl <sub>3</sub> .6H <sub>2</sub> O taken	Al <sub>2</sub> O <sub>3</sub> by standard	Fe <sub>2</sub> O <sub>3</sub> present as chloride	Al <sub>2</sub> O <sub>3</sub> found	Error
$\mathrm{cm}^3$	grm.	grm.	grm.	grm.
15	0.0592	0.0373	0.0597	+0.0005
15	0.0592	0.0373	0.0602	+0.0010
15	0.0592	0.0746	0.0600	+0.0008
15	0.0592	0.0746	0.0602	+0.0010
15	0.0592	0.0373	0.0603	+0.0011
15	0.0592	0.0373	0.0606	+0.0014

Many efforts were made to purify the contaminated acetyl chloride, by redistilling after refluxing (for six or seven hours) with a return condenser over sodium acetate;\* over manganese dioxide, or over lead dioxide; but the product in every case gave a test for phosphoric acid when hydrolyzed with water, evaporated with nitric acid, and treated with the solution of ammonium molybdate in nitric acid. Phosphorus-free acetyl chloride was finally prepared by passing a rapid stream of hydrogen chloride either through a mixture of glacial acetic acid and phosphorus pentoxide† or, preferably, through purified acetic anhydride kept at 100°.‡ Distillation over anhydrous sodium acetate easily removes contaminating phosphorus compounds from the acetic anhydride.

Satisfactory results were obtained by the use of the pure acetyl chloride when as much as 1.3 grm. of the AlCl<sub>s</sub>.6H<sub>2</sub>O

\* Richter, i, 301 (1909 edition). † Richter. i, 300. ‡ Beilstein's Handbuch, i, 462. was present in a mixture of 2 grm. of the hydrous chlorides. No determinations of the iron in the filtrate were made when the pure acetyl chloride was used.

#### TABLE IV.

	Solution of AlCl <sub>3</sub> 6H <sub>2</sub> O taken cm <sup>3</sup> .	$Al_2O_3$ by standard grm.	Fe <sub>2</sub> O <sub>3</sub> used, present as chloride grm.	Al₂O₃ found grm.	Error Al <sub>2</sub> O <sub>3</sub> grm.
1.	15	0.1661	0.0373	0.1662	+0.0001
2.	15	0.1661	0.0746	0.1666	+0.0005
3.	15	0.1661	0.1492	0.1661	0.0000
4.	30	0.1854	0.0746	0.1852	-0.0005
5.	30	0.1854	0.1119	0.1860	+0.0006
6.	30	0.1854	0.1865	0.1862	+0.0008
7.	30	0.1854	0.1865	0.1856	+0.0005
8.	30	0.1854	0.3730	0.1856	+0.0005
* 9.	30	0.1854	0.2611	0.1856	+0.0005
*10.	30	0.1854	0.3730	0.1839	-0.0012
11.	45	0.2781	0.0746	0.2779	0.0005
12.	45	0.2781	0.0746	0.2787	+0.0006

\* After decanting the acetone-acetyl chloride solution of iron through the filter and washing the precipitate of the hydrous aluminium chloride with the precipitating mixture to remove as much of the iron as possible, the precipitate in the beaker was dissolved in the smallest possible quantity of water and reprecipitated by the acetone-acetyl chloride mixture. There is great danger of mechanical loss due to the creeping tendency of the ferric chloride in acetone-acetyl chloride solution and the separation is sharp enough to obviate any necessity of the second precipitation to avoid danger of inclusion of the iron.

The precipitation of hydrous aluminium chloride by the use of the acetone-acetyl chloride [4:1] mixture is very simple, quick and accurate and affords an easy method for the exact determination of aluminium associated with iron.

In conclusion it remains to thank Professor Gooch for his kind advice and suggestions throughout the course of the work.

# ART. XIII.—On the Solar Constant; by FRANK W. VERY.

In his article in the September (1914) issue of this Journal,<sup>\*</sup> Professor Bigelow employs two different methods for obtaining the solar constant and obtains by each a value of four gram calories per square centimeter per minute. This value may not be seriously in error, but the arguments on which it rests are not entirely convincing.

By the first method, "the pyrheliometer at any station observes the 'effective' radiation I, and never the solar constant, which is A = 2I on the upper level where  $J_a = 0$ " (op. cit., p. 281). Here  $J_a$  denotes the selective radiation of the atmosphere, and where the atmospheric radiation is zero, the atmospheric absorption must also be lacking; but why must the solar constant "on the upper level," that is, at the outer limit of the absorbent atmosphere, be twice as great as the radiation measured by a pyrheliometer in this situation? Apparently because the pyrheliometer is supposed to be a very thin, flat, black body which experiences a certain thermal effect from solar radiation received normally on only one surface, but whose own heat is radiated from two such surfaces, which alike possess the quality of the black body, whence the extra heat of the black body, derived from solar radiation, is only half as great as it would be were the radiation issuing from the rear surface to be suppressed. This argument, though not stated in so many words, is implied by the form of the radiation equation and shows a complete misconception of what we mean by a pyrheliometer. The ideal pyrheliometer is an instrument having only one efficient surface, which is that exposed to the sunshine. Where, as in some actinometers, the wholly blackened spherical bulb of a thermometer is used as a receiver, the factor 4 is always introduced in the reductions in allowing for the four-fold radiating surface of the receiver. The original pyrheliometer of Pouillet was an approximation to a single-surfaced, flat radiator, because, while the front surface was blackened, the rear was of silver, polished as brilliantly as possible. As a radiant body, this very nearly fulfilled the ideal specification. If the instrument could be used in a vacuum, or outside the atmosphere, it would leave little to be desired; but convection losses, which are large, affect both the black and polished surfaces, so that the theory is not as simple as we have supposed.

\*" The Determination of the 'Solar Constant' by Means of Computations Based on the Data of Balloon Ascensions," by Frank H. Bigelow; this Journal (4), vol. xxxviii, pp. 277-281.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 230.—February, 1915. 14 If the supposition were correct that  $A = 2I + J_a$ , the solar constant would have to be much larger than 4, since, as I have shown by the reduction of an observation by Violle,\* a value of I as great as 2.86 is reached at the altitude of 13.7 km. Twice this would be 5.72 without including anything for  $J_a$ .+

For his second method, Bigelow employs that of spectrobolographic energy-curves and the determination of the effective solar temperature from the maximum ordinate. This method, which I have discussed recently in this Journal,; seems to me the one least open to objection. Here Bigelow has obtained ratios by dividing the summed ordinates of the energy-curves by that for a temperature of 6900° Abs. C. These ratios are compared with those for  $J_a/A$ , which are quite similar, and the author concludes that "this shows that the energy lost in bolometer spectrum is the same as  $J_a$ , and it is absorbed in the lower levels" (op. cit., p. 281). This conclusion involves the assumption that all of the depletion suffered by the solar rays is produced by that atmospheric absorption on which J<sub>a</sub> depends. This assumption is certainly incorrect, since a large part of the lost radiation is reflected and does not enter into the thermodynamic equations of the atmosphere in any way. It is true that if the losses by reflection and by absorption were proportional at every level in the atmosphere, the above ratios would be the same as if the whole process were absorptive, and the indications are that there is such an approximate proportionality; but the proportionality need not be exact, and the approach to exactness probably varies with the season. The following are the observed ratios:

Station	Washington	Mt. Wilson	Mt. Whitney
Altitude above sea-level	64 <sup>m</sup>	1780 <sup>m</sup>	4420 <sup>m</sup>
Ratio from the bolometer spectru	m •363	·258	•236
" by thermodynamic theory.	•362	.287	·225

About 2/3 of the atmosphere remain above Mt. Whitney and also 2/3 of the depletion; hence there is no evidence that the depletion takes place "in the lower levels," except in the general sense that the atmosphere itself exists principally at

\* "A High-level Measurement of Solar Radiation," Astrophysical Journal, vol. xxxvii, pp. 25-30, January, 1913.

<sup>+</sup> My determination has been criticised by Mr. Abbot in the Astrophysical Journal for March, 1913. Only one objection is relevant, namely, that concerning the rate of cooling of black copper, and this is not justified, as would be evident if my investigation of the theory of the observations could be given in full. Unfortunately, this would require a lengthy discussion, and I have not behind me the power of a great institution, which can afford to publish such work *in extenso*.

<sup>+</sup> "Solar Radiation," this Journal (4), vol. xxxvi, December, 1913, cf. especially pp. 610-614.

these levels; nor is there any certain evidence of proportionality between depletion and atmospheric mass at still higher altitudes. If a distinction were to be made between reflective depletion and absorption, the former must come principally from the dust and air molecules of the lower air, while the principal selective absorption of solar rays is found at higher levels. Granting the equality of spectrobolometric and thermodynamic ratios, since the Mt. Wilson observations are the best, they favor a lower value than 4 for the constant, or about  $\frac{258}{287} \times 4 = 3.6$ , which agrees with the value obtained by Savélief to which I have ascribed exceptional merit for reasons given in my paper, "A Criterion of Accuracy in Measurements of Atmospheric Transmission of Solar Radiation."\*

I am of the opinion that the sums of various thermodynamic and radiant data for the entire atmospheric column which purport to be given in gram cal./cm<sup>2</sup> min., where the numerical value of the sum in each case approximates to 4, have nothing whatever to do with the solar constant; because, in the first place, the conversion from M. K. S. mechanical values into C. G. Min. thermal values has been incorrectly made. For example, values which were originally obtained in M. K. S. mechanical units have evidently been converted into C. G. Min. (thermal) units by multiplying by 0.000014337. But 1 joule/m<sup>2</sup>sec. = 10<sup>7</sup> ergs/m<sup>2</sup>sec. (mechanical) =  $\frac{10^7}{4\cdot185 \times 10^7}$ gram cal./m<sup>2</sup> sec. (thermal), which is equivalent to

$$\frac{10^7 \times 60}{10^4 \times 4.185 \times 10^7} = 0.0014337$$

for the C. G. Min. System, and the factor should be 100 times greater than that actually used. The mistake has arisen because in the original equations certain quantities were stated in values *per unit mass*, which was entirely permissible, but the calorie is a mass unit, and when quantities are given in thermal measure it is not allowable to eliminate mass, except where the mass is always unity, which is not the case here. Consequently, the mass of each specified section of the air column should be restored in making the thermal conversion. Elimination of nonessentials is a very convenient procedure, but it must never be forgotten that the eliminated quantities are only in abeyance, and that they must be restored whenever the conditions under which their omission was permissible no longer hold good.

In the next place, the passage of radiation through the atmosphere is a flux of a fairly definite amount of radiant

\* Astrophysical Journal, vol. xxxvii, pp. 31-47, January, 1913.

energy (in spite of a certain distinction which will be explained presently), which is not entirely constant at all levels because certain layers of air add their own radiation, while others absorb more than they emit; but the quantity which needs to be considered in a comparison with the continuous flux of solar radiation is the average flux through the entire air column, and not the sum of the fluxes through so many kilometer layers; that is to say, these sums should be taken. but should be divided by the number of layers if the numbers are to represent a flux of radiant energy measured in "gram cal./ cm<sup>2</sup> min."

Although the numbers given (op. cit., p. 278) are in this sense wrong, their ratios may be right, provided the arithmetical work of the similarly erroneous computations has always been performed in the same way; and thus it is of interest to note that the thermal properties of the atmosphere as a whole. derived from the thermodynamic equations, agree with those of a black body computed by Stefan's law, although the atmospheric selective radiation is only a little more than one-third as great. This result is in general agreement with that which I announced in my "Note on Atmospheric Radiation." \*

The form in which Bigelow states his radiant equation,

$$\mathbf{I} + \mathbf{J}_{\mathbf{a}} + \mathbf{B} = \mathbf{A},$$

is not unlike that which is introduced in my paper on "The Solar Constant," + where, however, B stands for *lost* radiation, either reflected from the atmosphere, or absorbed in lines too fine to be discriminated by the bolometer, or in broad hazy bands of such indefinite limits that they are not easily recognized. In this case B increases from nothing at the outer limit of the atmosphere to a value which may be greater than I at sea-level. This represents a fact of nature. My measures of the Earth's albedo<sup>‡</sup> show that a fraction of the solar rays which is equivalent to a thermal quantity of this order is reflected back to space by the Earth, and chiefly by the atmosphere of the Earth; but the losses by reflection can not possibly enter into any *thermal* equation of earth or air, and can not possibly be determined from the equations of atmospheric thermodynamics, which is Bigelow's proposition, because the reflected radiation has never been absorbed by material substances and can not affect their temperature in the slightest.

If Bigelow's B represented loss by reflection from successive layers of the air, it would increase gradually from zero at

<sup>\*</sup>This Journal (4), vol. xxxiv, pp. 533-538, December, 1912. + Monthly Weather Review for August, 1901; reprinted as Weather Bureau Publication No. 254, cf. p. 26-27. ‡"The Earth's Albedo," by Frank W. Very; Astronomische Nachrich-ten, N<sup>r</sup>. 4696, cxcvi, 269-290, November, 1913.

the outer limit to a quantity which might approximate to the value of I near the Earth's surface, though there is no reason why B should exactly equal I even then. But actually Bigelow makes his B diminish from 2 at the top to 1.27 at the bottom of the air, 1.27 being the value of I=B at sea-level under a vertical sun. Hence his B can not represent loss by reflection. Moreover, everywhere and at all times B=I, becoming zero after sunset, the whole relating to a purely diurnal phenomenon, although the thermodynamic facts on which it is supposed to be based are true of the night as well as the day.

In connecting the thermodynamic and radiant quantities for the entire atmospheric column, the solar rays have been treated in the paper under discussion as if they belonged to the atmosphere, and the atmospheric heat as if it were directly and immediately produced by the solar rays, while I and B appear to be treated in the radiant equation as if they pertained to two equal quantities relating to two halves of an atmospheric process. In reality they relate to the erroneous theory of an instrument, as has been shown above.

A relation of approximate equality is also assumed between the heat produced by the solar radiation at a surface and the heat simultaneously exhibited throughout an air column. But it is not correct to equate the solar radiation received by an air column in one minute, even though it be absorbed by the air, to the thermal energy maintained in that column during the same interval of time and deduced from thermodynamic data, for the latter represents the accumulated radiant energy from many hours of sunshine; and no such relation would have been found if the computations had been made correctly. The solar rays from a zenithal sun, passing through a vertical column of 1 sq. cm. section for 1 min., and varying, according to Bigelow, between a thermal equivalent of 4.00 and 1.27gram cal. at top and bottom of the column, have suffered losses which are largely reflective, and the atmospheric heat derived from them after the elimination of all purely reflective losses must suffice for maintaining the temperature of the air at night as well as by day, so that the effective heating of the entire air column by the radiation absorbed in the interval of a single minute is only a fraction of a calorie.

Let us take the height of a homogeneous atmosphere at 0° C. and 760<sup>mm</sup> pressure, as 7.991 km. Then, neglecting latent heat of evaporation of air, since it is very small at the mean temperature of the air, and assuming that the specific heat of the atmosphere averages 0.238, the mass of a column of 1 sq. cm. section at an average temperature of  $\Sigma\rho T/\Sigma\rho=255^{\circ}$  Abs. C. is

 $7.991 \times 10^{5} \times 0.001276 = 1020$  grams,

and the heat required to maintain the air column in its gaseous state at the given temperature is

### $1020 \times 0.238 \times 255 = 61904$ gram cal.

To produce this heat during a diurnal period of  $12^{h}$ , or 720 min., 86 gram cal. would have to be communicated to the air column every minute. Besides this, the interchange of heat with surrounding bodies must be considered, and the radiation from such a column would be very great because its surface is large compared with its volume. The solar rays (averaging day and night) probably do not impart more than 1/5 gram cal. per min. to each air column of 1 sq. cm. section. The permanent heat of the atmosphere is about 400 times this amount and represents the accumulation of nearly 7 hours of sunshine. But this, as we have seen, is much too small, since it supposes that no heat is lost by radiation from the air. If the thermodynamic reduction to C. G. Min. units had been correctly performed, it would have given 400 gram cal., instead of 4, which indicates that between two and three days of sunshine are necessary to give the accumulated heat of the atmosphere.

The table on page 278 exhibits some obscurity in the use of Thus the sum of the pressure differences for the terms. entire atmosphere, that is to say, the atmospheric pressure, is given as approximately 1.45 "gram cal./ cm<sup>2</sup> min." But thermal units are not appropriate for the expression of pres-What has really been done is this: The average sures. atmospheric pressure, in C.G.S. gravitational force units, is 1,013,235 dynes per sq. cm. This pressure exerted during 1 min. throughout 1 cubic cm. of volume, produces a volume energy of 60,794,100 erg minutes, equivalent to 1.452 gram cal./ cm<sup>2</sup> min. This may be compared with the volume energy of atmospheric radiation, because, although the solar radiation is never anything else than a continuous flux, the air radiates in a discontinuous, or step-by-step fashion; and this is as if a definite quantity of radiant energy lingered for a time in a given volume of air, the duration being not that of the radiant transference, which is practically instantaneous, but that of the mechanism of molecular absorption, conduction and reradiation, indefinitely repeated, which requires time. The volume energy of solar radiation (C. G. S.) is the energy received on 1 sq. cm. in 1 sec., distributed through a column of ether  $3 \times 10^{10}$  cm. long. The complex and much retarded process to which the name air radiation is assigned has no such enormous velocity as light, and may be summed, as Bigelow has done, in successive small columns in which it varies progressively, but should then be distinguished from surface radiation in the ordinary sense. When the sum is

taken of the change of volume energy from layer to layer' computed with the values of T, c and a by the ingenious method developed by Professor Bigelow in his article in this Journal for March, 1913, \* values of about 1.460 are obtained, which are in agreement with the volume energy derived from the pressure. Consequently, the thermal energy which gives the air pressure is maintained by the internal radiation between the air molecules, and this is the real meaning of the consistent numbers given by the computation.

The air radiation (internal) is obtained from the absolute temperature T, by the equation,

# $J_a = cT^a$ ,

where the coefficient c and the exponent a are given by thermodynamic computations. In the article now under discussion, Professor Bigelow has arbitrarily modified this equation by substituting for a the value 4 demanded by Stefan's law for an ideal black body, but leaving the constant c and the temperature T unchanged. This amounts to assuming that the air radiates like a black body, and on summing the change of volume energy from layer to layer computed by this new formula, a result is obtained a little less than three times as great as before, this being the ratio of black-body radiation to air radiation, as I have already shown. When this sum is compared with the sum of the ratios of volume energy corresponding to pressure change divided by the mean density, they are found to agree. Professor Bigelow appears to attach great significance to this relation, but it is not entirely clear what this significance is. It is of course impossible that the air should radiate precisely like a black body, for it would also absorb radiation like a black body in that case and would be wholly opaque to outside radiation. Nevertheless, within the narrow range of its own limited radiations, the air does behave like a black body. Dr. Paschen has shown that the summits of the bands in a bolograph of the spectrum of a radiating gas, where the gas layer is of sufficient depth to exert its maximum radiating power, coincide with points on the continuous curve of black radiation at the same temperature. + Thus the radiation of the air to space, wherever it is free to radiate, must agree in this respect with black radiation. But the air can not radiate freely to space from its lower layers, because the selective absorption by the higher layers is a complete barrier to the selective

+"Ueber die Emission der Gase", von F. Paschen; Annalen der Physik und Chemie, N. F., vol. li, pp. 1-39, 1894.

<sup>\* &#</sup>x27;'On the Coefficients and Exponent of the Radiation Equation,  $K_{10} = cT_{10}^{a}$ , in the Earth's Atmosphere." By Frank H. Bigelow; (4), vol. xxxv, pp. 254-266.

emission of the same waves by the lower layers, whereas the hypothetical equation with exponent 4 requires such emission. This part of the subject is still very obscure.

In conclusion, it seems to me that the bolographic argument for a value of the solar constant approaching 4 calories is sound, but the primary pyrheliometric reduction employed by Bigelow involves the same erroneous assumption of a constant diurnal coefficient of transmission which has vitiated the work of Pouillet and of Abbot; while the doubling of the value given by this primary or preliminary reduction, although in approximate agreement with what may be obtained by means of a rational theory, is in the present instance a completely arbitrary procedure.

Westwood Astrophysical Observatory, Westwood, Massachusetts, October, 1914.

# ART. XIV.—An Eocene Ancestor of the Zapodilla; by E. W. BERRY. With Plate I.

I HAVE had in my possession for several years a large fossil seed collected by Mr. A. F. Crider from the Upper Claiborne deposits (middle Eocene) of Holmes County, Mississippi, which in the press of other duties remained undetermined until the recent appearance of a paper by Mr. Henry Pittier \* led me to compare it with the seeds of the Sapotaceæ, more especially those of the large-fruited genera Achras, Vitellaria, Lucuma, Calocarpum, etc.

The fossil seed, while it has the general characters of the seeds of the genera enumerated above, is not exactly like any of them. In size and form it is perhaps most like the seeds of *Achras* but in the latter the umbilical area is narrow and shortened, while in the fossil this area is the full length of the seed and wide as in the genus *Calocarpum*. A real difficulty encountered in giving a name to the fossil arises, not out of any uncertainty with regard to its relationship to still existing forms, but out of the purely taxonomic tangle that involves these forms and a lack of knowledge regarding the relationship of these among themselves and their true generic limits.

For example, *Achras* is a monotypic genus in the existing flora, artificially distributed in prehistoric times and now cultivated in all tropical countries. Its single species has served as the type of at least two genera, i. e. *Achras* Linné

\* Pittier, H., Cont. U. S. Natl. Herbarium, vol. xviii, part 2, pp. 76-86, 1914. See also Cook, O. F., ibidem, vol. xvi, pp. 279-282, 1913.





(1753) and Sapota Miller (1759), the latter usage giving its name to the family Sapotaceae. Moreover Achras differs from the fossil in the extent of its umbilical area. The genus obviously has had a geological history, as yet unknown, and it is quite possible that the umbilical character of the seeds may have differed in the unknown fossil ancestors of the existing form. At the same time it does not seem proper to amplify what is one of the diagnostic characters of the recent genus to include hypothetical fossil species. The fossil agrees with the seeds of Calocarpum in the character of the umbilicus but is smaller in size and more compressed. There are only two known species of Calocarpum, one described as recently as 1914, and the other, known since 1762, has been placed successively in the genera Achras (by Linné in 1762), Sideroxylon (by Jacquin in 1762), Lucuma (by Gærtner in 1805), Vitellaria (by Radlkofer in 1882), Calospernum (by Pierre in 1890), Achradelpha (by Cook in 1913), and still more recently (1914) Pittier has taken up the generic name Calocarpum, first proposed by Pierre in 1904. It will be seen that the paleobotanist can readily use a generic name for the present fossil seed that will bring up either a different concept of the plant that bore it in mind of each botanist according to his taxonomic taste, or else no concept whatever. Moreover it is the acme of improbability to suppose that the existing genera Achras, Calocarpum, Lucuma, Vitellaria, Sideroxylon and Chrysophyllum were all fully differentiated as early as the middle Eccene and that they have maintained their existing limits since that time, an interval estimated by geologists as something like three millions of years. Whatever credence the reader may care to place in the latter estimate it is certain that the fossil seed is older than the Pyrenees, the Swiss Alps or the Himalayas. A further emphasis of the remoteness of the fossil seed is furnished by the statement that the contemporaneous tiny mountain horses (Orohippus), well known from homotaxial deposits in the West, had five toes on their fore feet and three toes on their hind feet.

In view of the foregoing considerations I propose to describe the fossil as the type of a new genus to be known as *Eoachras* and I use this name in preference to Eocalocarpum or Eolucuma because *Achras* has but one living species and botanists are therefore in agreement regarding its characters and affinities, and its name is not likely to change hereafter. Moreover since this single living species may be regarded as the type of the family, *Eoachras* may be considered to represent the ancestral line that probably gave rise to more than one of the modern genera enumerated above. The fossil may be described as follows :—

# Eoachras eocenica gen. et sp. nov.

Description.—Seed of large size, compressed laterally, obliquely elliptical in outline when viewed from the side, proximal end more broadly rounded than the distal end. Length about 3.6<sup>cm</sup>; maximum height from dorsal to ventral margin about 2.2<sup>cm</sup>; maximum thickness about 1.5<sup>cm</sup>. The seed has been subjected to pressure after burial by sediments and this has destroyed the symmetry between the lateral surfaces. Dorsal margin broadly rounded, sigmoid in outline with a restricted but pronounced sinus toward the distal end. Ventral margin thickened, considerably deformed, curved in outlines : the umbilical sinus open, extending the whole length of the seed.

Occurrence.-Near Lexington, Holmes County, Mississippi. Discussion.-This seed differs from those of Achras zapote in its slightly larger size, in its more open umbilicus which also extends the whole length of the seed. As I have interpreted the orientation of the fossil, its smaller end is distal and not proximal as in Achras, but this is a negligible feature. Seeds of Achras are shown in figs. 4, 5. The seeds of Calocarpum are, as a rule, much larger, fusiform and not compressed : the umbilicus occupies the whole inner face and this feature as shown in figs. 6, 7, 9 may be profitably compared with that of the fossil. The seeds of Lucuma are also very similar to the fossil as may be seen in fig. 10. A fact of interest in the present connection is the presence in the Upper Eocene of Texas (Wellborn Sandstone of Jackson age) of leaves that agree exactly with those of the existing Calocarpum viride Pittier.

It is not possible to suggest the character of the foliage in Eoachras. Achras has a dense cover of smooth, thin-veined, coriaceous, evergreen leaves. Calocarpum on the other hand has very large, ovate-lanceolate, coarse, deciduous leaves. There are a considerable number of leaf remains associated with the seed of *Eoachras* but none of these can be definitely correlated with the latter. There are none that are comparable with those of Achras. There are fragments of large leaves, tentatively referred to the genus *Terminalia*, that might possibly represent Calocarpum-like leaves.

Regarding the environment of *Eoachras* it may be said that the Middle Eocene (Claiborne) flora of the Mississippi embayment is a coastal tropical flora \* embracing such types as Thrinax, Coccolobis, Pisonia, Inga, Copaifera, Šophora, Fagara, Sapindus, Reynosia, Sterculia, Cinnamomum, Nectandra, Rhizophora, Myrcia, Conocarpus, etc. It will thus

\*Berry, E. W., An Eccene flora in Georgia and the indicated physical conditions; Bot. Gaz., vol. 1, pp. 202-208, figs. 1, 2, 1910. Berry, E. W., Prof. Paper U. S. Geol. Surv., No. 84, pp. 129-163, 1914.

be seen that the environment indicated offers no difficulties in the interpretation of the fossil seed as representing a progenitor of the existing zapote (sapote) and zapodilla (sapodilla). The former is now predominantly an upland form while the latter is not. The fossil records of the family Sapotaceae may now be briefly passed in review. The family contains about 32 genera and nearly four hundred existing species of all tropical countries. About half of the existing species are American. There are eleven genera confined to America, seven to Africa, three to Australia, two to New Caledonia, two to Asia and Malayasia, two to Malayasia, and one to Asia. The three large genera, Sideroxylon, Chrysophyllon, and Mimusops, are represented in all tropical countries. There are four genera and twelve species represented in the Lower Eocene flora of the Mississippi embayment. The largest of these genera is Bumelia Swartz with six well-marked species. The genus Bumelia with about a score of existing species is confined to America, ranging from the southern United States through the West Indies and Central America to Brazil. It has numerous fossil species, the oldest coming from the Upper Cretaceous (Dakota sandstone) of the western interior. In addition to the six American Lower Eocene species which are the prototypes of still existing forms, there are two Eocene species (Ypresian) in southern England. There are about a dozen Oligocene species, ten of which are widespread in Europe, one is found in the Apalachicola Group of western Florida, and two forms, represented by both leaves and fruit, are found in the Vicksburg Group of Louisiana and Texas. There are seven or eight Miocene species widely distributed in Europe and one is recorded from the late Miocene of Colorado (Florissant).

The genus *Chrysophyllum* Linné, with about 60 existing species found in all tropical countries, but the majority being American, has a supposed species in the Upper Cretaceous of Saxony (Niederscheena); a well-marked species in the American Lower Eocene; three Oligocene and six Miocene species in Europe and a species in the Tertiary of Colombia.

The genus *Mimusops* Linné, with about 40 existing species in all tropics, has three well-marked species in the Lower Eocene of the Mississippi embayment and a fourth in the Middle Eocene of the same area. To it has been referred a form from the Upper Cretaceous of Saxony (Niederschœna) and it is undoubtedly represented in the Upper Cretaceous of the embayment region as well as elsewhere by the leaves that have been referred to the form-genus *Sapotacites*.

The genus *Sideroxylon* Linné, with about 80 existing species in the oriental tropics and about fifteen species in the American tropics, has two species in the Lower Eocene of the Mississippi embayment which are the oldest representatives of this genus thus far discovered. To this genus have been referred four Oligocene and one or two Miocene species from the European area.

Isonandra Wright, a small modern genus of the Malayan region, is represented in the Tertiary of Borneo by Isonandrophyllum of Geyler: the genus Achras has three fossil species recorded by Unger and Pilar from the European Miocene. These are based upon leaves found in Styria and Croatia and are probably referable to Chrysophyllum or Pisonia. The genus Labatia Swartz, with six existing species in the American tropics, has been doubtfully determined in the Miocene of Prussia and Italy. Felix has described two forms of petrified wood which he refers to this family under the name Sapotoxylon, one from Germany and the other from an unknown locality and horizon.

A large number of fossil forms of Sapotaceæ have been referred to the form-genus Sapotacites proposed by Ettingshausen (also Sapotophyllum). There are at least ten Upper Cretaceous forms widespread in North America and represented in Europe in the Perucer beds of Bohemia and the Credneria stage of southern Saxony (Cenomanian). Three of these Upper Cretaceous forms are from the Tuscaloosa formation of Alabama and undoubtedly represent the ancestors of some of the Lower Eocene Sapotaceæ that have been found in this region. There are about ten species of Sapotacites recorded from the Eocene of France and southern England; and there are about a score of Oligocene and Miocene forms most of which are European. There is, however, an undescribed species in the Apalachicola Group of western Florida. In the Pliocene there are species in southern Europe and on the Island of Java.

Notwithstanding the incompleteness of the record, it is obvious that the family became well differentiated during the Upper Cretaceous, and while it would not be safe in the present state of our knowledge to assign its place of origin to the American region, it is probable that at least several of the genera such as *Bumelia*, *Achras* and *Calocarpum* originated in this region.

It will be noted that the large genera of Sapotaceæ with many existing species and relatively small fruits are found in more than one continental area. They are also more or less well represented in the Lower Eocene and in some cases even in the Upper Cretaceous, and they are unquestionably older than genera like *Achras* or *Calocarpum* with their relatively enormous fruits. It is a strictly reasonable assumption that these large-fruited genera have been derived from the smallfruited genera, and in the present state of our knowledge *Eoachras* is the earliest of the large fruited forms.

Regarding the existing distribution of Achras and Calocarpum, this is masked by prehistoric cultivation. Both genera are endemic in the American tropics. Achras is indigenous in Mexico south of the Isthmus of Tehuantepec, in Guatemala, Salvador and northern Honduras. Pittier says that it is especially abundant in the lowlands of Tabasco and Chiapas and in western Yucatan. Throughout the balance of Central America and the West Indies it has not been definitely decided whether it is endemic or not. It appears to be also native in Colombia and Venezuela. The two existing species of Calocarpum are natives of Central America, and possibly the West Indies and the northern part of South America.

Johns Hopkins University, Baltimore.

#### EXPLANATION OF PLATE I.

FIG. 1.—*Eoachras eocenica* gen. et sp. nov.—lateral view, natural size, from the Middle Eocene (Claiborne Group) of Mississippi. FIG. 2.—The same, distal view.

FIG. 3.—The same showing the umbilical area. FIG. 4, 5.—Achras zapota Linné (after Pittier).

FIGS. 6, 7.-Calocarpum viride Pittier (after Pittier).

FIGS. 8, 9.—Calocarpum mammosum (Linné) Pierre (after Pittier).

FIG. 10. -Lucuma salicifolia H. B. K. (after Pittier).

# SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. The Molecular Weight of Sodium Carbonate and the Atomic Weight of Carbon Referred to Silver and Bromine.— RICHARDS and HOOVER introduce their account of this research by the remarks, that the investigations concerning radio-activity have increased rather than diminished the interest in atomic weights; that the recent indications that the atomic weight of lead may be variable stimulates further research; that whether or not the atomic weights may vary in a few cases they still remain the most fundamental figures that are known to science; and that no amount of trouble is too great to secure a satisfactory knowledge of these numbers.

Using the greatest care and skill, the account of which is fascinating reading, these investigators have started with pure sodium

213

carbonate, neutralized this with pure hydrobromic acid, and have then found the amounts of silver and silver bromide corresponding to the sodium carbonate. It was found that 29:43501 g. of sodium carbonate were equivalent to 59:91676 g. of silver and also to a weight of hydrobromic acid solution which could precipitate 104:3023 g. of silver bromide. From these results, if silver is 107:88, sodium carbonate becomes 105:995 and carbon 12:005. This work, by connecting various ratios in a new way, shows the consistency of a great variety of earlier work done by and under the direction of Professor Richards.—Jour. Amer. Chem. Soc., xxxvii, 95. H. L. W.

2. The Molecular Weight of Sodium Sulphate and the Atomic Weight of Sulphur.-Having worked out a method for the preparation of pure sodium carbonate in connection with the investigation referred to in the previous notice, RICHARDS and HOOVER have extended the work by neutralizing sodium carbonate with sulphuric acid and comparing the weights of the two salts. The ratio of the carbonate to the sulphate was found to be 1.00000: 1.340155. Assuming  $Na_{a}CO_{a} = 105.995$ , as found in the preceding research (Ag = 107.880) the molecular weight of sodium sulphate becomes 142.050, and the atomic weight of sulphur becomes This is very close to the value 32.069 previously obtained 32.060. by Richards, which is practically the value (32.07) of the International Table. The authors say that the mean value 32.065 may perhaps be taken as the most trustworthy value for the atomic weight of sulphur thus far recorded.-Jour. Amer. Chem. Soc., xxvii, 108. H. L. W.

3. The Separation of Tungsten and Molybdenum. - The analytical separation of these comparatively rare metals which frequently occur together has become more important of late on account of their extensive technical application. E. E. MARBAKER has studied this somewhat difficult problem and has worked out an apparently satisfactory method for the determination of the two elements, chiefly by the combination of previously known processes. He prefers to start with sodium tungstate and molybdate rather than with the ammonium salts. The tungsten is precipitated, according to Mdivani's method, with a carefully regulated quantity of stannous chloride in the presence of hydrochloric acid in the form of the blue oxide W<sub>2</sub>O<sub>5</sub>. This is filtered off, washed with very dilute hydrochloric acid, ignited and weighed as WO<sub>s</sub>. The filtrate is concentrated, treated with granulated zinc, whereby the tin is removed as metal. Then the filtrate from this precipitation is passed through a Jones "reductor" into a solution of ferric sulphate and titrated in the presence of phosphoric acid, manganese sulphate, and sulphuric acid by means of potassium permanganate solution, according to the method for the determination of molybdenum devised by Randall and published in this Journal in 1907. The test analyses show remarkably accurate results.-Jour. Amer. Chem. Soc., xxvii, 86. H. L. W.

4. The Standardization of Acidimetric Solutions .- FRANCIS D. DODGE has introduced a new substance for use in standardizing volumetric alkaline solutions. This is acid potassium phthalate, which does not appear to have been described previously, but which may be easily prepared by exactly neutralizing re-sublimed phthalic anhydride with pure potassium hydroxide, adding as much more of the phthalic anhydride as was used at first, crystallizing by cooling the hot solution and re-crystallizing the product. The salt has the formula HKC, H, O, it has no water of crystallization and may, be dried at 110° C. It has a number of advantages over the substances usually employed for the purpose in being easily obtained in a pure condition, in being unalterable in the air, in being fairly soluble in water, and in having a high formula weight.-Jour. Indust. and Eng. Chem., vii, 29. H. L. W.

5. Chemical Technology and Analysis of Oils, Fats and Waxes; by J. LEWKOWITSCH. Fifth edition, vol. ii, edited by GEORGE II. WARBURTON. 8vo, pp. 944. London, 1914 (Macmillan and Co. Price \$6.50).—The author of this standard work, whose services to industrial chemistry have been so important, died shortly after the appearance of the first volume of the present rewritten and enlarged edition. The second volume now being considered has been edited in a very satisfactory manner by Mr. Warburton, who was for a long time associated with the late author.

This volume takes up the commercial preparation of the raw materials in a general way, and then proceeds to describe very fully a large number of oils, fats and waxes of both vegetable and animal origin. Much information is given in regard to the sources, manufacture, commercial importance and uses of the individual products, thus making the book of much interest to the general reader, while the tabular statements of the physical and chemical characteristics of the substances are very extensive and particularly important for chemists. H. L. W.

6. The High Frequency Spectra of the Elements.—The wavelengths of the characteristic radiations of the K type for elements of low atomic weight and of the L type for heavy atoms have been determined experimentally by Moseley. The data obtained brought out a very important relation, namely, that the frequencies of the radiation of the different elements admit of being arranged in series such that the square root of the frequency in each series increases by a constant from element to element in the periodic system. It is a matter of considerable importance to find out if the two K-series can be extended to the heaviest atoms and if the constancy just mentioned continues throughout the system. This interesting problem has been successfully attacked by IVAR MALMER. The elements studied (with their "atomic numbers") were yttrium (39), zirconium (40), molybdenum (42), ruthenium (44), palladium (46), silver (47), cadmium (48), indium (49), tin (50), antimony (51), barium (56), lanthanum (57), and cerium (58).

The chief experimental difficulty consisted in keeping the X-ray bulb sufficiently "hard" when the anticathode was covered with metals of low melting points, such as indium ( $\leq 200^{\circ}$  C.). This was overcome by causing a stream of cold water to play against the back of the cathode and by running the Gaede mercury pump continuously, charcoal in carbon dioxide and ether being used simultaneously. A rock-salt crystal was employed in the usual way to analyze the radiations.

When the square roots of the frequencies are plotted as ordinates against the associated atomic numbers as abscissæ it is found that the points lie close to two straight lines which correspond respectively to the  $\alpha$  and  $\beta$  spectral lines. On the contrary, these right lines have not the same slopes as the lines derived from Moseley's data. Consequently the relation  $\left[\nu = \frac{3}{4}\nu_{0} (N-1)^{2}\right]$  discovered by Moseley for the elements from aluminium to zinc does not continue to hold good throughout the Furthermore, it should be series of the heavier elements. remarked that antimony fits in with the rest of the elements investigated by Malmer only when it is assigned the atomic number 52, whereas it must have the value 51 to agree with the L-series. If this be true, an element may have one atomic number in the K-series and a different number in the L-series. In the case of cerium no lines of the K-series were found, although the bulb was extremely hard. Finally, the lines of silver were studied in detail to find out if they are doublets such as have been recorded by Bragg for rhodium and by Rawlinson for nickel. The first negative showed two a-lines and also duplicity in the direct image. This doubling was due to the fact that the cathode rays were not focussed in only one point of the target. "Consequently, the bulb was placed in such a position that the X-rays used were emitted at a minimal angle with the surface of the target, and now both the direct and the reflected lines were simple." "Possibly former cases of double lines may be referred to the same cause."-Phil. Mag., xxviii, p. 787, December, 1914. H. S. U.

7. The Bifilar Property of Twisted Strips.—When a strip of phosphor-bronze, carrying an inertia bar, is twisted and then allowed to oscillate, its period of vibration is found to depend upon the load. As is well known, the period of a bifilar suspension depends upon the load and hence it has been suggested that a bifilar action is present in strips and accounts, in part at least, for their behavior. Since the results obtained by Campbell and by Pealing were not altogether concordant, the question has been taken up both theoretically and experimentally by J. C. BUCKLEY.

The formula  $C = \frac{16bd^3n}{3l} + \frac{2Tb^3}{3l}$  is first derived, where 2b =

horizontal breadth of strip, 2d = thickness of strip, l = length, n = constant of torsional rigidity, C = restoring couple per unit angular displacement, and T = tension per cm. The first term of the right-hand side of the equation corresponds to the twisting of

the strip in the form of a helicoid, when the bifilar couple (the second term) is negligible.

The influence of the bifilar term would be most pronounced when the torsional rigidity is small. Preliminary experiments showed that the period of vibration was proportional to the tension for strips of aluminium, celluloid, mica, paper, and xylonite. On the other hand, ribbons of steel and phosphor-bronze did not show this effect. Plotting values of T as abscissæ and the corresponding values of C as ordinates, the points for a xylonite strip  $(15.75 \times 3 \times 0.05^{\text{cm}})$  fall close to a straight line. This is consistent with the above equation. The slope

of the line gives  $\frac{dC}{dT} = 0.1425$ , which is in excellent agreement

with  $\frac{2b^3}{3l} = 0.1429$ . The intercept of the line on the axis of

ordinates (T=0) gives  $C=132\ 000\ dyne-cm.$ , or  $n=1.589\times10^{\circ}$ . It is thus seen that this method affords a means of obtaining the value of the coefficient of rigidity for suitable substances. Very

good agreement between the values of  $\frac{dC}{dT}$  and  $\frac{2b^3}{3l}$  is shown by

the data tabulated for five different widths of paper and two of celluloid. Aluminium behaved similarly but gave trouble because of the rapid damping of its vibrations. [C was always obtained from the period,  $P = 2\pi \sqrt{I/C}$ .] The straight lines in the first diagram for paper practically pass through the origin. This is due to the very small value of n, for when T = 0 we would expect to find  $C \propto b$ . The lines on the second diagram for paper intersect the axis of ordinates at finite distances above the origin. In this case, the paper was cut in another direction. In fact, it was found that two ribbons of paper cut from the same sheet, but in perpendicular directions, showed a considerable difference in rigidity, though the bifilar effect was the same for both strips. "This means that the distribution of tension producing the bifilar effect is independent of the fibrous structure of the material of the strip; whereas the rigidity depends greatly upon the structure." As a further test of the formula *l* and *T* were kept constant for paper so cut as to make *n* negligible. The experi-

mental data verified the relation  $\frac{C}{b^3} = \text{constant}.$ 

When the ribbon is made of a very thin piece of material having a large coefficient of rigidity the two terms of the right member of the general equation may attain comparable values. For a steel tape of dimensions  $41.9 \times 1.26 \times 0.01^{\text{cm}}$  the data obtained were  $\frac{dC}{dT} = 0.007$ ,  $\frac{2b^3}{3l} = 0.008$ ,  $n = 8.351 \times 10^{11}$ , and  $C = 25\ 000$  for T = 0. With another specimen of steel, AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 230.—FEBRUARY, 1915. 15  $31\cdot3 \times 1\cdot59 \times 0.022^{\text{cm}}$ , it was found that  $\frac{dC}{dT} = 0.0256, \frac{2b^3}{3l} = 0.0214$ ,

 $C_o = 308\ 500$ , and  $n = 8.555 \times 10^{11}$ . "In the strip  $0.01^{\rm cm}$  thick the restoring couple under the greatest tension is 48.5 per cent above that under least tension: this shows the necessity of allowing for the bifilar effect when obtaining the rigidity of materials by experiments with strips." It is thus seen that, in general, the complete formula gives very satisfactory results. The outstanding anomalies found by other observers may be accounted for as due to overstraining the materials employed.—*Phil. Mag.*, xxviii, p. 778, December 1914. H. S. U.

8. Volatility of Thorium D.-The behavior of thorium D at different temperatures and when treated with nitric acid and hydrochloric acid has been recently studied in detail by A. B. WOOD. The forms of the electric furnace and  $\beta$ -ray electroscope are not novel and hence a description of the apparatus would be superfluous in this place. The results obtained may be briefly summarized as follows : The temperature of volatilization of thorium D was found to be 520° C., both when this element had not been treated with acid and when it had been dissolved in pure nitric acid. On the other hand, when thorium D had been treated with hydrochloric acid the temperature of volatilization assumed the much lower value 270° C. The views of earlier investigators concerning the formation of definite chemical compounds of the active deposits of the various radio-active elements are confirmed by the work of Wood. This investigator also found that thorium D recoils from thorium C in the *atomic* form, irrespective of whether the parent thorium C was free or combined with acids. Finally, in the case of thorium D recoiling from the active deposit of thorium dissolved in hydrochloric acid, evidence was obtained that a portion of the recoiling atoms recombine with the free chlorine which is liberated when the molecules of thorium chloride disintegrate. - Phil. Mag., xxviii, p. 808, December, 1914.

H. S. U.

9. Lecture Experiment on Dispersion.-The following brief account of the experimental demonstration of the irrationality of dispersion is taken from a paper by SILVANUS P. THOMPSON. Light from an electric arc is focussed on a small round or square hole in an opaque diaphragm and a horizontal spectrum of this source is projected on the screen or wall by means of a diffraction grating having about 12,000 lines to the inch. "On interposing a prism to disperse the light vertically upwards, the resultant oblique spectrum is finely curved, being concave upwards." The curvature observed is due to the irrationality of dispersion of the particular prism employed, since for all known kinds of glass the refrangibility of the blue and violet waves is disproportionately large. The demonstration is enhanced either by using the carbons supplied for commercial "flame arcs" or by tamping an alloy of lithium, thallium, and zinc in the positive carbon. This scheme is obviously preferable to Newton's method of crossed

prisms because it isolates the effect due to a single prism and does not involve the resultant dispersion of two prisms.—*Proc. Phys.* Soc. London, xxvi, p. 154, April, 1914. H. s. U.

10. Experimental Studies in Electricity and Magnetism; by FRANCIS E. NIPHER. Pp. 73, with 29 figures and 11 plates. Philadelphia, 1914 (P. Blakiston's Son and Co.).-At the suggestion of Thomas R. Lyle, F.R.S., Professor Nipher decided to present in book form a consecutive account of the results of his investigations which have appeared heretofore only in the Transactions of the Academy of Science of St. Louis. The subject matter is arranged in two parts or chapters which deal respectively with "Experimental Evidence for the One-fluid Theory of Electricity" and with the "Causes of Local Magnetic Storms." The discussions are so intimately associated with the descriptions and figures pertaining to the discrete experiments as to preclude the possibility of giving an outline of the work in a few sentences. Many of the experiments possess novel features and all of them were most ingeniously devised and skilfully performed. Most of the text-figures and all of the plates of the first chapter are very clear half-tone reproductions of excellent photographs of electrical discharges which took place under widely different conditions. The plate and paragraphs pertaining to the artificial production of ball lightning are especially striking. The last four plates show automatically registered graphs of a magnetic storm due to wind, of a magnetic storm due to rain, of the magnetic effect of cloud shadows, and of a very pronounced magnetic storm at sunset. Although the first part of the monograph contains much of interest and value primarily to the physicist and the second to the meteorologist, the entire text may be perused with profit by the general scientific reader. H. S. U.

11. Smithsonian Physical Tables. Sixth Revised Edition; prepared by FREDERICK E. FOWLE. (Publication 2269.) Pp. xxxvi, 355, with 407 tables and an index. Washington, 1914. Smithsonian Misc. Collections, vol. 63, No. 6.—The revision of this very useful book, commenced for the fifth edition (1910), has been continued; a large proportion of the tables have been rechecked, typographical errors corrected, later data inserted, and 72 new tables added. Among the last named may be noted a new set of wire tables from the Bureau of Standards, new mathematical tables, and tables of data pertaining to Röntgen rays, radioactivity, radiation, international standard wave-lengths, etc. Much credit is due to Mr. Fowle and his collaborators for the close approximation which they have made to perfection in a work of this kind. H. S. U.

# II. GEOLOGY AND MINERALOGY.

1. The "Fern Ledges" Carboniferous Flora of St. John, New Brunswick; by MARIE C. STOPES. Memoir 41, Geol. Surv. Canada, 1914. Pp. 168, 25 plates, 21 text figs.—In the suburbs

of the city of St. John, New Brunswick, and chiefly in the suburb of Lancaster, occur tilted and metamorphosed sandstones with thin dark shale partings. These beds in 1861 attracted the attention of G. F. Matthew and C. F. Hartt, who collected fossil plants from them, and they have been known ever since as the "Fern Ledges" of the Little River group. Matthew and Hartt held the age of this flora to be Devonian, and sent their material to Sir William Dawson at the time he was studying the Perry, Gaspé, and New York plants, which are undoubtedly Devonian. He put all the collections together and described them as of a single period, the Devonian. Thus arose great confusion, and even though many paleontologists in the past fifteen years have pointed out that these "Fern Ledges" are of Pennsylvanian time, there is still one who holds that they are of the Silurian. The first to dissent from Dawson's age determination was the able German paleontologist, Geinitz, who held in 1866 that the associated insects, described by Scudder as of Devonian time, did not belong to this period, but rather to the Coal Measures. This view has since been backed up by Kidston, David White, Ami, Zeiller, Handlirsch, Jongmans, and now decidedly by Doctor Stopes.

The author of the contribution under discussion has done her work with the greatest care, having made collections at St. John, under the guidance of Doctor Matthew, and then studied the original material described by Dawson, Hartt, and Matthew. Finally, all the good material was taken to the British Museum, where it could be compared with large and authentic collections, and where a complete library was accessible. Not only this, but Doctor Stopes called to her assistance all paleobotanists who could help in the work, so that the available specimens might be accurately identified.

The flora of the "Fern Ledges" had risen to eighty described species, but of these Doctor Stopes finds "only about forty that are of value and that are determined on a sufficiently sound basis to make them of any real use in the comparison of this flora with others." The final list is reduced to twenty-nine "good species," and twelve others that have "some stratigraphic significance."

The plants of the Little River group constitute "a single flora, in the sense that they represent a period of time no longer than a single main division of the Carboniferous." White regarded the flora as of Upper Pottsville time, and Kidston referred it to the European Lower Coal Measures. The present author, however, concludes that "the 'Fern Ledges' represent plant debris from differing ecological situations which were all growing in that period of time in the Coal Measures which is best known as the *Westphalian*, and that probably it corresponds in point of time most nearly to the lowest zone of the middle Westphalian."

The Little River flora is not the usual swamp flora of the Pennsylvanian, but is "the remains of the inland flora of the period, and one which had travelled down stream as debris for some distance before being entombed." This is especially well seen in the great scarcity of such swamp forms as Sigillaria and Lepidodendron, of which no recognizable species has been determined.

This monograph is a beginning toward a satisfactory determination of the Coal Measures of eastern Canada, and their correlation with equivalent strata in the rest of the world. c. s.

2. Pre-Cambrian Algonkian Algal Flora; by CHARLES D. WALCOTT. Smithson. Misc. Coll., vol. lxiv, No. 2, pp. 77-156, pls. 4-23, 1914.—In this paper are described and well illustrated eight new genera (Newlandia, Camasia, Weedia, Collenia, Greysonia, Copperia, Kinneyia, and Gallatinia) and fourteen new species of calcareous deposits formed by plants allied to the bluegreen algæ (Cyanophyceæ). Although the fossils are from the Belt series (Upper Proterozoic) of Montana, they have been studied in connection with living forms. Similar fossils have long been noted by Walcott at various localities as Cryptozoons, but it was only recently that he obtained material revealing their internal structure. It is now apparent that these organic deposits are far more abundant and of greater chronologic importance than was formerly known; a wide field of endeavor is thus opened up.

The author holds that these fossils were formed in "nonmarine bodies of water" and that "the Algonkian period in North America with its great epicontinental formations was a time of continental elevation and largely terrigenous [= continental] sedimentation." In other words, that the known deposits yielding fossils are of freshwater origin and were laid down in lakes comparable to the Great Lakes. He says further, "A great work of the future will be the finding of marine deposits of Algonkian time and their contained life." The reviewer does not subscribe to these views and holds that the rocks with these algal formations were formed like those of the Ordovician with Cryptozoon, and that they are of marine origin; but why the ancestors of the Cambrian animals fail to be present in the Proterozoic strata still remains unanswered. The thick limestones of the Proterozoic (Newland, 2000 feet), but more especially of the Archeozoic (the Grenville series has a thickness of 50,000 feet of limestones), are seemingly not the deposits of freshwater lakes but of shallow and warm-water seas. All known freshwater limestones are thin deposits and limited in area, while those of the Algonkian have the physical characteristics of the marine limestones of the Paleozoic.

Walcott's paper once more raises the long discussed questions: Is *Eozoon canadense* Dawson of the Archeozoic (Grenville) an organism? Are these objects to be regarded as highly metamorphosed Cryptozoons? These masses, alone, as seen in museums, cannot answer the questions, but their field relations compared with those of the Belt and Ordovician strata may give a decisive answer and an organic vista into the supposedly unfossiliferous Archeozoic era. . C. S.

3. On the Petrology of the Orijärvi Region in Southwestern Finland; by P. Eskola. Bull. d. Comm. Géol. de Finlande, No. 40. Pp. 277, 2 maps, 6 pls., 55 figs. Helsingfors, 1914 .--This work covers the results of a detailed geological study of an area in southern Finland about  $40 \times 20$  miles in area. It consists of a complex of gneisses, called leptites, with some limestones intruded by bodies of granite, diorite, gabbro, and peridotite, also amphibolites of igneous origin. The different varieties of these rocks have been carefully mapped, studied in thin section, and chemically analyzed. One of the granite masses has produced a more or less extensive contact zone in the older leptites. amphibolites, and lime-carbonate rocks with production of a varied group of gneisses carrying cordierite, anthophyllite, andalusite, etc., cummingtonite-amphibolite and a lime series with tremolite, pyroxene, and andradite. The region has some economic interest from the occurrence of sulphide ores and bodies of iron oxides, which have not been much developed. The author states as his conclusion that the characters of the contact rocks are mostly due to pneumatolytic agencies which have brought about a metasomatic replacement of lime, soda, and potash by iron oxides and magnesia. This peculiarity holds without regard to the original nature of the intruded rocks. The ores are thought to have been formed in the same way and at this time. This is an accurate, thoughtful piece of work, of more than local interest, whose perusal will especially repay those engaged in the deciphering of metamorphic-igneous complexes. L. V. P.

4. The Crowsnest Volcanics, by J. D. MACKENZIE. Mus. Bull. No. 4, Geol. Series No. 20, Geol. Surv. Dep't. Mines, Ottawa, 1914, pp. 33; Pl. I.—The occurrence of alkalic rocks described in this paper has been previously mentioned by C. W. Knight in the Canadian Record of Science (vol. ix, p. 265, 1905) as occurring in the southwest corner of Alberta; he showed that in considerable part the volcanic ejections consisted of analcite, often occurring in crystals of considerable size, and held to be of primary origin. The author has investigated and mapped the areal extent of these rocks, which originally covered a probable field of some 50 by 15 miles with a maximum thickness of about 1000 feet. They are thought to have fallen mostly in shallow water toward the end of the Dakota. No definite vents have been found. The rocktypes are trachytes, latite, and the analcite-bearing rock which Knight has termed *blairmorite*, from the adjacent town of Blairmore. The blairmorite, of which several varieties occur, is found as bowlders, often of considerable size, in the water-laid breccias. The most interesting variety consists of a porphyry in which the phenocrysts are well-crystallized analcites an inch in diameter and of a red color, and an equal volume of dark green groundmass. Occasional phenocrysts of glassy sanidine and small melanites were observed. The groundmass was determined microscopically to consist of 50 per cent analcite with ægirite, augite, and unaltered nephelite and sanidine.

By measurements and by specific gravity determinations the mineral proportions of the rock were found to be:

 Anale.
 Æg.-aug.
 Neph.
 San.
 Mel.
 Ti.
 Hem.
 Cal.
  $H_2O$ 
 $71\cdot0$   $14\cdot0$   $5\cdot0$   $4\cdot0$   $1\cdot0$   $0\cdot5$   $1\cdot0$   $2\cdot0$   $1\cdot5 = 100\cdot0$ 

A chemical analysis of this type by M. F. Connor gave :

The specific gravity is 239. The other varieties differ chiefly in the amount of analcite, texture, etc. The author appears to hold with Knight that the analcite is primary, as shown by its crystal form and association with unaltered orthoclase and nephelite.

From the descriptions given by the two authors cited it seems not altogether certain that the analcite is primary; if it is so, this is a most surprising occurrence of an igneous rock. Hitherto it has been considered that the habitat of primary analcite was in the intrusive rocks where the pressure would tend to restrain the escape of the water vapor and force it to take part in the crystallization; here, however, it would appear to have been formed in the lavas undergoing explosion. If primary, the lava might be considered the effusive form of the analcite-syenite described by Tyrrell from Ayrshire, Scotland (Geol. Mag., vol. ix, p. 70, 1912), except that the latter contains much more feldspar; had the blairmorite crystallized anhydrously it would have formed chiefly albite and nephelite, a mariupolite.

The doubt concerning the primary nature of the analcite arises from the conclusion of the investigators that these pyroclastics were laid down in sea-water. If so, their original heat would have caused them for a long time to have been digesting in warm solutions of sodium salts, under which circumstances Lemberg's experiments show that leucite is converted into analcite. Whether under these conditions the feldspars would have also been attacked is less certain. The question thus arises whether the lavas may not have been originally leucitic ?

5. On the Mineral Empressite; by W. M. BRADLEY. (Communicated.)—In the number of this Journal for August, 1914 (p. 163) there was given a discussion and analyses of a silver-tellurium mineral known as *empressite*. A letter recently received from Mr. E. J. Dittus of the Colorado School of Mines contained the results of his analyses of a silver-tellurium mineral which was donated to the Geological Department of the Colorado School of Mines, by Mr. Frank Leavitt of Bonanza, from the Kerber Creek District, Colo. The analyses which follow show exceptionally close agreement to those given for empressite and help to confirm the conclusion that the formula of empressite is AgTe:

	I	II	Ave.	Mol. ratios
Insoluble	0.32	0.34	0.335	
Ag	43.71	43.68	43.695	0.40203
Te	53.86	53.81	53.835	0.43710
Fe	2.17	2.16	2.165	0.03800
CaO	trace	trace	trace	
		<u> </u>		Ag : Te = 1 : 1.08
Total	100.06	99.99	100.03	Ŭ

6. Report of the Director of the Bureau of Mines, JOSEPH A. HOLMES, for the fiscal year ended June 30, 1914. Pp. 101. Washington, 1914 .- The work of the Bureau of Mines keeps expanding in the two lines towards which its energies are being especially directed : the increase in the safety of mining, and the more effective conservation of the mineral resources of the country. This breadth of field is made possible by the act of February, 1913, which enlarged the earlier field of the Bureau. How much is being accomplished for the safety of mine workers, particularly in coal mines where the danger is greatest, is shown by the summary given by the director (pp. 13, 14) of the many important kinds of work accomplished with this object during the year. In conducting the campaign for the increase in safety and efficiency in mining, it is proposed that the National Government shall carry on the general inquiries and investigations; that each State shall enact the legislation needed and make provision for mining inspection; that mine owners shall introduce improvements looking in the directions named as rapidly as their practicability is demonstrated; and that miners and mine managers shall cooperate in making and enforcing all safety rules and regulations shown to be practicable.

The enormous loss in the present methods of mining is dwelt upon, and the estimate is given that in mining 600 million tons of coal during the last calendar year, one-half the amount was wasted or left underground in unminable condition, while of this yearly waste, 200 million tons might have been prevented under existing economic conditions. The value of the natural gas waste is estimated at \$50,000,000. The director also discusses at length the necessity for greater national aid for the mining industry, and shows how the development of the latter has lagged far behind in relation to the rapid increase in population.

The publications of the Bureau for the year include some eighteen bulletins and also a long series of tcchnical papers and miners' circulars; recent bulletins are as follows (see also vol. xxxviii, 102):

No. 38. The origin of coal; by DAVID WHITE and RHEIN-HARDT THIESSEN. With a chapter on the formation of peat; by CHARLES A. DAVIS. Pp. 390; 54 pls.

No. 73. Brass-furnace practice in the United States; by H. W. GILLETT. Pp. 298; 2 pls., 23 figs.

No. 76. United States coals available for export trade; by VAN. H. MANNING. Pp. 15, with map.

No. 77. The electric furnace in metallurgical work; by D. A. LYON, R. M. KEENEY and J. F. CULLEN. Pp. 216; 56 figs.

No. 82. International conference of mine-experiment stations. Pittsburgh, Pa., September 14-21, 1912; compiled by GEORGE S. RICE. Pp. 99; 4 figs.

No. 83. The humidity of mine air, with especial reference to coal mines in Illinois ; by R. Y. WILLIAMS. Pp. 69.

No. 85. Analysis of mine and car samples of coal collected in

the fiscal year 1911 to 1913; by A. C. FIELDNER, H. I. SMITH, A. H. FAY, and S. SANFORD. Pp. ix, 444; 2 figs.

# III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Annual Report of the Secretary of Commerce, W. C. REDFIELD, 1914. Pp. 210; with map, plates and text figures. Washington, 1914.—The second annual report of the Secretary of Commerce covers the work of the Department through the fiscal year ending June 30, 1914, with a general statement extending through October, 1914. The Department includes nine bureaus, viz.: those of Foreign and Domestic Commerce, Corporations, Standards, Census, Fisheries, Lighthouses, Coast and Geodetic Survey, Steamboat-Inspection Service, and Navigation. By the recent creation of the Federal Trade Commission the Bureau of Corporations will be detached from the Department when that commission is organized and will form its administrative nucleus.

A general introductory summary of the work accomplished in these various directions is given and then follow separate chapters devoted to the individual bureaus.

As noted below, the Secretary wisely devotes especial attention to the bureau which is conspicuous from the importance of its work and its need of greater financial support, viz. that of the Coast and Geodetic Survey.

It is stated that the enlargement of the Commerce Building was completed in July so that it now embraces the Bureau of the Census. A new building, for which the land has already been purchased, is contemplated and the Secretary urges that it be planned to contain the Coast and Geodetic Survey and the administrative portion of the Bureau of Fisheries.

2. The Work and Needs of the United States Coast and Geodetic Survey.—In the recently issued Annual Report of the Secretary of Commerce, the Secretary, Hon. W. C. REDFIELD, calls particular attention to the pressing needs of the Survey. He speaks of it as "the oldest scientific service of the Government, the greatest of its kind in the world, while the efficiency of its work is as marked as its extent, taking into consideration what the Survey accomplishes both for humanity and for commerce." The Secretary affirms further "that the past attitude of the Government toward the Coast and Geodetic Survey—if the magnitude of its task be considered and the quality of its work be weighed has been both with respect to its housing, its vessels, and to the necessary apparatus for its serious tasks, and particularly as regards the Pacific coast and Alaska, like that of a wealthy and prosperous man refusing to give to his loyal children the necessaries of life."

Those closely familiar with the work of the Survey, in the past as in the present, will appreciate the truth of the vigorous and well-timed words of Mr. Redfield. The great extent of the country, the long coast lines on the two oceans, with the very great additions to them of the difficult coasts of Alaska, the Philippine Islands. and our other dependencies, make the magnitude of the work of the Survey vastly greater than that of any other nation. Alaska alone offers several times more coast line than Great Britain and Ireland combined.

It is at once surprising and disappointing that the value of what the Survey has accomplished and the still great amount of important work to be done are not more adequately appreciated by those to whom it must look for the funds for its support. Doubtless many have the impression that work once finished need not be revised, and hence the time may be looked forward to when the labors of the Survey shall be completed. This, however, is very far from being true. The constantly changing conditions in all our harbors and rivers make continual vigilance necessary, while the increase of the draught of the vessels employed in commerce calls for a more minute and exhaustive search for possible perils to navigation. As illustrating this last point, it is interesting to note the results of the "wire-drag method," by which a long wire, maintained at any desired distance below the surface, is towed over the area to be examined, while a number of attached buoys indicate at once the presence of any obstructions. This work is slow but thorough, and has been carried on extensively in southern waters in winter and in northern waters in summer. By this means, since 1906, it is stated that 3,300 rocks have been located which have less water over them than the charts showed, and some 900 of these have been proved to be distinct menaces to navigation. A long list is given of wrecks in Alaskan waters, disastrous to property and in some cases to life, which might have been prevented if proper surveys had been made. No one will question the remark of the Secretary that "The plan of discovering hidden rocks by running vessels on them, still in vogue, does not commend itself as a business proposition, apart from the humanity of the case." But so little has the importance of the work spoken of been appreciated that the appropriations for the current fiscal year were reduced by Congress, making it impossible, for example, to provide suitable vessels to take the place of the long antiquated ones still in service in Alaska, while the extension of the wire-drag system has necessitated the cutting down of important expenditures in other directions.

The work of the Survey, however, is not limited to our coasts. What has been thus far accomplished over the land in primary triangulation and in precise leveling, leaves nothing to be desired as to accuracy but is painfully restricted as to amount, in consequence of the limited funds available. Primary triangulation, for example, now covers 100 per cent of Great Britain, Italy, and Japan, 83 per cent of Germany, 70 per cent of Austria, 40 per cent of France, 35 per cent of India, but only 12 per cent of the United States, while practically nothing in this line has been done in Alaska. As regards precise leveling, the United States is no better off in number of miles than India, while the amount accomplished in Germany, Great Britain, and Japan is respectively 16, 10.6, and 5.2 times greater. In Alaska again nothing has been done, although several thousand miles of leveling are needed at once. It would seem that nothing more than a full understanding of the situation with respect to the limitations of the Survey at present, and the demands upon it for the future, should be needed to insure its receiving adequate appropriations.

Besides the account of the work of the Survey, covering pp. 130-171 of the Report of the Secretary of Commerce, the Annual Report of the Superintendent, O. H. Tittmann, has also been issued (pp. 132, 16 illustrations), giving a concise statement of the work accomplished during the year in its special lines, particularly those of hydrography and topography, geodetic and magnetic. Special publications include the following:

No. 19.—Primary triangulation on the One Hundred and Fourth Meridian, and on the Thirty-ninth Parallel in Colorado, Utah and Nevada; by William Bowie. Pp. 163; 17 illustrations.

No. 22.—Precise Leveling from Brigham, Utah, to San Francisco, California; by WILLIAM BOWIE. Pp. 67; 5 illustrations.

3. Report of the Secretary of the Smithsonian Institution, CHARLES D. WALCOTT, for the year ending June 30, 1914. Pp. 117; 4 pls., 1 fig. Washington, 1914.—The activities of the Smithsonian Institution are so varied that the Annual Report by the Secretary, in which the year's work is summarized, is always of much interest. In the direction of researches and explorations, one point to be noted is the reopening of the laboratory for the study of the problems of aerodromics, particularly those of aerodynamics. This laboratory is to be named for Professor Langley, who studied this subject so profoundly and first placed the matter of air flight on a successful basis. As already noted in the public press, his original aeroplane ("aerodrome"), after being refitted, made a successful flight at Lake Keuka in June 1914 in the hands of Mr. Glenn H. Curtiss. Other explorations now being carried on include those by the Secretary at Robson Peak, the geological survey of Panama, etc.; an account of the varied ethnological researches, under the auspices of the Institution, is given in detail in Appendix 2, by F. W. Hodge, ethnologist in charge.

It is stated that the plans for the "George Washington Memorial Building" have been completed and a plate gives the accepted design. The cost is to be not less than \$2,000,000, and \$500,000 must be provided for maintenance; the work of construction will not be commenced until a sum of \$1,000,000 has been raised. The building is to serve as the gathering place and headquarters of patriotic, scientific, medical, and other organizations interested in promoting the welfare of the American people.

A detailed account of the work of the National Museum is given in Appendix 1, by Mr. Richard Rathbun; also a report on the Astrophysical Observatory, by the director, Mr. C. G. Abbot, in Appendix 5; from the latter the following summary is taken: "Progress has been made in the measurement of the effects produced by atmospheric water vapor on solar and terrestrial radiation. New apparatus for measuring sky radiation has been devised and perfected. Special pyrheliometers have been constructed and caused to record solar radiation with considerable success at great altitudes when attached to free balloons. The results obtained tend to confirm the adopted value of the solar constant of radiation. Further results from balloon pyrheliometry are expected. A tower telescope has been erected and put in operation on Mount Wilson. By means of it the variability of the sun has been independently confirmed, for it appears that changes of the distribution of radiation over the sun's disk occur in correlation with the changes of the sun's total radiation."

An interesting account of the Explorations and Field-work of the Smithsonian Institution in 1913 is given in a special publication, being No. 8 of vol. 63 of the Miscellaneous Collections. A sixth revised edition of the Smithsonian Physical Tables, prepared by FREDERICK E. FOWLE, has recently been issued as No. 6 of the same series, pp. xxxvi, 355, 405 tables. (See page 219.)

4. Annual Report of the Board of Regents of the Smithsonian Institution showing the Operations, Expenditures, and Condition of the Institution for the Year ending June 30, 1913. Pp. xi, 804, with numerous plates and figures. Washington, 1914.—This annual volume of the Smithsonian Institution contains the report of the Secretary, already noticed in this Journal (March, 1914, p. 286). The General Appendix (pp. 145–789) embraces thirty-six papers in the different departments of science, covering the more important lines of scientific progress.

5. Proceedings of the National Academy of Sciences. Volume I, No. 1. Pp. 1–58, with one plate. January, 1915 (The Waverly Press, Baltimore).-The first number of the Proceedings of the National Academy of Sciences (see this Journal, Dec. 1914, p. 572) has recently appeared, and fulfills all the promises made in the prospectus; it also leaves nothing to be desired on the typographical side. The editorial work is chiefly in the hands of Professor A. A. Noyes as chairman of the editorial board, and Professor E. B. Wilson as managing editor; Dr. A. L.Day, Home Secretary, and Dr.George E. Hale, Foreign Secretary of the Academy, are associated with them, and also fifteen gentlemen in different departments of science. Seventeen papers are included in this number, three in mathematics, six in astronomy, two in botany and genetics, and one each in chemistry, physiology, ethnology, and anthropology. These Proceedings will be of great assistance to the science of the country by giving opportunity for prompt announcement, in brief, of important results. As an example may be noted (p. 12) the account by S. B. Nicholson of the discovery of a ninth satellite of Jupiter at the Lick Observatory; this is estimated as of the nineteenth magnitude.

6. Memoirs of the National Academy of Sciences. Volume XII. Part I. Monograph of the Bombycine Moths of North America, including their transformations and origin of the larval markings and armature. Part III. Families Ceratocampidæ (exclusive of Ceratocampinæ), Saturniidæ, Hemileucidæ, and Brahmæidæ; by ALPHEUS S. PACKARD, edited by THEODORE D. A. COCKERELL. Pp. ix, 516; 113 pls.—Earlier parts of this great work by the late Professor Packard are contained in volumes VII and IX of these Memoirs.

7. Samuel Franklin Emmons Memorial Fellowship. - The friends of the late Dr. Emmons have established a fund whose income may be used in support of a fellowship to promote investigations in geology, especially on the economic side. The choice of the fellow and expenditure of the income are entrusted to a committee consisting of Professors J. F. Kemp, J. D. Irving, and Waldemar Lindgren. The committee is prepared to award in March, 1915, a fellowship of \$1,000 for the year July 1, 1915, to June 30, 1916, inclusive. Applications, stating the problem proposed for study, must be made on blanks furnished by the Secretary of Columbia University, New York City. These, accompanied by testimonials and statements of the applicant's qualifications, will be submitted to the committee on March 1, 1915. The investigation (to be made under the oversight of the committee) may be taken at any place or institution preferred by the holder of the fellowship and approved by the committee. The applicant must give his entire time and energies to the problem selected, but the results may be used as a dissertation for the degree of Ph. D. in an approved university.

8. Feeblemindedness: Its Causes and Consequences; by HENRY HERBERT GODDARD, Ph.D. Pp. 599. New York, 1914 (The Macmillan Co.).—This book will take its place by Seguin's "Idiocy and its Treatment by the Physiological Method," as one of the distinctive contributions of America to the many-sided subject of feeblemindness. Dr. Goddard is Director of the department of Research of the Vineland (N. J.) Training School for feebleminded boys and girls, and this new publication is a report of five years of investigation into the origin of feeblemindness.

The work is in the nature of a case book : in it 327 unselected cases of high, low and middle grade mental defect are described and family-charted (pp. 47-435) as the basis for a statistical and critical analysis of the causes of feeblemindedness. Of all causes feeblemindedness in the ancestors is the most potent, accounting for about 65 per cent of all the cases. The author considers direct heredity the cause least open to question. Neuropathic ancestry (insanity, epilepsy, neuroses, migraine, etc.) also plays a large part in the production of feeblemindedness, but the data cast doubt on the importance of alcohol, syphilis, and traumatism as causative factors.

The question "Is Feeblemindedness a Unit Character?" is raised and answered somewhat hesitatingly in the affirmative; tables and figures are presented showing that feeblemindedness tends to follow the Mendelian Law of Inheritance. Though this is a rather striking and novel idea, the temper of its discussion is conservative.

The chapters on Eugenics and Practical Conclusions emphasize the hereditary aspect of the problem and the necessity of control through wise segregative treatment rather than through the sterilization of defectives.

The many-sidedness of the subject is well reflected in Dr. Goddard's treatment and many pages will appeal to the general Crime, pauperism, prostitution and other "conreader. sequences" are considered in their relation to underlying mental The biographical character of the data, the abundant defect. photographs and the case method of presentation give the volume human interest; and will make it a kind of source book for students of the problem. ARNOLD GESELL.

9. Awards by the Franklin Institute.-It is announced that the Franklin Institute has awarded a certificate of merit to Mr. George P. Vanier, of Steelton, Pa., for his potash bulb. Fur-ther, the John Scott Legacy Medal and Premium have been awarded to Dr. Charles Edouard Guillaume, of Serves, France, for his alloy invar.

#### OBITUARY.

DR. CHARLES SEDGWICK MINOT, professor of comparative anatomy in the Harvard Medical School, died on November 19 at the age of sixty-two years. His contributions to biology, especially in histology and embryology, had placed him in the very first rank among American men of science.

DR. ALBERT CHARLES PEALE, the geologist and paleobotanist, died on December 6 in his sixty-fifth year. He was for many years connected with the United States Geological Survey ; since 1898 his work had been in the section of paleobotany of the U. S. National Museum.

JOHN MUIR, the well-known nature-lover, explorer and naturalist, died at Los Angeles on December 24 at the age of seventysix years.

PROFESSOR DR. JOHANN WILHELM HITTORF, the veteran Ger-

man physicist, died recently at the age of ninety years. DR. NILS CHRISTOFFER DUNÉR, professor of astronomy and director of the observatory at Upsala, Sweden, died on November 10 in his seventy-sixth year.

DR. MORDECAI C. COOKE, the veteran mycologist, died on November 12 at Southsea, England, at the age of eighty-nine years.

DR. J. BORGMANN, professor of physics in the University of Petrograd, died recently at the age of sixty-five years.
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#### CONTENTS.

	Page
ART. VII.—Physiography and Glacial Geology of the North- ern Catskill Mountains; by J. L. RICH	137
VIII.—Outbreak of Mauna Loa, Hawaii, 1914; by T. A. JAGGAR, JR.	- 167
IXCarboniferous Plant Tissue; by E. H. BARBOUR	173
X.—Crystallization—Differentiation in Silicate Liquids; by N. L. BOWEN	175
XIBottom Currents in Lake Ontario ; by E. M. KINDLE .	192
XII.—Separation and Estimation of Aluminium associated with Iron, by the Action of Acetyl Chloride in Acetone;	
by H. D. MINNIG.	197
XIIISolar Constant ; by F. W. VERY.	201
XIV.—An Eccene Ancestor of the Zapodilla; by E. W. BERRY. (With Plate I)	208

#### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Molecular Weight of Sodium Carbonate and the Atomic Weight of Carbon referred to Silver and Bromine, RICHARDS and HOOVER, 213.—Molecular Weight of Sodium Sulphate and Atomic Weight of Sulphur, RICHARDS and HOOVER: Separation of Tungsten and Molydenum, E. E. MARBAKER, 214.—Standardization of Acidimetric Solutions, E. D. DODGE: Chemical Technology and Analysis of Oils, Fats and Waxes (J. Lewkowitsch), G. H. WARBURTON: High Frequency Spectra of the Elements, 215.—Biflar Property of Twisted Strips, J. C. BUCKLEY, 216.—Volatility of Thorium D, A. B. WOOD: Lecture Experiment on Dispersion, S. P. THOMPSON, 218.—Experimental Studies in Electricity and Magnetism, F. E. NIPHER: Smithsonian Physical Tables, F. E. FOWLE, 219.
- Geology and Mineralogy—"Ferns Ledges" Carboniferous Flora of St. John, N. B., M. C. STOPES, 219.—Pre-Cambrian Algonkian Algal Flora, C. D. WALCOTT: Petrology of the Orijärvi Region in Southwestern Finland, P. ESKOLA, 221.—The Crowsnest Volcanics, J. D. MACKENZIE, 222.— Mineral Empressite, W. M. BRADLEY, 223.—Report of Director of Bureau of Mines, J. A. HOLMES, 224.
- Miscellaneous Scientific Intelligence—Annual Report of the Secretary of Commerce, W. C. REDFIELD: Work and Needs of the United States Coast and Geodetic Survey, 225.—Report of Secretary of Smithsonian Institution, C. D. WALCOTT, 227.—Annual Report of Board of Regents of Smithsonian Institution: Proceedings of the National Academy of Sciences, 238.—Memoirs of the National Academy of Sciences: Samuel Franklin Emmons Memorial Fellowship: Feeblemindedness: Its Causes and Con sequences, H. H. GODDARD, 229.—Awards by the Franklin Institute, 230<sup>-</sup>

Obituary-C. S. Minot : A. C. Peale : J. Muir : J. W. Hittorf : N. Cristoffer Dunér : M.C. Cooke : J. Borgmann, 230. VOL. XXXIX.

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#### FOURTH SERIES

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## AMERICAN JOURNAL OF SCIENCE

#### [FOURTH SERIES.]

ART. XV.-The Salton Sea;\* by DR. D. T. MACDOUGAL.

EXTENSIVE basins occur in various parts of North America. Australia. Africa, and Asia, in which the climatic and hydrographic conditions are such that the lowermost parts of the depressions are at times occupied by bodies of water, which may disappear or show wide fluctuations of level or volume. Alternations of this kind are followed, of course, by the annihilation of the terrestrial vegetation, as lakes are formed or as they increase, and by the revegetation of emersed areas laid bare by receding waters. It is fairly evident that occurrences of this kind have taken place in the great basins of Nevada and Utah, in the Oteri and other depressions in New Mexico and Arizona, in the Pattie basin in Mexico, and in the Cahuilla basin in southern California. In some the alternations date far back in geologic time and many thousands of years must have elapsed since the last change occurred. In others, such as the Pattie and Cahuilla basins, the transformations follow each other rapidly, and although they may have begun far back in time, yet they continue up to the present.

The Cahuilla Basin lies in the most arid part of North America, and although the making of the lake in the Salton Sink, or portion of the basin below sea-level, may be finally due to climatic factors, yet it is caused directly by overflow from the channel of the Colorado River. The geological record seems to indicate that the sink has been filled and dried out at intervals over a long period extending up to the present time.

\* \* The present article was prepared from Publication 193, Carnegie Institution of Washington, 1914, in compliance with the request of the editor of this Journal. No attempt has been made to assign paragraphs, which have been cited intact, to the collaborators in the volume, or to indicate the portions that have been abstracted. The reader is referred to the original treatises for details. The data obtained by the eighth annual analysis of the water of the lake in 1914 have been added to the table on page 241, and some other matter not included in the volume has been given.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 231.—MARCH, 1915.

Circumstantial evidence points to the conclusion that hardly twenty years have passed without some inflow from the river into the Sink, but the only available record of any other inundation, beside the one the effects of which are considered, is that of the overflow of 1891, when the passage from the river to the small lake formed in the Sink was made by a single man in a boat on the inflowing current for the purpose of ascertaining the source of the water forming the lake.

The formation of the lake in 1905, 1906, and 1907 occurred under circumstances that gave unexcelled opportunities for a study of the attendant phenomena. The Desert Laboratory of the Carnegie Institution of Washington had completed its organization and was able to focus the attention of members of the staff and to secure collaborators upon the more important problems which would be offered by the recession of the lake level: these may be briefly stated as follows:

1. Composition and nature of the flora of the basin with chief attention to the species inhabiting the Sink.

2. Influence of the lake upon vegetation above the flood level, either in increased humidity or hemmed underflow.

3. Endurance and survival of the vegetation in the shallower marginal portions of the flooded area.

4. Geographical relations of the Sink with especial consideration of the contributing drainage.

5. Physical and chemical analyses of soils of the Sink, with comparisons between those unaffected by the recent submergence and those taken from the bared strands.

6. Composition of the water of the lake as varying with its concentration.

7. Algal and bacterial flora of the lake, and influence of these plants upon the composition of the water.

8. Alterations in plant tissues induced by submergence.

9. Reoccupation of the bared strands left by the receding lake by plants.

10. Alternations or successions in the plant inhabitants of the strands with increasing aridity.

11. Environic response of plants gaining a foothold on the strand and later becoming subject to desiccation.

12. Pioneer occupants of sterilized islands emerging from the water as a result of lowered level.

13. Agencies effective in carrying seeds, spores, and propagula to bared strands and isolated areas on islands.

14. Introductions, or invasions of the Sink by species not hitherto native to the region.

The Cahuilla basin is a structural trough lying immediately to the eastward of an abruptly rising mountain range which separates it from the Pacific. The depression is shaped much like the bowl of a spoon, the tip of which comes to within a short distance of the Gulf of California. An ancient beachline, lying a few feet above present sea-level, encloses an area of about 2,200 square miles; and this lowermost portion of the basis has been designated the Salton Sink in the present paper. (See the map accompanying the original memoir.)

The original depression was of unknown depth; it has been filled to within 284 feet below the mean tide-level by the alluvial outwash from the slopes of the mountains which bound it on three sides. Borings to a depth of 1,700 feet show a series of interbedded sands and clavs, such as might be encountered in any one of the similar troughs in central Arizona. which had been filled by material worn down by wind and water from the mountain slopes. The bottom of the basin obviously lies far below the present level of the gulf; yet it is clear that "Blake Sea," the ancient body of water which filled the basin to the level of the highest beach, was composed of fresh water, at least during a part of its existence; as evidenced by the heavy layer of travertine formed on the rocks beneath its surface at the highest level, by the presence of fresh-water shells, and by the composition of the saline layer on the bottom of the sink; evidently derived by condensation of fresh water rather than from evaporation of sea water.

The Cahuilla Basin is subject to a mixed type of climate. It lies far enough inland so that overheating should result in a continental type of climate, particularly with respect to the rainfall. Its great bowl, however, lies immediately in the lee of a great mountain range which rises abruptly from its southwestern side, with the result that fringes of mountain storms reach out over part of its area at times, while the topographical conditions favor the development of the intense and localized precipitation known as cloudbursts.

The annual average rainfall from data covering 36 years is 2.74 inches and the character of the precipitation phenomena suggests a high degree of aridity. The maximum amount received in one year was 7.10 inches (1906) and the lowest, a "trace" (less than 01 inch) in 1904, giving a variation as 1 to 1000, a proportion occurring in deserts of a pronounced degree of aridity only. In addition to this expression, the ratio of possible evaporation from a free-water surface to the annual amount of precipitation has been useful in characterizing deserts. About 116 inches of water would evaporate from the surface of a small vessel on the ground in the open in the Cahuilla during a year; this is 15 times the amount which has fallen in any one year, 43 times the average, and many thousands of times the minimum. The possible evaporation in northern Africa at Algiers is about 60 inches annually, but in the interior of the Sahara it is much greater.

The Alamo and New rivers are the natural channels by which the Colorado river overflowed into the Sink before recent engineering operations were undertaken. The Alamo was the most direct, but its connection with the Colorado was in general rather obscure and liable to obstruction and obliteration by vegetation and the deposition of silt. The flow of water was intermittent and irregular and only occurred in seasons of extremely high water. The New River flow did not come directly from the Colorado, but partly from the Alamo by way of the Garza and other sloughs, and partly as overflow from the shallow cachement basin of Volcano Lake. This lake was itself filled, in seasons of normal high water, through the channels of the Paredones, the Pescadero, and other less clearly defined waterways. Normally the whole efflux from the lake went directly into the Hardy, and so into tidewater, but in seasons of exceptionally high water it would be forced also to right and left-into New River on the one hand and into the lower Pescadero on the other, and so into the lower Hardy and the Gulf. The influence of the tides is noticeable in the Hardy as far as the point of the Cucopa Mountains and has at times been instrumental in forcing a part of this Hardy and Paredones flood-water into the Pattie Basin.

The Hardy, with its associated sloughs, backwaters, and lagoons, has always occupied the position of relief channel for the flooded and surcharged delta in times of high water, filling thus a somewhat analogous position to that of the Bahr el Zaraf in the economy of the Upper Nile.

Since 1901 the flow of water in the Delta has been greatly changed, as will be detailed later, owing to the various engineering operations carried out by or on behalf of the irrigation companies and settlers in the Imperial Valley.

During the summer of 1890 the water from the Colorado River filled many of the small channels and lagoons toward the southwest, and in 1891 flowed through into the Salton Sink and forced a lake several miles in length. The intervening region was comparatively little known and its drainage system hardly comprehended at that time, and the appearance of such a large body of water in close proximity to the Southern Pacific Railroad attracted much attention and gave rise to some of the wildest of rumors and hypotheses as to its origin. William Convers, followed by one or two others, succeeded in making the journey by boat from the Colorado to the lake, and so the mystery was solved.

Mr. H. T. Cory, who has a comprehensive knowledge of the conditions in the Delta of the Colorado, concludes that some flood water has found its way down the channel of New River toward the Salton every year since the inundation of 1891, and cites opinions of old settlers who allege that water came into the Salton in 1840, 1842, 1852, 1859, 1862 and 1867. The mail stage service between Yuma and San Diego was interrupted by the flood of 1862 and a flatboat was used for crossing New River for several weeks in the summer of that year.\*

In 1900, a company having been formed for the purpose, work was begun upon the task of connecting and clearing the various channels which formed the natural waterway between the river and the basin; and by the middle of 1901 water was flowing upon the irrigable lands of what has since become known as the Imperial Valley. It had been deemed advisable by the promoters of the scheme to take the water from the river in the United States territory, and so the upper section of the canal was cut almost parallel to the river for several miles and with a very low gradient. This circumstance, together with the general unsuitability of the site selected for the head works, caused considerable trouble for two or three years, as more and more water was required to fulfill the demands of the growing communities in the desert; and so various openings were made between the river and the canal in order to furnish a more adequate supply.

Then in the winter of 1904–05, one of the infrequent winter floods in the Colorado, coincident with a tremendous rush of storm waters from the Gila, found before itself the unprotected head and comparatively steep downward grade of the canal, and at once began to cut and enlarge the channel. The ordinary summer flood of 1905 also poured its water through the opening, and it was soon realized that the outpour had got beyond control.

Practically the whole of the Colorado was now flowing into the Salton Basin and another flood in the following November (1905) made the task of closing the breach seem almost hopeless, although the most strenuous efforts were being made by the engineers; and it was not until February 1907 that the Colorado was finally returned into its former channel. Here, again, however, the vigorous vegetation of the Delta had played its part, for the river bed had in the meantime become so choked by plant growth and the deposition of silt that the water has since made repeated attempts to escape, first towards the southeast through the Santa Clara Slough, directly towards the head of the Gulf, and since—in spite of some rather hastily planned and inadequate efforts to control it in that direction---into the head of Bee River and the Pescadero and so by various ways into the Hardy, which is now, in its lower reaches, carrying virtually the whole volume of the Colorado. This surcharging of the Hardy Channel has had the further

\* Proc. Amer. Soc. Civil Engineers, vol. xxxviii, p. 1371, 1912.

effect of allowing a large quantity of water to flow over its western bank and towards the Pattie Basin, and a large lake has now filled the lower part of this depression.

During the summer of 1906, and at the time when the maximum inpour was reaching the Salton Sink, the channels of the Alamo and the New River began to cut backward from the lower end, and the soluble, loess-like soil along their courses was carried into the lake, leaving the deep precipitous-sided valleys through which the present streams flow.

Some idea of the magnitude of this displacement and redistribution of material may be obtained from a statement made by H. T. Cory,\* that the total yardage thus moved is over

#### FIG. 1.



FIG. 1. Northeastern shore of Salton sea, Feb. 1907, with tongues of water extending up the channels of desert washes: hills forming islands in distance.

450,000,000 cubic yards, or almost twice that of the Panama Canal.

A good deal of water still passes through both the Alamo and the New River, but this is merely the overflow from the irrigation canals, and it is quite improbable that with the interests now at stake in the Imperial Valley and the close watch kept upon the river by the engineers, any further uncontrolled incursion of water will be allowed to take place.

In the region of the lower Delta, however, conditions are very different; here we have a large, wayward, and silt-laden river, thrown out of balance by a temporary diversion, and

\* Proceedings of American Society of Civil Engineers, vol. xxxviii, No. 9, p. 1457, 1912.

always hampered at its mouth by great and violent tides, wandering at present virtually unchecked over a large area of friable alluvium with downward grades in several directions.

All these conditions tend, as may be readily imagined, toward a condition of instability and possible geographical change; in fact, it is probable that even if the Colorado and the general drainage conditions through the Alamo and its associated channels had not been interfered with in any way by the operations of the irrigation engineers, another diversion of the river water towards the west was about due from the natural causes outlined above, and would in any case have ensued within a few years.

It is furthermore evident that as so much of the flow of the river during the growing season of the early Spring is now diverted and utilized for agricultural purposes, and as the bed of the river in its lower reaches is left practically dry during the period of most rapid growth of the Delta vegetation, its obstruction and elevation will be more rapid and the stability of the irrigation and protective works menaced more and more unless adequate measures are taken for controlling and storing the flood waters of the early summer upon the upper Colorado.

The recent maximum level of Salton Sea was reached on Feb. 10, 1907, on which date an expedition from the Desert Laboratory which had started from Mecca near its northwestern extremity in a sailboat on Feb. 7, landed near the Carrizo sand dunes and made a camp for the purpose of observing shore phenomena and relative humidity. At this time the sea contained about seven cubic miles of water, which covered an area of about 450 square miles, with the deepest sounding showing about 84 feet. This indicated a surface of about 200 feet below sea-level (U. S. G. S. datum). The loose, flaky surface of the desert moistened by the water made boggy shores, which made landing extremely difficult until sorting and solidification by wave action had taken place. In places the water extended out into the channels of the dry washes for as much as a quarter of a mile or even farther, and the footing near these was uncomfortable and even dangerous (fig. 1).

The inundation had covered up the salt deposit in the lowest part of the Sink, which was being worked and the product marketed (fig. 2). A group of mud-volcanoes near the northeastern shore, which had at various times displayed much activity, was covered to a depth of nearly forty feet and no disturbance of the surface above them was noted.\*

\*Veatch, J. A.: Notes on a visit to the "Mud Volcanoes in the Colorado Desert in the month of July, 1857," this Journal (2), xxvi, 288, 1858. See also Le Conte: An Account of Some Volcanic Springs in the Desert of Colorado in Southern California, ibid., (2), xix, i, 1855. The species of higher plants in the Sink number something less than a hundred and fifty, yet in places the mesquite (*Prosopis gradulosa*) and the screw-bean (*P. pubescens*) and a halfdozen small trees and shrubs madé open forests over considerable areas which had been covered, and the emergence of these was expected to furnish evidence of value in the interpretation of the earlier stages of fossilization of woody tissues.

The greater part of the inflow from the Colorado river having been cut off, the phase of the history of the Salton sea or lake with which this discussion is concerned began, and the greater part of the facts of interest are results of the recession of the water level. The factors which would tend to lower the



FIG. 2. Salt deposit at bottom of sink, February, 1903.

level of the lake include the evaporation, which would amount to about 116 inches yearly, and the seepage of which no estimate could be made. Some supply of water would be contributed by the uncapped artesian wells in the northwestern part of the Sink, by numerous saline and brackish springs, by the underflow from the mountains which bound the Basin, by the run-off from the infrequent rains, and by the wastage and seepage which continued to find its way down the inflow channels of the Alamo and New rivers, and from the tailings of power plants and irrigation systems. The variation in the level of the water from the beginning of the inflow until July, 1912, is shown by the tracing in fig. 3, which is reproduced by permission of Mr. H. T. Cory. It was found that the recession from 1907 to 1912 amounted to 40 to 59 inches annually, the maximum occurring in 1910.

FIG. 2.

#### D. T. MacDougal—The Salton Sea.

Evaporation was the chief factor in determining the rate of variation of the level in the earlier history of the lake, and consequently the surface fell slowest from November to February and most rapidly during the midsummer. The extension of the controlled use of water in the southeastern part of the basin known as the Imperial Valley has been followed by an irregularly increasing amount of wastage escaping into the lake with the result that variations in level are no longer to be directly correlated with the seasons. Thus no measurable



FIG. 3.

FIG. 3. Diagrams showing variations in level of Salton sea, and probable amount of inflow, 1905-1912. After H. T. Cory.

recession occurred in the period of six months from December to June, 1914. The record for the year, however, will show a net loss, but this may be expected to decrease each year until the waste irrigation waters balance the evaporation and other losses, which will probably result in a permanent body of water of an area of nearly three hundred square miles with irregular fluctuations in a level of a foot or two.

The composition of the water was of course a prime consideration in all physical and biological work connected with the lake and its problems. The rapid inflow of silt-laden river water first covered the saline beds at the bottom of the Sink, dissolving the salts in the surface layers and then leaching out the contents of the alluvium beneath. This process followed so slowly that samples taken at a depth of 60 feet in February, 1907, nearly fourteen months after the salt deposits were flooded, contained 352 parts in a hundred thousand of dissolved material as compared with 330 parts at the surface of the lake.

As might be expected, those samples were found most salty which were taken from shallow regions overlying saline flats, while samples taken from the surface in deep parts of the lake contained less amount of salts. Thus, on June 10, 1906, when the greatest depth of the lake was about 35 feet, a sample taken  $1\frac{1}{2}$  miles from shore near Mecca was found to contain 401.6 parts of total solids in 100,000; a second sample, taken at the same time from a point 100 feet from shore, contained 697.4 parts of solids; and a third sample, collected a short time before within a few feet of the shore near Travertine Point, showed a salt content of 1152.8 parts. The water at this point was very shallow and covered a saline deposit.

Within the next few months a marked increase in uniformity took place, as shown by the analysis of two samples collected on October 11. One of these taken from shallow water near the shore contained 363.2 parts of solids in 100,000, while a half-mile from shore a sample yielded 359.6 parts.

The dates on which the samples were collected and the results of the eight yearly analyses are given in the following table. Instead of aiming to give a statement of the constituents which occur in solution, the analysis of each sample was made to represent rather the composition of the anhydrous inorganic matter which is left when the water is evaporated to dryness. Those elements, like silicon, iron, and aluminium, which occur in the residue in the form of their oxides, are represented as such, but all other coustituents which occur in combination as salts are expressed in the ionic form. In this way the necessity for making assumptions regarding the way in which the constituents are combined is avoided.

With the exception of the first year period, the yearly percentages of increase of the constituents are seen to increase progressively. This result is to be expected, for as the volume of the lake becomes smaller an equal loss of water by evaporation will produce a greater increase in concentration of the constituents.

The difference, however, in the fall of the surface of the lake between the first and second year periods is not great enough to correspond to the difference found between the total constituents for the same periods, and it may therefore be con-

				Parts	per 100,00		•	-
	June 3, 1907.	May 25, 1908.	June 8, 1909.	May 22, 1910.	June 3, 1911.	June 3, 1912.	June 18, 1913.	June, 1914.
Total solids (dried at 110° C.) plus water of occlusion and hydration	364.8 111.05 2.30	$\frac{437\cdot20}{134\cdot26}$	$519.40 \\ 17.50 \\ 160.33 \\ 3.24$	$\begin{array}{c} 603 \cdot 80 \\ 22 \cdot 56 \\ 189 \cdot 28 \\ 3 \cdot 53 \end{array}$	718·00 20·84 227·81 3·81	$\begin{array}{c} 846.55\\ 23.9\\ 270.71\\ 3.81\end{array}$	$1002.56 \\ 32.6 \\ 323.08 \\ 3.45 \\ 3.45 \\$	$\begin{array}{c} 1179.6\\ 36.2\\ 381.47\\ 4.01\end{array}$
Lithium, Li Calcium, Ca Magnesium, Mg Mannesium, Mg Ferrio oxide, Fe <sub>2</sub> O <sub>3</sub> .	trace 9-95 6-43 0-056 0-007 0-92	$\begin{array}{c} 0.013\\ 11.87\\ 7.63\\ 0.065\\ 0.009\\ 0.93\end{array}$	$\begin{array}{c} 0.017\\ 12.70\\ 8.96\\ 0.1117\\ 0.0114\\ 1.04\end{array}$	$\begin{array}{c} 0.021\\ 13.67\\ 9.84\\ 0.075\\ 0.075\\ 0.011\\ 1.01\end{array}$	$\begin{array}{c} 0.025\\ 15.62\\ 11.68\\ 0.168\\ 0.051\\ 1.19\end{array}$	$\begin{array}{c} 17\cdot28\\ 13\cdot62\\ 0\cdot100\\ 0\cdot042\\ 1\cdot79\end{array}$	$\begin{array}{c} 19.75\\ 16.22\\ 0.125\\ 0.038\\ 2.18\end{array}$	$\begin{array}{c} 2222\\ 2222\\ 19.03\\ 0.140\\ 0.012\\ 2.42\end{array}$
Manganese, Mn	169.75	204.05	240-90	trace 280.93	trace 339.42	395.44	473.89	559.66
Iodine, I	$\begin{array}{c} 47.60\\ 6.58\\ 0.009\\ 0.18\\ 0.093\end{array}$	56.74 7.66 0.011 0.20 0.059	65.87 7.34 0.01 0.006	76.36 6.38 0.013 0.045	91.67 5.78 trace 0.063	106.83 12.09 trace trace 0.072	134-65 11-28 trace 0-110	148°10 10°96
Total constituents.	354.93	426.27	500.61	581.17	697-28	821.78	974.77	1157

Eight Complete Analyses of the Salton Sea Water.

D. T. MacDougal—The Salton Sea.

241

cluded that the high value found for the first year increase of the constituents was largely caused by leaching of salts from the bottom of the lake, as already stated.

An inspection of the results of the analyses given above shows that the calcium and potassium do not follow the course of concentration of the total solids, or of sodium, the principal constituent of the residues. The percentages of increase of the total solids and of these two elements are as below:

	Total solids	Calcium	Potassium
1908	20.9	19.3	20.9
1909	16.2	7.	16.7
1910	17.4	7.7	9.
1911	18.9	14.2	7.3
1912	17.5	10.6	0.0
1913	17.7	14.5	9. (loss)
1914	18.1	12.05	16.3

Nothing in the results obtained by a study of the Salton yielded positive evidence as to the fate of the potassium, but the deposition of the calcium on twigs and objects near the surface of the water was observed as early as 1910, at which time the concentration of this element in solution fell farthest behind that of the other constituents. Furthermore the thickness of the deposit now being formed on branches and other objects at the surface is less than in 1910 and 1911, although the actual concentration of the calcium is greater. Without rehearsing the detail of this matter which is given in the volume on the Salton, the deposition of calcium takes place under conditions favorable to the existence of certain bacteria and algæ. These conditions in the Salton include a concentration of 5 to 6 per cent and the presence of some organic matter. The environment necessary for a plexus which would have the end effect of precipitating calcium might be entirely different in other cases, and undoubtedly is so in the Great Salt Lake, in the water of the Atlantic, near the Florida keys and in other places in which this matter has been studied. The direct interest in the present connection is the probable origin of the travertine which forms a coating on the rocks at certain places near the ancient high level of Blake sea. This layer is but a few inches in thickness near the high level, increases to a point 30 to 40 feet below, then thins again. It is as if Blake sea were full, then began to recede, the deposition of calcium increasing to a maximum rate when a certain concentration was reached, then slowing down as concentration continued. It is by no means certain, however, that such was the case, and it may well be that the thickest part of the

242

#### D. T. MacDougal—The Salton Sea.

travertine marks the under-surface layer of water for a longer time than at the high level. (Fig. 4.) The geologist may no longer assume that calcium is precipitated from saturated solutions in lakes as in a test tube and the trend of recent work seems to be accurately represented by the conclusion of Walcott, "that the origin of the Cordilleran Algonkian limestones is largely owing to the action of lime-secreting algæ and bacteria, and that precipitation of calcium and magnesium bicarbonates from a saturated solution is of very rare occurrence and not an important agent of deposition in geologic time and that marine waters are not necessary for the deposition of magnesian limestone" (Smithsonian Misc. Coll., vol. 64, No. 2, p. 84, 1914).

FIG. 4.



FIG. 4. View southward near Travertine point showing high beach line of Blake sea on rocks at right and Salton lake at level of 1912. The lighter zone fringing the shore is the strip laid bare by the recession of the water from 1907 to 1912.

The special studies made of the changes in the stems and branches of trees submerged by the Salton demonstrated the fact that hydrolyzation of cell walls of cortical and other unlignified tissues occurred in material submerged one to five years, and that this action did not take place when sterilized Salton water was used for experimental tests in the laboratory. The disintegration of the walls seemed to be due to an enzyme produced by organisms of the Amylobacter group. The woody cylinders of such stems might be held together submerged for indefinite periods and would pass into the fossil condition minus the cortical cells and the phlœm. In anticipation of possible future condition of the Salton, some attention was devoted to the organisms inhabiting the pools and ponds along the shore of San Francisco bay which pass with the season from a fresh to a brackish condition, and finally concentrate to crystalline salt. These included species of Dunaliella, Pyramimonas, and a red chromogenic bacterium none of which, however, have yet been found in the Salton.

An examination of the portion of the basin below the ancient beach line and above the present level of the lake leads to the conclusion that the vegetation which was destroyed when the lake was formed included ahout 8 species of trees, 33 shrubs and woody perennials, and 81 herbs, most of which were of the characteristic desert types and hence were sparsely distributed over the 450 square miles that were submerged. The shores of the present lake cut across various soil formations and slopes with gradients ranging from 1 in 8 or 10 to 1 in 300 or more. The yearly recession therefore laid bare an encircling strip which varied in width from a few feet to three or four hundred yards.

Four main observational areas were selected along the shores and the yearly extensions of these were followed down the slopes as the lake receded in order to ascertain the mechanism of revegetation of such emersed areas. The following conditions had to be considered at every stage of the process :

1. The observational areas selected represent widely different habitats as to soil composition and other environic factors or components.

2. The lake rose quickly to its maximum level and receded rapidly.

3. The infiltration and leaching of the soil varied year by year as affected by the concentration of the water on one hand and the time of submergence on the other.

4. The salt content of the water was least during 1907 and increased about 18 to 20 per cent in each succeeding year.

5. Every emersed strand would therefore be saturated with a soil-solution resulting from the infiltration of the lake water of the concentration and composition prevalent in the period preceding emergence.

6. The desiccation of the emersed strands would proceed at a rate determined by the character of the soil and by the composition of the infiltrated water.

7. The rising water of the lake picked up seeds lying on the surface, and their survival constituted a means of revegetation, chiefly of the strand bared in 1907.

8. The rates of evaporation and of recession of the lake varied with the season; being most rapid in June to August and slowest in December and January. The possible total may be estimated at 116 inches per year.

9. The rainfall data of the Sink, obtained from the records of the U. S. Weather Bureau made at Indio, which is located near the extreme northwestern end of the Sink, only a few feet below sea-level, show an average of 2.74 inches per year.

10. Rapid recession of the water would result in separating stranded seeds quickly from the margin of the water with consequent rapid desiccation of the surface layer of soil, which would be unfavorable to germination and survival.

11. The shallow water lying on wide mud flats fringing the shores was raised to a much higher temperature  $(15^{\circ} \text{ to } 20^{\circ} \text{ F.})$  than the body of the lake during even the winter season, thereby greatly increasing its toxicity for seeds, plantlets, and propagating bodies. The greater number of the seeds falling into the lake would be subjected to this action. The muddy flats fringing the shores at all stages of the lake must, therefore, be considered as a barrier of some magnitude which would be crossed by a plant carried out into the lake and again when deposited on a beach.

Practically all of the species inhabiting the Cahuilla Basin, including those native to the alpine slopes of the San Jacinto Mountains, are to be included among the forms, the seeds of which might be carried by run-off streams, winds or other agencies down to the unoccupied areas around the receding lake. The differences in climatic conditions and in the soil, however, would obviously constitute an effectual barrier to the greater number of the plants native to the rocky slopes of the mountains. Some of the barriers affecting the dispersal of species on mountain slopes are much too subtle to be This is detected by available methods of geographic survey. well illustrated by the cultures made at the Desert Laboratory, in which many species abundant on the higher slopes of the Santa Catalina Mountains in positions from which their seeds must have been carried to the lowlands in myriads for centuries, are not found below a certain limit, although when the seeds are transported by man to the lower lands the plantlets survive and in some instances, such as that of Juglans, ontstrip the lowland species in growth-activity.

The species inhabiting the bajadas or detrital slopes of the basin, or of the lowermost part of it included in the Salton Sink, would be the most important elements in any invasion of surfaces left bare by the receding waters of the lake.

A number of introduced species and weeds would constitute another element, and plants of this kind would be carried along the line of the Southern Pacific Railroad, which runs at varying distances from the shore of the lake for about threefourths of its length. The water actually washed the ends of the ties for many miles of the line at the maximum level. It will be recalled also that a long stretch of the track previously ran below the maximum level and was moved up the slope to evade the rising waters. The other element to be considered would be the species native to the valley of the Colorado River. The entrance from this region would be principally by flotation. The number of species included would be too large to be discussed in detail. Only those with seeds which would be uninjured by long immersion would constitute potentialities in invasion from this source. The census of the invasions from 1907 to 1912 inclusive includes 60 species.

Many physical agencies would operate to carry seeds toward the sterilized beaches, and it will be profitable to consider some of the possibilities upon which only inferential evidence may be offered.

The Colorado River at the time that it poured the greatest volume of water into the lake was in a state of flood and had spread out over the lowlands along its course, lifting millions of seeds from their resting-place on the ground; these would be carried toward the lake. Some kinds, however, because of their specific gravity, would sink and these would have very little chance of reaching the strands of the lake, as they would soon be covered with silt. Others which might float at first would soon become softened and by the imbibition of water would swell as if for germination, with the result that these also would be destroyed before they passed through the long overflow channel leading from the main channel into the Salton Sink, and some might actually proceed to germination, the plantlets being carried still farther.

Some of the heavy seeds might adhere to trunks of trees and other floating objects and be carried with them to a final resting-place on the strands. In all cases, however, seeds of any kind would be subjected to the action of the saline water as soon as they were thrown into the waters of the lake. Seeds with indurated outer coats might be picked up by the water and carried the entire distance, or the seedlings might endure aquatic conditions for extended periods.

The heavy winds from the southeast, southwest and northwest would lift and carry a large variety of seeds (such as those of *Baccharis* and *Pluchea*) long distances. Some might fall to the ground directly on the bared strand exactly at a time when the germination conditions were most favorable. Much greater numbers would tend to fall on the surface of the stream and of the lake itself. Once in the water, their further transportation would depend upon wave-action, which would be produced by wind.

Traveling animals, especially birds, might bring seeds attached to their feathers or imbedded in mud clinging to their feet. In the present instances the principal birds were the pelican, cormorant, and various species of ducks. The first two feed upon fish and habitually alight either on rocks or branches of trees rising above the level of the water, or upon the arid rocky soil about their nests as noted on various islands. In one case the seeds would be dropped in the water and their origin would escape analysis, while in the second instance the soil would be too dry to induce germination, which if it did take place would end disastrously, since the surface about the nesting-grounds was trampled and worn so that green plants had little chance of survival.

The lake occupied the bottom of the Cahuilla Basin and streamways from all of the converging slopes led toward it. In none of these, however, were there constant streams. The run-off or surface flow resulted from the precipitation accompanying the heavier storms, and when the streams were formed in this manner the water rushing down the steep slopes of the bajadas undoubtedly would pick up the accumulation of seeds lying in the shallow channels and carry them down into the lake, or perhaps cover some with sand and silt which with the implied moisture would be very favorable to germination and survival. The invasions thus facilitated would result simply in the advance of species down the slopes crossing the strands at right angles, generally in places perhaps occupied previous to the making of the lake. Such action was of course noticeable on the uppermost beaches left bare during the first year's recession of the lake, and transportation by this method became less and less efficient as the distance from the maximum-level shoreline was left behind.

The flotation by run-off streams becomes a more effective method for carrying plants onto the bared strands, especially from the fact that no prolonged subjecting to soaking would be endured. The subjection of the seeds to the brief action of the ephemeral stream and its subsequent contact with the moistened sand or soil would be of a character highly favorable to survival. It is evident that the soil conditions of the beaches during the first year of recession were different from those offered in any following year. Briefly stated, the surface layer had been leached to a slight depth by water containing the lowest proportion of salts. Another thing bearing upon the comparatively heavy vegetation of the emersion due to the first year was the fact that the rapid rise of the lake would have lifted seeds from the ground and thus at the theoretical moment, when the lake was at its maximum level, the number of floating seeds which might be driven ashore by wind and wave action was greater than at any subsequent time in the history of the lake. The toxic activity of the water itself was least at the maximum level and began to increase at once. As was noted in the history of the earliest strand,

Am. Jour. Sci. – Fourth Series, Vol. XXXIX, No. 231. – March, 1915.

the dead stems of some species remaining erect in place held aloft fruits which were not all cast off until after the waters had receded.

The fact that 4 out of a total of 60 species which found place on the strands exhibited modifications of structures not observed elsewhere led directly to a consideration of the endemic species of the Sink. Atriplex saltonensis Parish, Sphæralcea orcutii Vasey and Rose, Cryptanthe costata Brandegee, Calandrinia ambigua Howell, Astragalus aridus A. Gray, and Chamæsyce saltonensis Millspaugh are to be included in this category. It is true that Calandrinia is found a short distance beyond the limits of the Sink, but the remaining 6 species are not known

#### FIG. 5.



FIG. 5. Big island, a hill surrounded by the waters of the lake in 1905. Several well-marked strands of Blake sea are visible.

to occur beyond and above the high beach line which marks the level of Blake sea, which filled the basin to this shore line within comparatively recent time. The situation suggests that these species originated in the Sink since it was last filled and the inference is strongly in favor of such a conclusion. If the possibility of the origination of these forms within the Sink be allowed, it is also suggested that other species might have originated in like manner but become disseminated over a wide area in such manner that their nativity is undiscoverable.

It became obvious during the course of the work that the origination of qualities or structures upon which dissemination would depend might, in many instances at least, have no possible connection in a causal way with the agencies themselves. Thus for example, the desert gourd which was carried about

248

the lake and deposited on various beaches owes this dissemination to structures which could hardly be attributed to any excitation action on the part of water or to any previous selecting action. The same mechanical qualities of flotation and dissemination are displayed by the fragments of pumice which were carried about at the same time.

The communal life and successions on the beaches showed some interesting diversities. The manner of the occupation of the zones laid bare by the receding waters was chiefly deter-



FIG. 6.

FIG. 6. Ranks of vegetation marking ancient strands near the high level of Blake sea.

mined by the water, and hence the first communities of plants were of the nature of strand-steppes. The history of such formations showed two distinct phases, both also determined chiefly by edaphic conditions. The strands of the more gently sloping alkaline beaches were at first occupied by a greater number of species than the bared strips on the steeper gravelly shores, and the pioneers gained a foothold earlier. This difference may be attributed in greater part to the fact that the narrower, more steeply sloping beaches were subject to the action of storm waves a longer period than the broader zones on the gentler slopes, and also to the fact that the latter actually presented a greater area of soil for the reception of seeds (fig 5).

The arrangement of the pioneers on any beach would be characterized as open, and on the gentler alkaline slopes the tendency in general was toward a decrease both in the number of species and individuals, with few or no secondary introductions, thus making a direct change toward the true open or desert formations. The gently sloping beach at Mecca, however, receiving some seepage water, did not exhibit such simple Steeply sloping beaches, as represented by the Traverresults. tine Terraces and the shores of Obsidian Island, showed two phases of succession, differing chiefly in degree. The open formations on the shores of Obsidian Island showed some tendency to becoming closer or denser in irregular areas, which soon began to thin in the final change toward the open desert formation (fig.6). The benches of Travertine Terrace were characterized by the development of dense ranks comprising a half dozen species or less at the upper margins of the annually bared strands, which were soon thinned in accordance with the general tendency toward desert formations, but at the same time the greater part of the surface of the terrace was knit together in a close formation by a mat of Distichlis. This closed formation, however, soon began to show the effects of desiccation and the progression toward the desert formation with the introduction of xerophytes would be seen within three or four years after the zone had been laid bare by the lake. The transition is so rapid and abrupt that species appearing on strands two years old are also included in ancient beach ranks marking the positions of strands 300 to 400 years old. The revegetation of the area submerged by the waters of the lake in Salton Sink is therefore seen to be chiefly influenced by water or other edaphic conditions during the first year or two after emersion, after which the formations become increasingly open in the progression toward the extreme desert type.

The evaporating power of the air becomes an agency of increasing importance, as the age of the plant-formation or the period since emersion lengthens.

Submergence and consequent extermination of the flora of portions of the Salton Sink has occurred many times in the last few centuries and the reoccupation of the bared strands has taken place with the complex interplay of biological and mechanical agencies partly suggested and partly described in the preceding pages. O. A. Derby-Stem Structure of Tietea Singularis. 251

#### ART. XVI.—Illustrations of the Stem Structure of Tietea Singularis; by ORVILLE A. DERBY.

[Preliminary note in advance of the "Annaes do Serviço Geologico e Mineralogico do Brazil."]

UNDER the name of *Tietea singularis* Count Solms-Laubach recently described and illustrated (Zeitschrift für Botanik, V, pp. 673–700) a fragment of fossil'wood of Permian age from the state of São Paulo, Brazil, which he found to present a variation from the Psaronius type of structure sufficiently important to justify a new generic denomination. Having temporarily in my possession the different slices into which the original specimen was cut, it seemed desirable to utilize the exceptional skill of Mr. Francisco Basto in the construction of general plots showing in a connected whole the essential structural features so ably worked out by the author of the genus and species, but which are of too complicated a character to be made readily comprehensible by a written description and isolated figures of a part of the cross sections.

The task proved an exceedingly difficult one, more especially in the matter of finding a satisfactory mode of representation, owing to the occurrence in a small space of a great number of individual strands belonging to different groups and arranged in successive ranks like a military troop on parade in close The process employed was to trace carefully with ink order. on photographs the vascular and tegumentary systems and then to wash out all the uninked parts of the photograph. A series of skeletonized cross sections were thus obtained and from these the features to be represented were transferred to the drawing by the processes of mechanical draughting, so that the imagination of the artist only came into operation in the joining up of the successive cross sections across the intervening concealed spaces. Fortunately the cross sections were so numerous and had been so judiciously spaced by Count Solms-Laubach, under whose direction the cutting was done, that the few cases of doubt regarding the course of a given strand from one plane to another could only affect questions of minor importance. On the completion of the work, which was done under my constant personal supervision but without any botanical preconceptions whatsoever, it was very gratifying to find that in the most essential particulars the result was a graphic representation of Count Solms-Laubach's written summary of the structural features of the stem.

The specimen which contains parts of two vertical rows of F organs is evidently a fractional portion of a polystichous stem which if approximately circular in outline would have

#### 252 O. A. Derby-Stem Structure of Tietea Singularis.

possessed six such rows, while if the outline was oval the number would be eight. An exceptionally fine and complete Psaronius stem in the collection of the Brazilian Geological Service, which will shortly be described by Prof. Pelourde of the Paris Museum, shows that the oval outline indicated by the fragments of several other species of Psaronius is an original feature, and not, as has generally been assumed, one due to the distortion of the trunk after the death of the plant. In this latter stem the number of rows is sixteen, and this seems to indicate that in the polystichous Psaronides (the ill-defined continuation of the di- and tetrastichous groups) multiples of four should be expected rather than haphazard numbers. On this hypothesis an oval eight-rowed stem rather than a circular six-rowed one should be postulated for *Tietea singularis*, and in accordance with this view the accompanying hypothetical restoration (fig. 1) has been made. As thus restored the stem has about the same dimensions as the sixteen-rowed Psaronius above mentioned with a less departure from the circular form normal to most tree trunks.

In fig. 1 an oval of the proper dimensions, deduced from the peripheral curve of the slices with exclusion of the root sheath, has been traced to represent the top of the missing lower part of the trunk from which the original specimen had been broken. Within this oval the lowest cross section at hand (14) has been fitted where it best conformed to the curve of the oval, and three of the most significant of the overlying sections have been projected down on to the same plane with their peripheries adjusted to the remaining portions of the curve. This gives schematically the general aspect of a complete cross section of the stem at plane 14, on which, of course, the vascular groups would take the numbers 1 to 8, and, except in the shaded portion, would present details different from those here shown. Of the sections utilized 2 and 10 are represented photographically in Count Solms-Laubach's paper.\*

Comparing this cross section with those of the several known representatives of the polystichous group of Psaronius, a fundamental agreement is found in the threefold character of the vascular system, accompanied by a fundamental difference due to the composite character of both the peripheral members of that system. It may be suspected that this difference will eventually prove to be of more than generic importance.

In fig. 2 corresponding portions of eight of the cross sections are plotted in sequence with a forward inclination of 15°

<sup>\*</sup>The comparative numeration used in the present paper and in that above cited is as follows: I = V, 2 = IVb (fig. 5), 3 = IVa, 4 = IIIb, 5 = IIIa (fig. 4), 6 = IIb (fig. 3), 7 = IIa (fig. 2, which was reverted by the photoengraver), 8 = I (fig. 1), 9 = -I, 10 = IIa (fig. 6), 11 = -IIb, 12 = -IIIa, 13 = -IIIb, 14 = -IIVa.

so as to permit the representation of a narrow zone at the front of each. In A the only completely preserved row of P strands is taken as a center and the plotting is continued laterally to



FIG. 1.

FIG. 1. 1/2 nat. size.

include a half of the two adjacent rows of F strands, while in B the F1 row is given the central place and is flanked on the right by the complete, on the left by the incomplete row of P strands. In both figures the F strands are drawn in black



254 O. A. Derby-Stem Structure of Tietea Singularis.

FIG. 2.

#### O. A. Derby-Stem Structure of Tietea Singularis. 255

while the P and C (seen only on the upper face) ones are simply outlined. The groups of strands on the different faces are hypothetically joined by heavy dotted lines for the F and by lighter lines for the P ones. The spacing is based on the thickness of the various slices with an allowance of  $2^{mm}$  for the saw cuts, except in the case of the interval between 7 and 6, from which a thin slice for microscopic preparations had evidently been taken before the three parts of the original specimen came into my hands to be forwarded to Count Solms-Laubach. Whether too great or too little space has been given to the saw cuts makes no material difference in the general accuracy of the plotting.

Beginning with the basal (14) section of A in fig. 2 the front of the trunk and the cross section of the root sheath are shown, but above this plane these features are discontinued and only those of the stem proper are plotted. Behind the stem rind lies, at the center and right, an elongated group of P strands which are interpreted as belonging to an older (P2) and a newer (P2') cluster which, coming up from below, were here in a senile and a youthful stage of growth respectively, the latter cluster being backed by a long curved sclerenchymous band. To the left of this group the stem rind describes a deep sigmoid curve, shown by a dotted line behind its extreme left end, and then extends in a straight course to the margin of the figure. In the deep broad indentation formed by this inflection of the rind on the outer surface of the stem, lies a many-stranded F organ which is here cut in a fully developed stage of growth, while behind it and inside the rind a row of small strands representing the embryonic stage of the p2'' cluster had appeared.

On the next plane above (12) a tendency towards extinction is shown in the inflection of the stem rind at the left as well as in the P2 and F1 groups of strands, and towards development in the p2'' group; but otherwise the features above enumerated are not materially changed. The f2 group, which in the drawing appears as a new feature, is really distinctly developed on the plane below, but its situation is so far in the background that it could not be represented.

On plane 10 are registered important modifications introduced in the growth from the plane below. At the right the immature  $f^2$  organ had developed into the adult (F2) stage of growth and had emerged laterally through the interruption, by its overlopping, of the stem rind in front of it, accompanied by the formation of a sclerenchymous layer behind it. Accompanying this change the internal sclerenchymous band of the lower planes swung around in a complicated curve to unite at its right border with the interrupted stem rind and at its left with the newly formed sclerenchymous layer behind F2 so as to give a continuous stem rind with a deep inflection corresponding to the one above noted on plane 14 to the right and back of the F1 organ. The latter organ had become so greatly reduced that it did not persist to the plane above, and is, therefore, represented as terminating at this level, as is also the case with the P2 cluster. The P2' cluster had suffered no material change, while the p2'' one had developed in width and in the size of its component parts.

As regards the features that enter into it from below, the next plane (8) differs principally in the considerable development of the p2'' and the appearance of senile characters in the P2' and F2 groups of strands. New features are the sclerenchymous band behind p2'' on the left and the beginning of a new (p2''') P cluster of strands on the right.

On plane 7 the strong inflection of the rind in the plane above has permitted the representation of what appears to be a new feature (f1') that in reality (see fig. 2, B) had presented itself on plane 14. Otherwise no great variation from the plane below is to be noted. The p2'' cluster had united into a single complicated strand which should here take the denomination of P2'' and which bears a striking resemblance to certain phases of the P strands in *Psaronius brasiliensis*, except that its concave face is directed outward instead of inward. This is the ear-shaped process of Count Solms-Laubach, who interpreted it, as is done here, as a vigorous member of the group to which it belongs, destined to supersede its senile companions.

At the level of plane 6, F2 and P2' were so near extinction that they did not persist to the plane above; f1' had emerged laterally as F1' in a manner similar to that above described for f2-F2, and a new (p2''') P cluster had appeared on the left.

The essential changes in the growth between planes 6 and 5 were the extinction of the F2 and P2' organs and an almost complete extinction of the inflection of the stem rind behind the former, corresponding to the similar change that took place on the left in the growth between planes 10 and 8.

To complete the figure, plane 2 instead of plane 1 has been selected because the latter, being a fractured face, does not show the structural features as clearly as does the cut and polished one below it. The distance between the two planes is so small that nothing of importance is lost by the resulting shortening of the figure. On this plane the features of the narrow frontal zone that could be represented on the planes below, show that no material changes had occurred in their growth upward from plane 5. Behind them appear an internal sclerenchymous band that commenced to form at about the level of plane 5; two groups of F strands of which f2' had commenced to be differentiated from the mother central strands between the levels 8 and 7 (see fig. 3), while f1'' had just begun the process of differentiation, and a number of central strands that, with individual changes unessential to the present study, had come up from plane 14.

In fig. 2B the F1 and P2 groups of strands with their successors are shown in their entirety together with the right portion of the P1 group, of which only a part is preserved in the specimen. The first of these groups appears in its adult condition on the three lower planes, but is lacking on those above. Its successor (f1'-F1') had evidently just begun to form below plane 14 on which it appears as a single row of small strands lying behind the slightly older formative stages of a new set of P clusters (p1'' + p2''). Before plane 10 was reached the nascent f strands had developed into two long rows, and the pones had commenced to separate into a right and left cluster that at plane 8 had reached, or nearly reached, their adult condition accompanied by the appearance behind them of sclerenchymous bands setting them off from the still immature F group of strands. At the level of plane 7 the latter had pushed far to the sides the sclerenchymous bands with the accompanying P clusters, and was nearly prepared for its lateral emergence that was effected between this plane and the one above. In the process of emergence the formation of stem rind in front of the organ ceased, probably from the overlapping of the latter that had previously risen erect from the vegetative disc, and a sclerenchymous band formed behind the group, which uniting with the incurved lateral bands reestablished the continuity of the stem covering. Before the level of plane 6 was reached a new group of P strands (p1'''+p2''') had commenced to form, but its accompanying F group (f1'') had not yet appeared so that it only presents itself on plane 5. The upper plane (2) is essentially a reproduction of the lower one (14) with some of the central strands added, so that by imagining the preserved portion of the F1' group prolonged by emending with it that of the F1' one, we have the entire basal portion of an F organ from its first inception up to the point where its dead free portion fell away from the living plant, leaving a persistent stalk base (compare *Psaronius brasiliensis*, this Journal, Nov. 1913). The older P clusters (P1, P2, P2') shown in this figure present no features that have not been sufficiently discussed in the study of fig. 2A.

In fig. 3 the peripheral members of the central group of strands that appear on plane 14 just behind the  $f^2$  group have been plotted up to plane 2. As will be seen by reference to fig. 1, these do not present on section 14 any features that

#### 258 O. A. Derby-Stem Structure of Tietea Singularis.

distinguish them from the more internal members of the group to which they belong, but on following them upwards it becomes



apparent that those in the middle are mother strands destined to give birth, by sprouting or subdivision, to future P and F strands, while those at the sides, distinguished by the letter C, are sterile. These last show evidence of having been formed, at least

FIG. 3.

#### O. A. Derby-Stem Structure of Tietea Singularis. 259

in part, by the coalescence of smaller strands and one of them came to end between planes 6 and 5, while at about the same level the other two seem to have taken on a new lease of life by subdivision, or perhaps more probably by sprouting, and at plane 2 they present substantially the same conditions as at plane 14. As it seemed reasonable to assume that the central strands in general would present essentially the same features as those here represented, two of the most prominent of the more centrally placed ones were plotted separately with the result that the correctness of this assumption was fully verified.

At plane 14 the four mother strands (f2') present no features to distinguish them from their neighbors of the central group. At plane 12 a new strand had appeared behind the third, counting from the left, of this group of four, which, on being traced upward, proved to be one of the progenitors of a new group of F strands (f2''). A companion to this, situated more to left, had already appeared on plane 14, but owing to its position in the background this set of strands could only be represented near its origin and, in a subdivided condition, on plane 2 where it presents an aspect quite similar to that of its predecessor on plane 14. Whether these new strands originate from the as vet undifferentiated ones in front of them or from the adjacent central strands behind them, could not be determined, but the latter hypothesis seems to be the most plausible one. Between planes 12 and 10 the two central  $f2^{\prime}$  strands had united and thrown off a vigorous branch to the left, while the one at the left of the group had given off a branch to the right which persisted to the higher levels after its companion came to an end between planes 7 and 6. At the level of plane 8 fine small strands had appeared in front of the central and right members of the f2' group from which they had evidently sprouted at a point above plane 10. These are the beginnings of a new pair of P organs, which, in order not to obscure the figure, are represented as cut off at this plane, their prolongation being shown in the separate figure at the right. Above plane 8 the f2' strands began to multiply by subdivision or sprouting and this process, continued nearly up to the level of plane 2, increased their number about eight-fold. At the latter plane, the group as a whole was nearly ready for its lateral emergence, being in a considerably more advanced stage of development than its predecessor at plane 14, as is shown by its greater dimensions and the wider space between the inner ends of the internal sclerenchymous bands in front of it. These bands had begun to form a little below the level of plane 5, so that it was probably about half way

between planes 5 and 2 that they, and the strand groups separated by them, were in the phase of development corresponding to that shown on plane 14.

The shading applied in fig. 3 to parts of the lower and upper planes does not represent a natural feature visible in the specimens, but is introduced to express diagrammatically the fact that the strands enclosed by the shaded areas are interrelated as component parts of the same organ, and not, as might be supposed at first sight, an appreciable differentiation in the parenchymous mass, represented by blank spaces, that surrounds the vascular and sclerenchymous parts to which the drawing has been limited. The differentiation that really exists but that could not be represented without unduly complicating the figures, is of two kinds of which only one is perceptible macroscopically. This, which has been discussed in Count Solms-Laubach's paper and is clearly shown in the photographs that accompany it, consists of the segregation of a large part, if not all, of the central parenchymous mass around the vascular strands as an outer covering. This feature which I had postulated hypothetically in the study of the crown structure of *Psaronius brasiliensis* (this Journal, Aug. 1914), is more distinct in the stem here considered than in any other Psaronide known to me, and it suggests a comparison with the closely appressed leaf-stalk portions of the trunks of Tubicaulis and Thamnopteris. The second differentiation established microscopically by Count Solms-Laubach is that due to the filamentary character of the parenchyma (Füllgewebe) outside of the stem rind, in the zone of the adventitious roots and of the emerged F organs, in contrast with the ordinary type of parenchyma within the rind.

In figs. 1 and 2 the stem rind is shown diagrammatically by simple thin lines, whereas its true appearance, better shown in fig. 3, is that of a moderately broad band of tolerably uniform thickness, except in the recesses occupied by the emerge d F organs, where it tends to thicken and eventually to become difficultly distinguishable from the broad parenchymous mass that, after the extinction of the organ, lies between it and the inner border of the root sheath.

Rio de Janeiro, Oct. 20th, 1914.

Page

#### ART. XVII.— Petrographic Evidence on the Origin of the Catahoula Sandstone of Texas; by MARCUS I. GOLDMAN.

#### CONTENTS :

Description	262
Undisintegrated rock	262
Macroscopic examination	262
Hand lans examination	262
Digiptograted rock	262
Machanical analyzia	202
Mechanical analysis	202
Quantitative results	200
General character of products	264
Microscopic examination	264
Rounding of the grains	264
General appearance	264
Proportion of rounded grains present	264
Lower limit of rounding	264
Ratio of feldspar to quartz	265
Weathering of the feldspars	265
General appearance	265
Batic of fresh to weathored foldeners	265
Datio of different encoder of foldener to	200
Ratio of uniferent species of feldspar to	000
each other	200
Heavy minerals	200
Proportion of heavy minerals	266
Species of heavy minerals present and	
their relative amounts	267
Interpretation	267
Sizing	267
Rounding	271
General character	271
Lower limit of rounding	271
Proportion of rounded grains present	273
Ratio of feldspar to quartz	273
Westboring of the foldspare	274
General appearance	974
Datio of fresh to weathered foldeners	974
Datio of different angeing of folder and to each other	070
Ratio of different species of feldspars to each other	210
Ratio of neavy to light minerals	270
The species of heavy minerals present and their ratios to	-
each other	277
Packing of the sand	280
Bedding	281
Arrangement of fossils	282
Clay galls	283
General character	283
Distribution .	284
Summary and conclusions	284

THE material used in this study was collected in Trinity County, Texas, by Charles L. Baker. An examination of the specimens with a view to obtaining evidence as to the conditions of origin of the sandstone yields the following results.

#### I. DESCRIPTION.

#### 1. Undisintegrated Rock.

*Macroscopic examination.*—The sandstone is light colored, yellowish, with faint lavender tinges and pale brownish patches irregularly distributed through it.

As a quartz sandstone it appears rather pure, though speckled with opaque white and with fairly abundant black grains. It is often very friable on an edge but not in larger fragments. Absence of bedding, or better perhaps of lamination, is evidently characteristic for the rock, as fragments of 4 inches or more in diameter show no trace of it in any direction. This is especially evident in the pieces containing impressions of fossil nuts. Here too, the lack of orientation is brought out by the nuts themselves, which lie with their long axes showing only the slightest evidence of parallelism. In some specimens impressions of fossil leaves show even more random arrangement as they are not only not parallel to each other, but even the surfaces of the individual leaf imprints are strongly curved or curled. Certain specimens, however, differ in these respects from the majority, for in them the leaf impressions are rather numerous and closely packed approximately parallel to each other. They are not, however, distributed on any bedding planes marked by difference of texture in the sand itself. Moreover, even where most pronounced this parallelism is not absolute, and the surfaces of the leaves are not perfectly flat.

Often associated with bunches of parallel leaves are rather abundant small grains or pellets (up to about 8 <sup>mm</sup> diameter) of a soft, crumbly, yellowish-white, argillaceous material.

Hand-lens examination.—The lavender tint is seen to be due to the cement, apparently of opal, binding the grains. Its distribution is very irregular, and where it is lacking the rock is friable. In places the cement is more opaque, whitish, resembling in appearance the clay pellets described above; where these are abundant the cement also takes this character. But the two types of cement, the opaline and argillaceous, grade imperceptibly into each other, and it is quite possible that the opaline variety is derived from the argillaceous.

#### 2. Disintegrated rock.

a. Mechanical analysis.—Whether opaline or argillaceous the cement should decompose on being boiled with a strong solution of KOH and trial showed that it does. A mechanical analysis
### M. I. Goldman—Catahoula Sandstone of Texas. 263

of the sands was therefore possible. This was made according to the method of Thoulet\* with only slight modification.

The method consists essentially of decanting off the muds and passing the sands thus obtained through bolting-cloth sieves of the following meshes and average sizes of openings.

Mesh	Size of opening	Name of product	diameter <sup>1</sup>
0.0	0.00mm	Coarse	$> l^{mm}$
30	0.89	Medium	$1-\frac{1}{2}$ mm
60	0.42		1 Imm
100	0.26	Fine	$\frac{1}{2} - \frac{1}{4}$
		Very fine	$\frac{1}{4} - 1/25^{mm}$
200	0.04	Extra fine	$< 1/25^{mm}$

<sup>1</sup> The approximate diameters in fractions given are for comparison later.

In the "very fine" portion the heavy minerals are then separated from the quartz and feldspar in a heavy solution of density between 2.7 and 2.8.

In the present instance the method was modified by ignoring the decanted portion, since it was very fine, mostly colloidal in appearance, there was very little of it, and being largely the product of decomposition by KOH it has no significance for the problem under consideration.

Quantitative results.—The results of the separation were:

	Weight in grams	Percentage
Total sand	9.340	
Products:		
Coarse (4 grains)	$(0.002 \pm)^{\dagger}$	tr.
Medium	0.975	10.4
Fine	4.995	53.4
Very fine	3.175	34.1
Extra fine	0.185	2.0
	9:330	99.9
	0 000	000

The accompanying diagrams (figs. 1 to 12, p. 269) show graphically the relation of these different portions.<sup>‡</sup>

\*Thoulet, J.: (1) Précis d'analyse des fonds sous-marins actuels et anciens. Paris: Chapelot et Cie., 1907, 220 pp. (2) Instructions pratique pour l'établissement d'une carte bathymétrique-lithologique sous-marine. Bull. de l'Inst. Océanogr. No. 169, Monaco, May 25, 1910, 29 pp. [A condensed statement of the method elaborated in (1), with some modifications.]

† The balance used does not weigh accurately quantities less than 0.005gm.
‡ These diagrams are made after the method of Mohr (E. C. Jul. Mohr,
" Die Mechanische Bodenanalyse," Bull. du Dépt. de l'Agr. aux Indes Néer-

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 231.—March, 1915. 18

## 264 M. I. Goldman-Catahoula Sandstone of Texas.

General character of products.—The coarse sand (4 grains as noted above) consists of agglomerations of sand in a dull olive-green matrix which did not effervesce in HCl but gave a yellow stain to the acid.

All the other portions, of which the characters are now to be described, consisted mainly of quartz and feldspar.

b. Microscopic Examination.—Rounding of the grains: General appearance.—The exquisitely perfect rounding and smoothing of many of its grains is a striking feature of this sandstone.

Proportion of rounded grains present.—A count, in the different portions, of the proportion of quartz grains that were rounded, gave the following results :\*

	Percentage of rounded grains in the portion <sup>+</sup>							•
Medium	27	=	2.8	per	cent	of	total	sand.
Fine	25	=	13.3	•••	"	"	• •	66
Very fine	35	=	11.9	"	"	"	66	66
Extra fine	35	=	0.2	"	"	"	"	"
			28.7	Pe	r cen grains	it ( s ii	of rou n the	ınded total

Lower limit of rounding.—The smallest rounded grains found measured about 0.035<sup>mm</sup> in diameter and were scarce, but grains of 0.05<sup>mm</sup> diameter were not uncommon.

sand.

landaises No. 41 Buitenzorg, 1910), who devised them independently. Entirely similar diagrams, however, differing only in scale, were used at an earlier date by Udden. (See footnote pp. 267, 268.) Their construction can be most readily grasped by conceiving of the vertical columns as being actually the portions of sediment they represent, set up side by side in cylindrical tubes of the same diameter. The columns are all of the same width and represent material ranging in size between the diameters indicated at each side of them, while the vertical distances represent percentages to scale.

side of them, while the vertical distances represent percentages to scale. \*The quartz was readily differentiated from the feldspar by immersing the grains on the slide in a liquid whose index of refraction was 1.548, the mean index of quartz.

+ In these counts all grains that might be called subrounded were counted with the round grains, while those that seemed more subangular were classed as angular. Largely this classification depended on the appearance of the upturned surface. As this could not be well studied under the high power (No. 7 objective) used on the "extra fine" sand, the count of this size is more uncertain. Perhaps that explains the high percentage of rounded grains counted there, where a lower proportion than in the coarser sizes would be expected.

In the "fine" sand a count was also made of only those grains that showed complete rounding and 12 per cent were found, i. e. just about half that given above. This relation therefore affords a factor that may be used for an approximate estimate of the proportion of completely rounded grains present in the entire sand. In the "fine" sand also a count of the ratio of all rounded grains (feldspar as well as quartz) to all angular, gave exactly the same proportion as for quartz only.

Ratio of Feldspar to Quartz.-A count in the "very fine" light portion gave:

> quartz : feldspar = 221 grains : 139 grains = 38.6per cent : 61.4 per cent.

Weathering of the feldspars.-This is a very important feature in the petrography of a sandstone, but the evidence here does not appear very coherent.

General appearance of weathering.—On a mere inspection of the sands I was at first struck by the great freshness of many of the feldspars, which were perfectly limpid with fresh faces and sharp angles.

Ratio of fresh to weathered feldspars.—But if the results of a count of fresh and weathered feldspars are compared with those given by Mackie,\* in his study of this feature, the weathering appears rather advanced. Of course such comparisons may be very misleading on account of differences in ideas of different observers as to what constitutes weathering in feldspar and above all as to the identification of completely weathered feldspars. Following is Mackie's statement of his method of procedure :\*

"Fragments giving a play of colors in polarized light have been counted as fresh. If they remained turbid or exhibited no play of colors, they have been counted as kaolinized. A third group, usually showing a low percentage of fragments, is marked off as showing intermediate character."

In this examination, however, only perfectly fresh, limpid feldspars were counted as fresh. As weathered were counted only those showing complete compound polarization.<sup>‡</sup> A third group contained those of intermediate character. From the results tabulated below it will be seen that this last differed from Mackie's intermediate group in being on an average about as large as each of the other two. It included all cloudy or impure-looking feldspars and those, not numerous, showing incipient compound polarization. Following Mackie,§ this intermediate group is distributed equally between fresh and weathered feldspars, though personally I should prefer to class it entirely with the weathered.

\* Mackie, Wm.: The feldspars present in sedimentary rocks as indicators of the conditions of contemporaneous climate, Trans. Edinburgh Geol. Soc., pp. 443-468, 1898.

† Mackie, loc. cit., pp. 457–458. ‡ Here is one of the important factors of uncertainty since other substances than kaolinized feldspar may well have that character. In general, however, the fact that the index of these fragments corresponded about to that of kaolin (1.54) supported the assumption. Furthermore, especially in the coarser sands, many of these grains were quite rectangular in outline, like feldspars, and one of them, separated from the "medium" sand, had quite the appearance of a cloudy feldspar grain but was too soft to scratch glass. SMackia loc git p. 468

§ Mackie, loc. cit., p. 468.

		No. of g	rains	P in ea	er cent .ch portion	Ec pe of w	quivalent rcentage /hole rock	Per d fe	centag lifferer eldspa	e of nt rs 1
Portion	Fresh	Medium	Weathered	Fresh	Weathered	Fresh	Weathered	Orth.	Micr.	Plag.
Medium	63	29	60	51	49	5.3 5.1		86	13	1
Fine	47	50	57	47	53	25.1	28.3	79	19	2
Very fine	48	4.7	55	5 48 52 16.3 17.7 8	55 48 52 16.3	87 13 0	87 13 0	0		
Extra fine	105	129	70	56	44	1.1	•9	93	2.5	4.5
Total						47.8	52.0			

The results are given in the accompanying table.

<sup>1</sup>Orthoclase means feldspar showing no twinning, microline means "grating structure" twinning, plagioclase means polysynthetic twinning.

Thus while obtained entirely without regard to each other the results for the different portions show a fairly good correspondence. The appearance of greater freshness in the "extra fine" which seems to be supported by the higher percentage of plagioclase in that portion may be due to errors of observation resulting from the smallness of the grains. Thus a small fragment out of a cloudy feldspar might appear fresh and in a small fragment of microcline the twinning in only one direction might appear.

Ratio of different species of feldspar to each other.—At best these figures for the proportion of the different kinds of feldspars are to be regarded only as the merest approximations. How much the number encountered is a matter of chance was shown by two slides of the "extra fine" sand, in one of which there were 9 plagioclases (only two of them regarded as doubtful) among 68 feldspars counted, while in another were only 2 (both doubtful) among 182 feldspars.

*Heavy Minerals: Proportion of heavy minerals.*—The separation of the heavy minerals from quartz and feldspar in the very fine sand gave the following percentages:

	Observed	Corrected*
Light	97·50%	98.90
Loss	0.95% 1.55%*	1.10
	100.00	100.00

\* The loss is due to the large amount of handling in this separation and if distributed pro rata gives the results in the second column.

Species of heavy minerals present and their relative amounts .-- The species of heavy minerals recognized were :

Magnetite: It is safe to estimate that this mineral is at least half of the heavy minerals present, but a further quantitative separation did not appear feasible or necessary.

Zircon: This mineral appeared nearly as abundant as magnetite so that the two together are the essential heavy minerals present. The zircon shows all conditions of wear from brilliantly fresh crystals to well-rounded grains. There are many variations of color, green, typical smoky hyacinth, and colorless.

The other minerals recognized, all scarce, were: Cyanite, corundum, epidote, tourmaline, muscovite, andalusite, biotite (1 grain), staurolite (1 grain), pleonaste (?) (dark blue green, isotropic, 1 grain), pyroxene, glauconite (?) (an ochrous botryoidal grain), many limonitic grains, and several other dirty colored opaque varieties of grains.\*

#### II. INTERPRETATION.

What evidence does each of the above facts give as to the conditions of origin of the Catahoula sandstone?

#### 1. Sizing.

In the accompanying figures (figs. 1-12) I havet presented in the form of diagrams the results of mechanical analyses of some types of sediments.<sup>‡</sup> These analyses are as yet too meager, and not sufficiently correlated with the exact

\* As it seemed possible, especially from the very unusual fact that the tourmaline was strongly corroded, that the KOH had destroyed some of the interval was strongly controlled, that the KOH had userolyed some of the "very fine" sand obtained by crushing. It yielded *tourmaline* perhaps a little more abundant and above all in good fresh prismatic form, showing that the KOH had acted on this mineral. A grain or two of *rutile* was also observed, but this mineral may merely have been missed in the sample obtained by decomposition. Otherwise no difference was noticed between the mineral contents of the crushed and of the decomposed sample.

<sup>†</sup> Where dimensions in the original analysis are not given in fractions, I have placed two rows of figures under the diagram. The upper row are those given by the author; the lower are the same rounded off in the nearest fractions that will permit ready comparison of different diagrams. For ready comparison I have also rounded off and combined quantities slightly in some of the diagrams.

<sup>‡</sup>For quantitative results of mechanical analysis including the analyses

<sup>‡</sup> For quantitative results of mechanical analysis including the analyses reproduced in the diagrams of this paper, p. 269, see the following: Mohr, E. C. Jul.: Ergebnisse mechanischer Analysen tropischer Böden. Bull. du Départ. de l'Agric. aux Indes. Néerlandaises No. 47 Buitenzorg, 1911. [Fig. 2, see p. 42; fig. 4, see p. 43; fig. 12, see p. 37.]
Oldham, R. D.: Note on the sandhills of Clifton near Karachi. Mem. G. S. Ind., xxxiv, pt. 3, pp. 148–150, 1903. [Figs. 3 and 7, see p. 150.]
Free, E. E. and S. C. Stuntz: The movement of soil material by the wind. U. S. Dent. Agric. Bureau of Soils Bull. 68, pp. 68–70, 1911. [Short discussion]

U. S. Dept. Agric., Bureau of Soils, Bull. 68, pp. 68-70, 1911. [Short dis-

geographic conditions under which the sediments were formed, to permit of direct matching of diagrams. But certain general factors and conditions can be distinguished. The principal features of the diagrams are the degree of the sizing, i.e., the extent to which a single size has been concentrated forming the maximum in the diagram; the relation of the amount of the other sizes to this maximum or, as Mohr calls it, the "curve" on each side of the maximum; and the size which forms the maximum. It must be noted, however, that even simple comparisons are made difficult by the differences in the limits of sizing used by different workers.

Mere inspection shows at once that the closest affinities of the Catahoula sandstone are with æolian and beach sands. Certainly neither Mohr's diagrams of stream deposits (i.e. flood-plain deposits) (fig. 12), nor the lagoonal stream sediments (figs. 10 and 11), nor the sediment off the Rhone delta (fig. 9) show as good sizing.

In the two analyses of beach sands given by Mohr, one of which is represented in fig. 2, 90 per cent and 98 per cent respectively of the samples is coarser than  $\frac{1}{4}$ <sup>mm</sup>, the big maximum being between  $\frac{1}{2}$  and  $\frac{1}{4}^{mm}$ . Oldham's analysis of beach sand (fig. 3), however, shows much less perfect sizing, but the exact conditions for his material are not known and the diagram strongly suggests weathering (see below).

Turning to dune sands, we find that the analyses to which references have been given practically all agree in indicating

Udden, J. A.: The mechanical composition of wind deposits. Augustana Library Publ. No. 1, Bock Island, Ill., 1898, especially diagrams, pp. 13-23, and summary, p. 61. [Fig. 5, see p. 23, table 14.] Thoulet, J.: Étude minéralogique d'un sable du Sahara. Bull. Soc. Min. Fr., iv, pp. 262-268, 1881. [Fig. 6, see p. 263.] Sabban, P.: Die Dünen der süd-westlichen Heide Mecklenburgs. Mitt.

Grosherz. Meckl. Geol. Landesanstalt, viii, pp. 1-49, 1897. Lehmann, Paul: Wanderungen u. Studien in Deutschlands grössten binnenländischen Dünengebiet [Posen]. Jahrb. Geog. Ges. Greifswald, x, pp. 351-379. 1905.

Atterberg, A.: Die rationelle Klassifikation der Sande u. Kiese. Chemztg., xxix, No. 15, pp. 194-198, 1905. Über die Korngrösse der Dünensande. Do. Do. No. 80, p. 1074.
Keilhack, K.: Einige Bemerkungen ü. die Korngrösse der Dünensande. Chemztg., xxix, No. 53, p. 723, 1905.
Thoulet, J.: Étude bathylithologique des côtes du Golfe du Lion. Annales de l'Inst. Océanogr., Monaco, iv, fasc. 6, 1912. [Fig. 8, see p. 53; fig. 9, see p. 55]

see p. 55.]

Sudry, L.: L'Étang de Thau. Annales de l'Inst. Océanogr, Monaco, i, fasc. 10, 1910. [Fig. 10, see p. 44; fig. 11, see p. 112.] Sorby, H. C.: On the application of quantitative methods to the study of the structure and history of rocks. Quart. Jour. Geol. Soc., lxiv, pp. 185-186, 1908.

Sudry, L.: Expériences sur la puissance de transport des courants d'eau et des courants d'air, etc. Annales de l'Inst. Océanogr., Monaco, IV, fasc. 4, 1912, especially p. 67.

cussion of æolian sands with full bibliography, from which some of the following references are taken.]



FIG. 1. Catahoula sandstone. FIG. 2. Fresh beach sand, East Indies, Mohr, No. 213. FIG. 3. Beach sand, Mouth of Indus, Oldham. FIG. 4. Deeply weathered beach sand, East Indies, Mohr, No. 250.



FIG. 5. Dune sand, average. Udden. FIG. 6. Sahara sand, Thoulet. FIG. 7. Dune at Mouth of Indus. average of two specs., Oldham. FIG. 8. Typical off-shore sediment, Gulf of Lyon, Thoulet.



FIG. 9. Off Rhone Delta, Thoulet, B40. FIG. 10. Lagoon of Thau, Sudry, No. 123. FIG. 11. Small Delta in Lagoon of Thau, Sudry, No. 110. FIG. 12. Stream sediment, Mohr, No. 696.

Figures in the vertical columns express percentages.

good sizing. In the analyses of dune sands published by Udden (cf. average presented in fig. 5) an average of 65 per cent is in the size between  $\frac{1}{4}$  and  $\frac{1}{8}$ <sup>mm</sup>, with the maximum, in almost all the numerous analyses presented, in that grade. Atterberg, on the contrary, believes that 0.6 to 0.2<sup>mm</sup> (nearly  $\frac{1}{2}$  to  $\frac{1}{5}$ ) is so characteristic and prevalent a size in dune sands that in his classification of sand sizes he would actually call that size "dune." But he admits in his answer\* to Keilhack's criticism that he considers only the dune ridges, where the material being least protected is naturally coarsest, and expresses the belief, moreover, that if derived from a more mixed and finer source material than was supplied to his coastal dunes the dunes themselves might contain more fine material. Lehmann's results, too, while not directly comparable on account of differences in sieve mesh, rather support Udden's results, though in one of his analyses there is 36 per cent even in a size so coarse as  $1-\frac{1}{2}$  mm, and in general there is much greater variation between different samples analyzed by him. Oldham's analyses, again (cf. average presented in fig. 7), as far as comparison is possible on account of the differences of sieve mesh, show a marked tendency to conform in the size of grain of the maximum to that of the. Catahoula sandstone, with in fact even a larger portion of material coarser than  $\frac{1}{4}$ <sup>mm</sup> than in the Catahoula sandstone. The same is true, to even a greater extent, of Thoulet's analysis of Sahara sand (fig. 6), of which only 5 per cent is finer than 0.21<sup>mm</sup>. Now it is noteworthy that while all the other analyses are of material from the temperate regions, these last two authors were dealing with samples from the tropics, so that their results tend to support Keilhack's contention that much depends on the prevalent force of the winds.

If we consider another factor brought out by Udden, that outside the maximum portion the greater part of the material in æolian sands tends to be in the next coarsest size, we find again a divergence from the composition of the Catahoula sandstone, but in view of the difference in the position of the maximum in his results and mine this fact may really be interpreted as well for or against similarity.

Comparison with any of the subaqueous deposits (figs. 8 to 12) shows at once two very significant differences; i. e., the presence of a considerable portion of "clay" in all of these (a constituent which is negligible in the Catahoula and practically absent in the beach and æolian sands) and the greater predominance of the finer sizes in them. Thus the typical analysis from 25 feet depth of water off the shore of the Gulf of Lyon (fig. 8) has all the characteristics of a beach sand

\* Atterberg, Chem. Ztg., xxix, No. 80, p. 1074, 1905.

except that its maximum is in a finer size, and that it contains clay. The reason for the similarities is evident enough-both types are the product of continuous strong wave action. And this leads to a summary statement of the most essential conclusion from the diagrams presented. Wind and strong wave action are both capable of producing marked sizing of sands. The Catahoula sandstone, therefore, is the product of one or both of these agencies. To say with assurance that one of the two was alone or predominant does not appear possible. But Mohr's analysis of a weathered beach sand draws attention to a factor which may help in the interpretation. There we see that as the result of weathering the amount of the maximum is decreased and its disintegrated constituents are added to the finer sizes, a process which very probably accounts for the large portion of material next finer than the maximum in the Catahoula sandstone.\* Furthermore, the relatively large amount of material in the size next coarser than the maximum makes the Catahoula sandstone resemble more nearly an æolian sand, so that in the decision between beach and æolian conditions the weight of evidence from the sizing of the material is slightly in favor of the æolian.

#### 2. Rounding.

General character.—For the interpretation of the form of grains, as for the topic just considered, the absence of abundant quantitative data justifies one in giving some weight to general impressions, and the rounding of these grains is striking, not, that is, so much in the proportion of rounded grains as in the degree of rounding of some of them which, in cases even in the "extra fine" sand, are almost perfect spheres. There are, however, some quantitative data for comparison. The most important of these are for the lower limit of rounding.

The lower limit of rounding, that is the diameter of the smallest grain that will be rounded under given conditions, is a definite physical factor depending on the specific gravity of the grain (in this case quartz), on its hardness, on the viscosity of the medium (in this case water or air), and possibly on surface tension and adhesion. Observational data on the lowest limit of rounding in aqueous and æolian deposits are scant and inconclusive. Daubrée<sup>†</sup> has concluded that since grains of quartz less than  $0.1^{\text{mm}}$  will float in water very slightly<sup>+</sup> agitated no

‡ Italics are mine.

<sup>\*</sup> By using Udden's method of determining the proportion of different sizes (by counting under the microscope) and then by counting only the quartz grains, the original sizing of the sand could be determined, but time was lacking for that.

<sup>+</sup> Daubrée, Géologie Expérimentale, 1879, p. 256, par. 2.

quartz grain smaller than this could be rounded. His words are: "any finer-grained sand would doubtless<sup>t</sup> be angular." Ziegler\* too, after some rather unconvincing experiments, himself does not dare say more than that "In view of the results it seems *improbable*<sup>±</sup> to the writer that grains less than 0.75<sup>mm</sup> in diameter could be well rounded under water." Strong evidence, however, that this conclusion is wrong is afforded by the observations of Worth<sup>†</sup> in the English Channel, where he found well-rounded grains of 0.5<sup>mm</sup> or less that had almost certainly been rounded by strong wave action.

As to the ratio of the lower limit of rounding in air to rounding in water, Mackie,§ from theoretical considerations in which, in addition to the factors enumerated above, the velocity of the grains is also taken into account, deduces that for wind at 8 miles an hour the lower limit of rounding will be one-fifth that for water at 2 miles an hour, but only for these two velocities. Since winds of much greater velocity are known, it would appear, if we accept even Ziegler's limit of 0.75<sup>mm</sup> for water, that the most minute grains might be rounded by wind. But Udden draws attention to the fact that the lower layer of the air, which acts directly on the surface material, is so much affected by friction that its velocity increases very slowly with increase in the velocity of the free wind (he thinks it probably never reaches three miles an hour).

From actual observations on the lower limit of rounding of sands in nature, the only figures I could find were in Früh's paper on loess. As an absolutely definite figure he gives 0.034<sup>mm</sup> diameter (sample 11) for a rounded grain in Pampas soil. Less definite figures are given for analyses 2 and 8 (European loess), which he states have rounded grains in material between 0.019 and 0.06mm, and 0.01 to 0.05mm diameter respectively; but that the smallest grains included in these sizes showed rounding is not stated, so that we must be satisfied with 0.034<sup>mm</sup>. However, this is exactly the diameter of the smallest well-rounded grain that I found in the Catahoula sandstone. Now Früh's samples are distinctly considered æolian, so that while we have for comparison no figures as to the lower limit of rounding in water-borne material, the fact that 0.034<sup>mm</sup> is the diameter of the smallest rounded grain

\* Ziegler, Victor: Factors influencing the rounding of sand grains, Jour.

of Geol., xix, p. 654, 1911. † Allen E. J., and Worth, R. H.: On the fauna and bottom deposits, etc., Jr. Marine Biol. Assoc., Plymonth, England. N. S., v, p. 385, 1899.

t Italics are mine. S Mackie, Wm. : On the laws that govern the rounding of particles of sand,

Trans. Edinb. Geol. Soc., vii, p. 310, 1897. Udden, loc. cit., p. 23-24. Früh: Der postglacialle Loess in St. Gallen, etc. Vierteljahreschrift naturf. Ges. Zürich, xliv, pp. 174-5, 1899.

found in known wind-borne material justifies the conclusion that at least part of the material of the Catahoula sandstone had been blown about by the wind.

Proportion of rounded grains present.—For the interpretation of what may be called the *amount* of rounding of the sand, Mackie\* has established a method and given some results which may be used for comparison. The method, essentially, consists in determining the proportion of rounded to angular grains. The results for quartz grains are :†

River sand of Spey	. Mostly angular
Sea sand, Lossiemouth	{ Round 33 per cent } Angular 67 per cent
Culbin [dune] sands	{ Round 78 per cent Angular 22 per cent
Catahoula sandstone	{ Round 29 per cent Angular 71 per cent

In the proportion of rounded quartz grains present, then, the Catahoula sandstone is much more like Mackie's sea sand than like his æolian sand.

## 3. Ratio of Feldspar to Quartz.

Efforts have been made to find some connection between the relative number of quartz and feldspar grains and the conditions of origin of sediments. It has been shown by Mackie‡ that soft minerals (that is above all feldspar as compared with quartz) tend to be eliminated by abrasion in water transportation. He gives for the average of the sands of four rivers near the sea 18 per cent feldspar, and for beach sand only 10 per cent. On the other hand, since wind is a less viscous transporting agent than water, this same process should be still more rapid in wind transportation ; and, in dune sands that have been blown about a long time this is so.§ But as Sherzer notes, this state is not generally reached in desert sand because unlike water-deposited sand it remains in the region in which it forms, and, therefore, constantly receives fresh additions of fragments from the decomposing country rocks.

While I have determined the ratio of feldspar to quartz only in the "very fine" light portion, it may be assumed that the ratio in other portions would not be very different. This

\* Mackie, Wm.: Rounding of particles of sand, cited above.

† In order to make his figures comparable with mine I have converted his factor into percentage values, distributing his subangular grains equally between rounded and angular.

<sup>‡</sup> Mackie, Wm.: The sands and sandstones of E. Moray, Trans. Geol. Soc. Edinburgh, vii, p. 149, 1896.

§ Sherzer, loc. cit., p. 640-1.

moreover is the method employed by Thoulet and the one followed in a study of the Upper Cretaceous sediments of Maryland \* so that direct comparison with the figures obtained in the latter is possible. This comparison makes the abundance of feldspars here even more striking, for the general ratio in most of those Cretaceous sediments is 10 per cent feldspar, running up to 25 per cent in only one sample. These Cretaceous sediments are undoubtedly all continental fringe deposits (deltas, lagoons, estuaries, and the off-shore marine belt) so that their bearing is significant.

The ratio of 39 per cent in the Catahoula sandstone is therefore seen to be high and may be taken to indicate, for the present, merely that the sandstone was deposited near the source from which its material was derived, and moreover that the ratio is so high as to suggest a very feldspathic rock as that source.

# 4. Weathering of the Feldspars.

General appearance.—The brilliant freshness of many of the feldspars even under the hand lens, where their lustrous cleavage surfaces show up strikingly, seems very significant aside from any attempt at a quantitative evaluation of the degree of weathering. This alone may indicate origin of the sandstone under conditions of mechanical rather than chemical disintegration. Unfortunately, however, neither any information I could obtain from the literature nor my own experience enables me to assert that such feldspars can not exist side by side with weathered ones in a sediment formed under conditions of predominantly chemical disintegration.

Ratio of fresh to weathered feldspars. - Quantitatively the ratio of fresh to weathered feldspars is inconclusive. For comparison there are available here the data gathered by Mackie,<sup>†</sup> though his paper contains only two analyses of sediments formed under conditions that may be regarded as known. <sup>‡</sup> One of these is a bowlder clay in which 86 per cent of the feldspars are fresh, the other is a sample of sand from the mouth of the river Spey in which 81 per cent of the feldspars are kaolinized. The Catahoula sandstone lies half way between them. With these analyses comes the general statement that "Professor Judd found in the deposits of the Nile delta a large proportion of remarkably fresh feldspars." Here then are three distinct types of deposits represented;

\* To appear in a volume on the Upper Cretaceous of Maryland, Maryland

Geol. Survey. † Mackie, Wm.: The feldspars present in sedimentary rocks as indicators of the conditions of contemporaneous climate. Trans. Geol. Soc. Edinburgh, vii, pp. 443-468, 1898.

‡Loc. cit., p. 445.

mechanically disintegrated glacial material; chemically decomposed, water-laid material of a modern temperate humid region; and water-deposited material originating mainly in a modern arid region.

But the largest part of Mackie's analyses was made on material from the Old Red of England,\* of which the conditions of origin can only be surmised. Yet in spite of that they are I think very significant, for a glance at his diagram shows at once a striking grouping of the results around two extremes. This general appearance is more significant than actual averages since in the absence of definite knowledge of the conditions of origin of the rocks those whose feldspars fall near the median line must be regarded as inconclusive; but even the averages support the point, giving 72 per cent for the kaolinized end and 81 per cent for the fresh. What is of special significance, however, is the fact that extremes are characteristic. Indeed I find it hard to conceive of theoretical reasons to account for the presence of appreciable quantities of feldspars of one condition where feldspars of the other condition prevail. That is, if the conditions are those of mechanical disintegration why should some of the feldspars be decomposed? If the answer is that under such conditions only those along joints or fissures would be decomposed, then at once the extent of fissuring of different rocks under the same external conditions becomes a factor opposing the external conditions. Or the effect of a previous condition of climate still retained in the superficial portion of a rock may, as Mackie himself points out, be preserved in the sediments formed under opposite conditions succeeding. Here too we have opposing factors capable of producing any degree of mixture in the product.

These considerations are presented only to draw attention to suggestions of possible complexities in the problem. For the present the indications that the condition of the feldspars tends to one or the other extreme may be accepted. Hence the intermediate condition of the feldspars in the Catahoula sandstone is after all significant; for if they were originally at one extreme then that extreme could have been only one of predominant freshness and the weathering, as may so easily have happened, took place after deposition of the material. While I do not mean for a moment to suggest a possible glacial origin for the Catahoula sandstone, it should be noted, since this paper aims to be a purely petrographic study, that there are as yet not known, to me at least, any criteria for distinguishing the effects of glacial from those of arid conditions in producing disintegration or decomposition of feldspars.

\* Loc. cit., diagram facing page 468.

#### M. I. Goldman—Catahoula Sandstone of Texas. 276

Ratio of different species of feldspars to each other.-Mackie \* gives as the order of weathering of the three main types of feldspars : plagioclase, orthoclase, microcline. The only quantitative data for their relation that I know of are in Thoulet's study of the Gulf of Lyon<sup>+</sup> and a few scattered through the volume of his pupil Sudry on the Lagoon of Thau. + These figures are only approximate, having in some cases a range as great as 50 per cent, but indeed the great variability of the ratio of plagioclase to orthoclase (microcline is not counted separately) justifies this rough counting. From an inspection of Thoulet's table it appears that in general the plagioclase is less abundant, but the great variability in the relative amounts suggests that this fact is to be ascribed largely to the original proportions in the source rock. It will be convenient to discuss this feature of the Catahoula sandstone more in detail in the following discussion of the heavy minerals.

## 5. Ratio of heavy to light minerals.

Following Thoulet, the ratio of heavy to light minerals (feldspar and quartz) has been determined for the "very fine" sands only; t but this suffices since the most available data for comparison are those given by Thoulet. Taking up first ordinary marine coastal deposits, I find that the average of 15 analyses selected at random from Thoulet's paper on the Gulf of Lyon§ gives 12.4 per cent of heavy minerals in the "very fine" sand while the lowest thus obtained is 1.1 per cent and the highest 26.6 per cent. Inspection of the table discloses a ratio as low as 0.23 per cent, but the very low ratios occur in sands with almost no "coarse," "medium," or "fine" sand; "very fine" and "extra fine" with "clay" making up almost the whole sample. Turning to another type of deposit, an analysis by Thoulet of a Sahara sand shows the proportion of heavy mineral in the very fine portion to be about 0.25 per cent.

\* Feldspars in sedimentary rocks, p. 448. +Op. cit.

‡ By an oversight the determination was also made for the "fine" sands and gave about 0.1 per cent, showing that as usual there is a much larger pro-portion of heavy minerals in the "very fine" sands than in coarser sizes. In the "extra fine" sand it is not practicable to make this separation by ordinary methods on account of the great fineness of the material. § Thoulet, J.: Étude bathylithologique des côtes du golfe du Lion. Annales

de l'Inst. Océanogr., Monaco, iv, fasc. 6, pp. 53-60, 1912. ||Thoulet, J.: Etude minéralogique d'un sable du Sahara, Bull. Soc. Min. Fr., iv, p. 266, 1881. || An obstacle to direct comparison with this analysis is the absence of any

portion corresponding exactly to the "very fine" sand, as "very fine" and "extra fine" together are about represented by " $\varepsilon$ " which includes all material below  $0.21^{mm}$  diameter. But as this portion is only 5 per cent it may be assumed that the amount of "extra fine" material in it is negligible. It is, moreover, noteworthy that in this sand the amount of heavy mineral is about the same in each portion.

Sabban in his paper, cited above, on the dunes of the Mecklenburg heath, and Retgers in a paper on the dunes of Holland,\* both give determinations of the proportions of heavy minerals present; but as these are for the entire sand or for portions that are not comparable with mine they too are not directly comparable. However, the high proportion in Retgers' average for the whole sand (5 per cent) and even the figure for Sabban's entire sand (average estimated over 1 per cent) show that in these dunes the proportion is much higher than in the Sahara sands, while the figures given by Sabban for some of his individual portions suggest a very marked similarity with the Catahoula sandstone.<sup>+</sup> Theoretical considerations alone suggest the more perfect separation of light and heavy minerals in æolian sands for the same reason that they are more perfectly sized, i. e. on account of the much lower viscosity and density of air as compared with water. However, in the absence of comparative data on this point I do not want to overemphasize it since there is an evident difference between desert and stream deposits, as pointed out by Sherzer and already noted above in the discussion of the percentage of feldspars present, in that the stream of water carries its material continuously in one direction and thus can leave the heavy material behind, while winds do not have this fixed direction and tend more to blow material about in the area in which it originated, so that there is less space for a horizontal separation. Another factor working toward a low percentage of heavy minerals in æolian sands will be presented under the next heading (Species of heavy minerals, etc.).

To sum up, it may be said that theory, as well as comparative data about the percentage of heavy minerals present, suggest æolian action as a factor in the formation of the Catahoula sandstone, while among the æolian sands with which it can be compared its greatest affinity is with dune sands.

## 6. The species of heavy minerals present and their ratios to each other.

Though I have not attempted to determine quantitatively the proportion of individual heavy minerals present, certain facts of their abundance are so pronounced as to permit of easy generalization. Magnetite makes up doubtless over half the sample and zircon most of the rest. It seems as though the predominance of these two minerals is so pronounced that it must have some significance independent of the composition

<sup>\*</sup> Retgers, J. W. : Über die mineralogische und chemische Zusammensetzung der Dünensande Hollands, etc. Neues Jahrb. Min., 1895, i. p. 27. † For additional references on the minerals in æolian sands see Free, loc.

cit., p. 68 footnote g.

of the source rock and related to the conditions under which the sandstone was formed. For its interpretation, however, I know of little information. The concentration of zircon can of course be readily justified on the grounds of its hardness, lack of parting or cleavage, chemical resistance and its rather high specific gravity (4.7). But as to the resistance of magnetite, I have not been able to find any data. It has no appreciable cleavage and is often free from parting, in which case it may be assumed to be mechanically resistant, though it is not very hard. As to its chemical resistance I can find no evidence, but its familiar prominence in many stream sands and above all in beach sands, and the frequency with which it forms an important constituent (between 15 and 20 per cent by weight of the heavy minerals) in sands of the Upper Cretaceous of Maryland that I have studied (believed to cover a range of types from delta to true marine sediments), justifies the conclusion that it is chemically resistant to atmospheric and aqueous agents of decomposition, at least in temperate regions.

Since the balance of the minerals, so very scantily present, are all more or less regular constituents of sedimentary rocks and are not, in this case, the product of any one kind of igneous or metamorphic rock, they contribute nothing of especial use for this discussion. But they do furnish certain negative evidence which is important, namely the striking scarcity of epidote, and the apparent absence of chlorite, two of the most common weathering products of crystalline rocks, and therefore, as a consequence of their wide distribution and chemical stability, two of the most persistent and often abundant constituents of sedimentary rocks. The absence of chlorite, however, must be grouped, from another point of view, with the absence of micas in general. Finally as a third negative character is the practical absence of ferromagnesian minerals, though their stability not being as great as that of epidote and chlorite they are under no conditions as likely to survive.

This evidence when combined points to the following conclusions. The scarcity of epidote and absence of chlorite indicate fresh source rocks and mechanical—that is arid or glacial—as against chemical disintegration. But the great scarcity of micas and of ferromagnesian minerals are two results distinctly characteristic of arid conditions alone. Goodchild\* explains the elimination of ferromagnesian minerals under arid conditions as resulting from their pronounced cleavages which tend to cause them to splinter up under the action of extreme temperature changes, so that they are readily

\* Goodchild, J. G.: Desert conditions in Britain, Trans. Geol. Soc. Edinburgh, vii, p. 206, 1896.

blown away. The flaky micas are of course still more readily carried off by the winds. This elimination of ferromagnesian minerals and micas is the additional factor, alluded to under the previous heading, to account in part for the low proportion of heavy minerals in general. Of course it can not be definitely asserted that these minerals have actually been eliminated in the process of formation of the sandstone since they may not have been present in the source rocks from which the grains of the sandstone were derived. Nor, reversing the process, is it, I think, safe to try to reconstruct the predominant source rock from those minerals that are present in the sandstone. Thus the meaning of the predominance of acid varieties among the feldspars and of the relative scarcity of microcline can not be determined without knowledge of the relation, under various geographic conditions, of their proportion in particular sediments to their proportion in the specific source rock or rocks from which the material of those sediments was derived. Moreover there is room for unlimited confusion through the mixing of material from different sources. In the case of the Catahoula sandstone there is perhaps less probability of such mixing since the proportion of feldspars present, as explained above, suggests the derivation of the material from near the place where it was deposited, but even here there is again the danger of reasoning in a circle since the high proportion of feldspar may be due to derivation from a very feldspathic rock at a greater distance.

Still in an attempt to draw the most probable conclusion we have as a basis of deduction the order of weathering given by Mackie, and Thoulet's tables for the relative amounts of orthoclase and plagioclase in the Gulf of Lyon. While the wide variation in the proportion of feldspars in a region so limited as that studied by Thoulet shows how local this feature is, yet at the same time this very local variability under conditions which must be regarded as uniform in all essentials suggests a close dependence upon source rock. Moreover the predominance, in several of the samples, of plagioclase over orthoclase shows that the plagioclase does not weather so much more readily as to destroy in all cases its original predominance, so that the high ratio of orthoclase to plagioclase in the Catahoula sandstone may be assumed to be largely original in the rocks from which the material was derived. This is made still more probable by the relatively small amount of microcline, for if this is the most resistant of the feldspars then its seemingly low ratio to the orthoclase indicates that there has not been enough weathering to obscure the original relations of the feldspars. Therefore the indications in the Catahoula sandstone favor slightly the assumption of an acid

AM. JOUR. Sci.-Fourth Series, Vol. XXXIX, No. 231.-March, 1915. 19 igneous rock as the principal source of its minerals, though there is enough microcline to indicate some contribution from metamorphic rocks. Somewhat more trustworthy evidence in the same direction is furnished by the zircons, which are of the igneous as against the metamorphic type.\*

But even if this reconstruction of the source rock were more trustworthy it still would not give assurance that there had been ferromagnesian minerals originally present and eliminated by the conditions under which the sandstone was formed, for if the rock had been, for example, a granite it might yet have been of the alaskitic type and so have contained no appreciable amounts of hornblende or consequently of the ferruginous weathering products epidote and chlorite. Thus the evidence afforded by the heavy minerals for arid conditions is only contributory and not by itself conclusive.

Here more than in any other part of this investigation is brought out the importance of founding the petrographic study of any sedimentary rock on study of its field relations and of the petrography of the rocks, crystalline and sedimen-tary, with which it is associated. The ways in which this might throw light on the particular sedimentary rock under investigation are too many to be enumerated; but to mention only one point it is evident that if we knew something about the rocks from which the material of the Catahoula sandstone might have been derived it would be possible to reach much more definite conclusions concerning the conditions to which those materials had been subjected in the process of its formation.

This completes the conclusions drawn from the mechanical and microscopic analysis of the Catahoula sandstone. There remain to be considered the macroscopic characters of the rocks, and of these may be taken up first its open texture.

## 7. Packing of the sand.

On this subject there is but little that can be said. Quantitative observations have not been made on it because those on modern sands with which it might be compared are for the present so inadequate. Very recently Monsen<sup>+</sup> has been investigating this question of the relation of pore space to the type of sedimentation. His conclusions, which are not always quite clear, seem to be that deeper-water marine sands are closely packed, as are also those of fresh water; near shore littoral marine deposits are more loosely packed, while dune

\*Chrustschoff, K. von: Beitrag zur Kenntnis der Zirkone in Gesteinen,

Tsch. Min. Petr. Mith., vii, pp. 423-442, 1886. † Monsen, Astrid: Über die Packung tertiärer. . . . Sande, etc. (Prelimin-ary paper) Centrblatt Min., etc., 1913, No. 8, pp. 242-245.

sands are loose when newly deposited but become more compacted under the pressure of overlying dune material. Examples of his figures are :

For deeper-lying dune sand : pore space is 37.5 per cent. For near-shore marine sand : pore space is 43.0 per cent. For beach sand : pore space is 35.0 per cent.

The limits of pore space for spheres of uniform size have been shown theoretically to be 25.9 to 47.64 per cent.<sup>\*</sup> Noetling, and more fully Atterberg, both point out that these theoretic quantities are of little significance in nature where sands are neither spherical nor of uniform size; and the variability in these two elements ought to be considered in conjunction with the measurement of the pore space for sands deposited under different conditions. It is for Monsen's failure to do this that Noetling, justly I think, criticises his work. I will leave this topic, then, merely with the remark that dune and beach sands are of those which are seemingly a little more likely than others to be open textured, so that, since the Catahoula sandstone appears to be loosely packed it may on that evidence belong to one of those two types.

#### 8. Bedding.

The entire absence of any lamination or of thin bedding in most of the specimens collected is a characteristic which is hard to interpret. Comparative data are entirely insufficient while, as in most problems of sedimentation, the factors are so complex that a theoretical analysis is very likely to be set at naught by later observations. Even Walther's generalization that "absence of bedding signifies uniformity of conditions of formation" except in its broadest sense requires qualification since it seems likely, for instance, that of material of varying size brought by a current of air or water into a body of water agitated by waves, all below a certain size (that resistant to the maximum prevailing wave intensity) might be eliminated and, thus, that original difference of texture in different layers which constitutes bedding, be destroyed. So we have conditions of deposition that do not meet Walther's requirement of uniformity, the lack of bedding being, in a way, secondary. On the other hand, the transporting agent may be uniform over only a very short time but near its maximum of power and thus form an unlaminated deposit of which at least the greater part will not

\* Free, loc. cit., p. 70; Atterberg, loc. cit., pp. 104-105; Noetling, Fritz, Die Packung losen Sandes (Criticism of Monsen), Centrblatt Min., etc., 1913, No. 21, pp. 681-683.

+ Walther, J.: Einleitung in die Geologie, p. 641, 1893-4.

be subsequently disturbed. That there is any type of sandy sediment which may be considered to be characterized by absence of bedding—unless it be beach sands as a product of the maximum of wave action as just suggested—seems improbable. Stream and delta deposits are stratified as the result of variations in the velocity of the stream, littoral deposits probably also from the same cause or from the larger variations in the intensity of wave action, and in the same way sand dunes show bedding due to variations in the velocity of the wind,\* though this bedding is often not thin enough, at least as far as the eye can distinguish it, to appear in hand specimens like those in question.<sup>+</sup> Of course beach sands also, even though not showing lamination, would in a larger way show variations in the grain of their material corresponding to minor fluctuations of the relative level of sea and land, which, as Philippi<sup>‡</sup> could show, produce that result even in deep sea deposits. In fact here is the crux of the matter, for bedding is only a relative term (wherefore I have preferred the word lamination), and even where there is information as to the presence of bedding in recent deposits figures for the fineness of the bedding are generally not given.

Still, to conclude by accepting Walther's principle, just quoted, as true for the final state in which sedimentary material is found, it may be concluded from the massive specimens of the Catahoula sandstone, that either their material was accumulated rapidly by a current of wind or water, or that it is a beach deposit.

## 9. Arrangement of fossils.

In this connection, as being in fact actually a part of the bedding, the arrangement of plant fossils in the sandstone must be considered. Here too conclusions are of necessity based mainly on speculation or the most general observations and I offer them with corresponding reserve. I think it may be said, however, that a wet leaf will be laid out only flat, perhaps folded on itself but still in a flat plane. Now, as noted above, many of the leaves are embedded in this sandstone in a curled condition and it seems to me a fairly safe conclusion that this indicates burial in wind-blown material. The leaf as it dried would curl and in this condition, rolled along by wind with the sand, would be gradually buried in whatever position it happened to be caught. Such a manner of burial has been assumed for the large Credneria leaves found in this condition in the Upper Cretaceous of Germany. As for the nuts they too should, if buried in a body of water,

\*Walther, loc. cit., p. 638 top. Udden : The mechanical composition of wind deposits, Augustana Library Publ. No. 1, p. 19, 1898. † Oral communication from Dr. Udden.

Philippi, E.: Über das Problem der Schichtung, etc., Zs. d. Deutsch. Geol. Ges., ix, pp. 346-377, 1908.

show an arrangement of their long axes parallel to the bottom and tranverse to the direction of current or wave motion. Only a violent current carrying masses of sand would seem capable of burying them in such chaotic condition, and I question whether such a current would allow these relatively light fruits to settle at all.

But the material as described macroscopically was not all of this massive type with random orientation of the plant fossils. The parallel arrangement of leaves in others of the specimens may be regarded as a kind of bedding or lamination of the including sand. This arrangement of leaves, as just explained in the discussion of the other type of occurrence, can, I believe, arise only under water. Furthermore the accumulation of the leaves in masses with general parallelism of the individual leaves suggests quiet water, at least absence of violent currents. At the same time the fact, noted in the macroscopic description, that even these leaves are not perfectly flat and parallel, suggests rapid accumulation of the enclosing sand. The same conclusion is suggested by the bunching of the leaves in a mass yet with sand between most of the individual ones, for the bunching indicates that they accumulated rapidly, yet the sand kept pace well enough to form thin films between many of them. If then the sand was accumulated rapidly and yet the water was moderately quiet, there is some suggestion that it was not the water that carried this pretty coarse sand but rather that the sand was brought in from the outside-that is by wind. However, in the absence of observational data on the burial of leaves in sands this conclusion too is very hypothetical.

#### 10. Clay Galls.

General character.—The last macroscopic character to be considered is the occurrence of a fine, whitish, pulverulent substance partly as matrix of the sandstone but more especially as small lumps up to about 4 inch diameter. These lumps or "clay galls" are especially abundant in the specimens with the masses of flat leaves.

Lumps and granules of this kind are found in regions of dunes, in river flood planes where sand blows about, on the desert shore of the Red Sea,\* etc. † They originate by the drying out of a deposit of clay resulting in the formation of larger or smaller flakes which are picked up by wind or water to be buried in the midst of sands. Enough fine material is present, even in dune sand, to form thin deposits of this kind when the dunes are washed by rains. It settles in the hollows between dunes, where it soon dries out to be

\* Walther, J.: Einleitung in die Geologie, III, p. 847, 1893-4.

+ Grabau, A. W.: Principles of stratigraphy, pp. 564, 711, 1913.

## 284 M. I. Goldman-Catahoula Sandstone of Texas.

carried away as described. Now the character of the clay galls in the Catahoula sandstone supports the belief that the material is derived from the washing out of æolian sand, for its lack of coherence proves it to be more a rock flour than true clay material.

Distribution.—There remains to be considered the special abundance of these "galls" in the flat leaf accumulations. It may be that this is due to the fact that the bodies of water in which these leaves are supposed to have accumulated were intermittent (field relations could throw much light on that question) and that the clay forming the "galls" remained from a previous filling of the same basin. But it seems more probable that if this had been the case the clay material would again have been spread over the bottom rather than have survived in the form of fragments to be distributed among the leaves during their accumulation. I think it is more likely that the general process deduced above for the burial of the leaves explains the "clay galls" also. That is, they were blown in with the sand, and the water being quiet and accumulation rapid they were buried without being disintegrated. In the subaërially accumulated sand they may be less abundant because here they did not come to rest but were blown about with the sand and so became more disseminated, or perhaps, not being very coherent, were disintegrated by the continued wear.

#### III. SUMMARY AND CONCLUSIONS.

In the first part of this paper I have described the petrographic characters of the Catahoula sandstone; in the second I have pointed out their possible interpretation as evidence of the conditions under which the sandstone originated. It remains now to bring together, compare, and weigh these various lines of evidence in order to draw the conclusion that seems to harmonize best with all the facts ascertained.

It may be well to begin by listing the factors considered. They are:

Proportion of different sizes of grains present.

Rounding.

General character.

Lower limit of rounding.

Proportion of rounded grains present.

Ratio of feldspar to quartz.

Weathering of the feldspars.

General character.

Ratio of fresh and weathered feldspars to each other Ratio of different energies of feldspar to each other

Ratio of different species of feldspar to each other Ratio of heavy to light minerals. Species of heavy minerals present. Ratio of different species of heavy minerals to each other. Pore space. Bedding.

Arrangement of fossils. Clay galls. General significance. Distribution.

The picture presented by the combination of these different factors appears somewhat as follows:

A sand flat, either coastal or inland, containing temporary or more permanent, but in either case small and quiet, bodies of water; the climate arid and perhaps tropical, with strong winds driving the sand about but not accumulating it characteristically in dunes, while nearby rocky hills or mountains crumbling under the effects of temperature changes constantly add fresh angular fragments to the sand.

To review the different characters, in the order given above, for their bearing on this conclusion we have, first, the important feature of sizing supporting the assumption of sorting of the sand by wind and probably by strong wind such as prevails in tropical regions, but the sorting probably not as perfect as would result in a region of well-developed dunes. In the very perfect rounding even of grains as small as 0.035mm there is pretty certain evidence of wind action, while the rather small proportion of rounded grains again indicates that dunes did not prevail here and that new angular material was being constantly added. This conclusion is strongly supported by the abundance of feldspar, which indicates moreover that the source of supply of this new material was near by. On the amount of weathering of the feldspars, however, which is one of the most important features for the determination of the climate, the evidence is particularly unsatisfactory. Still I shall accept as working hypothesis the tentative conclusion, arrived at above, that the feldspars were predominantly fresh when deposited. Then we have in them also evidence of mechanical disintegration, that is of arid conditions.\*

The proportion of heavy minerals was seen to lie between that characteristic of normal subaqueous deposits and a desert sand, and to be most like that of dune sands. The negligible proportion of micaceous minerals points to wind action; the small amount of epidote, and absence of chlorite to absence of

<sup>\*</sup> As stated above there is no basis, in the condition of the feldspars themselves, for choosing between arid and glacial climate. I reject glacial simply because all our other knowledge about the period, as well as other evidence presented in this paper, especially that from the heavy minerals, precludes such an assumption. How easy it is to be misled by the feldspars is shown by Mackie's paper on the subject, in which he concludes for glacial conditions in formations which are now generally believed to have originated in an arid climate.

## 286 M. I. Goldman-Catahoula Sandstone of Texas.

chemical conditions of weathering; the scarcity of ferromagnesian minerals to insolation in an arid region; and the predominance of the two resistant minerals magnetite and zircon to strong mechanical wear such as, under the circumstances, is most likely to have resulted from æolian action. In the seeming porosity of the rock there was some support for the assumption of subaërial deposition. The interpretation of absence of lamination was uncertain, but it seemed likely to be due to rapid deposition such as might be caused by wind or by emptying of a strong current into a quiet body of water. The arrangement of fossils is of two types, one indicating subaërial burial in blown sand, the other also probably burial by wind but in a quiet body of water. It was shown that clay galls in general are produced in regions of loose sand, arid or at least without vegetation, and where there is occasional flooding or washing by rain. Their concentration with the masses of flat leaves is taken to confirm the assumption that the water was quiet and that the burial was by wind-blown material, though it may also indicate that these bodies of water were intermittent or variable in their extension.

In this paper I trust I have made it clear that I do not, under present conditions of knowledge, consider any one of the lines of evidence discussed as in itself decisive, and that it is only in so far as they combine to point to certain conclusions that any weight is to be ascribed to these conclusions.

But it must be borne in mind, as brought out by Sorby,\* that when obtained in this way most of the evidence derived from the constituents of a sedimentary rock is inconclusive because there is a distinction to be made between the history of the material composing a sedimentary rock and the history of the rock itself. Thus of all the lines of analytic and microscopic evidence above the only ones that might not merely survive from an older sedimentary rock are freshness of the feldspars and the ratio of feldspar to quartz. As for the macroscopic characters while they are primary and inherent it should be noted that they throw no light on one of the most fundamental problems, that is whether the Catahoula sandstone was deposited under an arid climate. For while they indicate wind deposition it is very important not to confuse æolian conditions, that is dune formation, with arid conditions. From scarcity of vegetation in both cases they do have certain characters in common, but dunes can and do exist in the most varied climatic regions, and, therefore, their occurrence throws no light in itself on the important problem of prevalent climate. But these considerations of doubt only help to bring out what is one of the principal conclusions from this paper.

\* Sorby, H. C.: On the structure and origin of non-calc. stratified rocks. Qt. Jr. Geol. Soc., xxxvi, p. 58, 1880.

In writing it, it has been as much my object to gather some of the principal lines of evidence available in the interpretation of a disintegrated sediment as to interpret the Catahoula sandstone. I hope I have shown that these lines of evidence are numerous and valuable; and if they do not, in this case, permit of a more positive conclusion it is largely because such an isolated study, and the general science of the petrography of the sedimentary rocks itself, are both too incomplete. Had it been possible to accompany this laboratory study by fuller field observations and by the laboratory study of the rocks associated with the Catahoula sandstone, it is evident that many of the conclusions would be much more certain. And furthermore, in order that the evidence when obtained may be interpreted with more confidence, it is necessary that there be available for comparison a much greater number of extensive descriptions of different types of modern sediments accompanied by critical consideration of the exact geographic conditions under which they were formed, and analyzed by methods so standardized that direct and sure comparison may be possible.

This investigation was made in connection with a paleobotanical study of the Catahoula formation by Professor Edward W. Berry of the Johns Hopkins University. A report by him and Mr. G. C. Matson will probably be published later by the United States Geological Survey. A brief preliminary statement, that he kindly furnished, concerning the peculiar flora and some of the leading faunal types is appended as of interest in connection with the above petrographic study.

The flora is almost entirely a strictly tropical coastal one. It contains at this locality: *Myristica* or nutmeg (fruits); *Phoenicites* or date palm (fruits); abundant fruits of an unidentified *palm*.

From the same formation in its wider extension are: Fagara, a tropical coastal genus of small trees (Rutaceae) with evergreen punctate leaves; two fern genera, Lygodium and Acrostichum, the latter a widespread, tropical, tidal marsh species; leaves of a fan palm, and seven species of petrified palm wood found in this formation in Texas and Alabama, and some also in the Oligocene of the Island of Antigua; species of fig (Ficus), rain tree (Pithecolobium) and coastal forms of Proteaceae (Embothrites), Rhamnaceae (Paliurus), Myrtaceae (Myrica), Combretaceae (Terminalia), and Sapotaceae (Bumelia).

Animal fossils from the formation in its wider extension are :

Camel bones. A small Ostrea. A Linthia (?) (Echinoidea). A Rhinoceros (?).

# ART. XVIII.—Age of the Igneous Rocks of the Adirondack Region; by H. P. CUSHING.

Introduction.-In discussing "Magmatic Differentiation and Assimilation in the Adirondack Region" in a recent paper, the author, Prof. W. J. Miller, mildly criticises certain views which I have published concerning the age of some of the Adirondack eruptives.\* The general paper deals with problems of differentiation and assimilation suggested by these eruptives, matters concerning which there is, so far as I know, little difference of opinion among those who have worked in the Adirondacks; in regard to which Dr. Miller is simply adding his own testimony to the published results of those who have preceded him there. But his work seems to have led him to the belief that all the great eruptive bodies of the Adirondacks are variants of a single period of intrusion, and are not of widely different age. At least in the paper referred to he so argues in regard to all the syenites and granites of the region. My reference of certain granite-gneisses in the Thousand Island region to the Laurentian does not meet with his approval, and he refers to them as "so-called" Laurentian. Lest silence on the part of those who disagree with his views should be misinterpreted as giving assent to them, it seems to me that a reply is necessary: not at all for the sake of being controversial, but in order that the dissent may be made as plain as possible.

Geology of the Region.—The Adirondack highland consists entirely of Precambrian rocks, which are rimmed by early Paleozoics except for a short interval at the outlet of Lake Ontario. But one Precambrian sedimentary series has been recognized, the Grenville series. Of this but shreds and patches are left, the whole having been torn to pieces by the intrusions which have invaded them. So far as known, all the igneous rocks of the district are younger than the Grenville. They consist of anorthosites, syenites, granites and gabbros. All are somewhat metamorphosed and some are heavily so. Metamorphism is more excessive on the east than on the west.

Since all are younger than the Grenville, and no other Precambrian sedimentary formation is present, the age of these eruptives can only be given in terms of their relations to one another.

Miller's Argument.—"With certain possible rather local exceptions, the great masses of syenite and granite which are the most abundant rocks in the Adirondack region, are regarded

\* Bull. Geol. Soc. Amer., vol. xxv, pp. 243-64.

as belonging to a single vast intrusive body. Evidences for this view are presented below."\*

Early in his paper Miller thus states his view. Search in the body of the paper for these promised evidences shows them to be:

(1) A table of chemical analyses, comprising eight analyses of syenite and three of granite, introduced to show their similarity in chemical composition. Nine of the eleven analyses were made by Prof. Morley, seven of them for me and two for Dr. Miller. Of the three granites one is a granite-porphyry variant of the syenite, and the other two are of rocks from the Thousand Island region, for which I have suggested a Laurentian age. The similarity of the rocks as shown by the analyses is not questioned. Whether kinship in age may be legitimately deduced from chemical similarity is quite another matter.

(2) A description of the known variations of the syenite magma, including its granitic phases. Since we have all recognized and described such variations, this calls for no comment except to point out that the presence of granite of such age and relationship has nothing whatever to do with the possibility of there being another of quite different age also present. And if there be more than one there is every reason why they should be akin chemically, since they probably have arisen from the same deep-seated source, and through the same rocks.

(3) In Dr. Miller's Adirondack experience he has in no case been able to find any evidence that any of the Adirondack granites are distinctly older than the syenite, while he has many times found that granites are only siliceous variations or phases of the normal syenite. He states that, in the Adirondacks, no definite case of syenite cutting granite has been found, and but one good case of granite cutting syenite. He seems to regard this lack as of special significance in support of his contention. He also argues that if such evidence were forthcoming it would not disprove his contention, since all igneous masses, when cooling, become cut by dikes of their own material.

It is because, in my Adirondack experience, I have found plenty of what to me seems very good evidence that there were at least two widely separated periods of granite intrusion in the region, that this paper is being written. In many times finding granites that are variants of the syenites, and describing them, my experience is on all-fours with Dr Miller's. But I have been more fortunate than he in making the acquaintance of other granites. He assumes all the syenite to be of the same age. I do not know how he knows that. I personally have a strong suspicion that both granites which I believe to exist in the region have symplectic phases, though I cannot prove it as yet.

There *is* a lack of good cases of syenite cutting granite in the Adirondack region, but there is a very good reason for this lack. Much of the syenite magma was apparently very hot, most of it shows marginal differentiation phases, and some of it gives evidence of marginal assimilation, as in the case of the syenite at Tupper Lake, which shows a basic border phase adjoining anorthosite, and an acid border phase against granitic gneisses.<sup>\*</sup> In my experience *much* of the syenite of the region shows a border phase of porphyritic granite, and the chief dikes which run out from the syenite masses into the surrounding rocks are of this porphyritic granite type. This is especially true where the bordering rocks are older granites, and accounts for the lack of syenite dikes cutting them. But there are numerous instances known to me of the one type of granite cutting the other.

All large igneous intrusions are attended by the production of dikes formed during the later stages of the intrusion, out of the unsolidified magma residuum. It is a part of the business of the field geologist to recognize such and to distinguish between them and the other dikes formed at an entirely different period. It is because I believe that I have successfully done just that, that I am combating Dr. Miller's view. He seems to fail to realize, if his contention be true, that there is a considerable amount of granite in the Adirondacks which is a variant of the syenite, and of substantially the same age, that a good case of such a granite cutting an older granite is just as significant as though normal syenite itself did the cutting. It was precisely such a relation, magnificently exhibited, in the Thousand Island region that led to my correlation.

Time Relations of the Adirondack Eruptives.—In the Adirondack highland there is a great group of eruptive bodies, consisting of anorthosite, syenite, granite and gabbro. So far as we know, the anorthosite is the oldest of the four, in this related group. The only case so far recorded in which the time relations between anorthosite and syenite have been determined is in the Tupper Lake region, where it has been shown that the syenite is the younger. The localities were visited by the International Committee in 1907, and the relations observed seemed conclusive to all members of the Committee. Away from the anorthosite, on its opposite side, the syenite develops a granitic border, and it is also cut by a similar granite. Dikes of similar granite are also found cutting the

\* Bull. 115, N. Y. State Museum, p. 478.

anorthosite in many places. The anorthosites themselves have gabbro borders and are also cut by gabbro dikes. The four eruptives seem all to be variants of the same magma, and not to differ greatly in age. They are metamorphosed but the metamorphism is not excessive, not so great as to destroy the original structures and textures except locally. They are not thoroughly granulated and gneissoid except in the extreme east. Metamorphism increases in severity going east.

There are also other eruptive masses, chiefly granite and gabbro, perhaps some syenite, so far as known no anorthosite, which are certainly older, far older, than the eruptives just considered. The younger eruptives cut these out across the strike, just as they do the Grenville rocks. They contain inclusions of them, just as they do of the Grenville rocks. My note books contain several instances of granite-gneiss inclusions in anorthosite, along the northwestern margin of the anorthosite mass, the only portion of this margin which I know in detail. Inclusions of granite-gneiss in the granitic border phases of the syenite are also recorded, though of necessity these are more difficult to distinguish than similar inclusions in the anorthosite. These eruptives are always more heavily metamorphosed than are those of the later group. The granites are completely granulated, are orthogneisses. The gabbros are entirely changed to amphibolites. It is also true, at least in the western Adirondacks, that the attack of the old granites upon the inclusions which they hold, with the production of soaked, and mixed, rocks, is much more prominent than is that of the intrusives of the younger group upon their inclusions. Though the only safe method of determining the relative age of these intrusives is by their field relations to one another, still each group has, at least in the western area, a facies of its own which may be used with caution in making an age determination.

Granite Relations in the Thousand Island Region.—On the New York side in the Thousand Island region both Smyth and I have shown the presence of two granites of entirely different age, and we are in entire agreement as to their relations.\* The correlation of the older of the two with the Laurentian I must assume the responsibility for. This older granite is an orthogneiss, which cuts the Grenville series. The younger granite, Picton granite, cuts out both. Exposures are extraordinarily abundant, and the field relations especially clear. Fortunately also the present erosion plane cuts the Picton granite on the very roof of the bathylith, so that it is full of fragments of the older rocks in their original attitudes, and the belts of Grenville quartzite and various schists, and

\*Bull. 145, N. Y. State Museum, pp. 41-43.

# 292 Cushing-Igneous Rocks of the Adirondack Region.

the orthogneisses as well, can be mapped right across the Picton granite surface just as accurately as though the granite were not there. The relations show clearly and unmistakably that the orthogneisses are much more closely related to the Grenville in age than they are to the Picton granite. The Picton is but slightly metamorphosed. Its margins and its dikes are fine-grained, and are difficult to distinguish from the orthogneiss, but as to the main mass the difference is marked. In the vicinity there is a small stock of syenite, which I called the Alexandria syenite, which has a border of porphyritic granite, and this also contains inclusions of orthogneiss.

The orthogneiss contains everywhere abundant inclusions of amphibolite, and inclusions of little else. It also is sometimes involved with larger masses of amphibolite, which it cuts. Some of these certainly represent ancient gabbros or basalts and are older than the orthogneiss.

I regard the Picton granite and the Alexandria syenite as local representatives of the great igneous bodies of the Adirondack region, the anorthosite-syenite group, and as of similar age. The orthogneiss is certainly an eruptive, a granite, and as certainly greatly older. In the table of analyses which he publishes, Dr. Miller lists two analyses of these orthogneisses, calling attention to their similarity with the syenites farther east.\* It is greatly to be regretted that he omitted the analysis of the Picton granite from this table. Anyone willing to take the trouble to look up this analysis and compare it with those of Miller's table, especially with Nos. 6 and 7, and at the same time reflect on the demonstrable age difference between the two granites near Alexandria Bay, will be in excellent position to appreciate how little bearing chemical similarity may have on age.<sup>+</sup>

Age of the Orthogneiss.—Having thus established to my satisfaction the occurrence of two granites of widely different age, and this in that part of the New York Precambrian which directly connects with the Canadian Precambrian across the river, I naturally cast about to see if any correlation could be legitimately suggested. The Picton granite could not be found cutting the Alexandria syenite, but I had little question about correlating them both with the general eruptive series of the Adirondacks. Then came the correlation of the orthogneiss. The geologists working in Ontario and in the Lake Superior region have shown that there are at least two granitic invasions there, one cutting the Keewatin, but older than the next younger series of sediments (Lower Huronian, Temiskaming, Sudbury), and the other cutting through that series. Though

\* Op. cit., p. 250, analyses 9 and 11.

+Bull. 145, N. Y. State Museum, p. 176, analysis 6.

the younger sediments are lacking in New York so that precise comparisons cannot be made, it nevertheless appeared to me that the mutual relationships of the two sets of eruptives were precisely those which prevailed in Canada, and that the orthogneisses of the Thousand Island vicinity were precisely like the Laurentian and Ottawa gneisses which I had seen in a host of Ontarian localities, under the guidance of Canadian geologists, chiefly Adams and Barlow. I therefore made the tentative correlation of the orthogneiss with the Laurentian. In eastern Canada Adams has described the anorthosite as holding inclusions of orthogneiss, correlated as Ottawa gneiss, and in a personal letter just received reiterates the statement that the Morin anorthosite has a number of large inclusions of the regular orthoclase gneiss through which it cuts. The Ottawa gneiss is regarded as of Laurentian age. In the Adirondacks the anorthosite is the oldest of the set of younger eruptives, so far as the evidence goes. Both in New York and in Canada, the anorthosite cuts out older granite gneiss along the foliation strike, and holds inclusions of it.

This old orthogneiss, which is everywhere associated with the Grenville in eastern Canada and in New York, and which further west has equally close association with the Keewatin, seems to me to represent a widespread granitic invasion whose separate masses cannot differ greatly in age. It also seems to me that, in Precambrian rocks, great periods of igneous activity, such as this, afford a safer basis of correlation than the sediments do. It is because the Grenville is older than this orthogneiss, which I correlate with the Laurentian, that I have for some time felt the impossibility of correlating it with any part of the Huronian, and believed it more akin to the Keewatin, as several of the Canadian geologists are now classifying it. I think the classification of the orthogneisses of the northwestern Adirondacks as Laurentian is as safe a correlation as can be made in Precambrian rocks. And even if this correlation is unjustifiable and erroneous, it would not alter the fact that, in this region, there are two granites which differ widely in age.

Quantity of the Orthogneiss in New York.—Dr. Miller states in his paper that "If any such older granite does exist, it must be small in amount, and the writer believes it could rarely be successfully mapped as a formation distinct from the granites, which are certainly only phases of the syenite."\*

Since I radically differ from both these statements, I am led to believe that a partial reason for the view that Dr. Miller holds may be that his detailed work has been chiefly confined to the

\* Op. cit., p. 252.

## 294 Cushing—Igneous Rocks of the Adirondack Region.

southern half of the region. In my judgment it is true that the orthogneisses bulk more largely in the northern half of the district, and the later intrusives in the southern. It is also true that metamorphism is more excessive in the latter district, so that the age relations of the intrusives are more masked than on the north. I can simply record my disagreement with his statement, and say that, in the northern Adirondacks, the older rocks far exceed the younger ones in quantity, and that, along the northern border, all across Clinton and Franklin counties, they constitute the bulk of the Precambrian. Here there is even very little Grenville; nothing but a monotonous repetition of granite gneiss and amphibolite, cut by occasional small stocks of syenite and of gabbro. Topographic maps still fail for most of this region, so that none of it has been mapped in detail. But the above statement rests on several years of reconnaissance work, which covered the whole region. In St. Lawrence County more Grenville comes in and separate bathylithic masses of the orthogneiss are readily mapped.

In so far as the possibility of separate mapping of the two sets of intrusions over the whole Adirondacks is concerned, that will very likely not be possible. The same difficulty is met on a vastly larger scale in Canada. But that does not alter the fact that at least two sets of intrusives are present there, and that, in many places they can be told apart and successfully mapped.

Summary.—There are, in the Adirondacks, great bodies of orthogneiss which have suffered severe regional metamorphism, along with the Grenville rocks, and which have, in common with the Grenville, been invaded by the later intrusives of the anorthosite-syenite group. The anorthosites cut out these orthogneisses, and hold inclusions of them. The syenites generally have granitic marginal phases, especially when in contact with the orthogneisses, but these later granites are frequently found cutting the orthogneisses and holding inclusions of them. The relations are especially clear in Jefferson and St. Lawrence counties, where metamorphism is less severe than on the southeast. Precisely the same relations obtain across the river on the Canada side. It is a mistake to attempt to class all these intrusives together, and to belittle the importance of the early group.

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## ART. XIX.—Unstable Chromium Sesquioxide, and Corrections of Previous Work on the Heat Effect of Chromium and Aluminum Sesquioxides in Fusions with Sodium Peroxide; by W. G. MIXTER.

[Contributions from the Sheffield Chemical Laboratory of Yale University.]

In a former paper\* the heat effect of 1 gram of amorphous chromium sesquioxide reacting with sodium peroxide is given as 867 and 878 cal. The writer regrets errors in the calculations. The corrected figures are 712 and 722 cal. A new determination, Experiment 1, p. 297, gives 726 cal. The average is 720 cal. For 1 gram molecule of chromium sesquioxide reacting with sodium peroxide the result is 109.4 The sesquioxide used in all the above determinations Cal. was made by heating the hydroxide over a blast lamp. Essentially the same valuet was found for the crystalline oxide. As the values are alike, the ignited oxide, which was apparently amorphous, may in reality be crystalline. for the heat of formation of a crystalline compound is commonly higher than an amorphous one. Professor Hastings, however, found in a very careful microscopic examination no appearance of crystals in oxide made by heating the hydroxide. Whether or not such oxide is made up of ultra microscopic crystals, it is to be regarded as the same polymer as the crystalline form, since, as shown later, both are condensation products of the unstable form of chromium sesquioxide.

As Moissan‡ states, chromium sesquioxide which has not been calcined oxidizes below a red heat in air and oxygen while the calcined oxide does not. It has long been known that chromium hydroxide glows when heated, that is, it suddenly becomes hotter than the surrounding medium. Endell and Rieke§ have studied the glowing of some hydroxides and have found when the temperature is raised 80° a minuté that "Chromoxydgel, heiss, gefällt, zeigt eine bei 500° einsetzenge und sich bis 610° hinziehende Wärmetönung und Verglimmen —Der Vorgang der Wärmeabgabe is irreversibel u. entsprich einer gewissen Kornervergrösserung." There is, therefore, a stable and an unstable chromium sesquioxide. The two forms differ in heat of formation, as will be shown later.

The chromium hydroxide used in the work was from Kahlbaum and had been in the laboratory some time. It was free

\* This Journal, xxvi, 125, 1908.

Ibid.

‡ Ann. Chim. Phys. (5), xxi, 199.

SCentralblatt f. Min. u. Geol., 1914, 246, Berlin, quotation from abstract in Chem. Zentralblatt, 1914, I, 1991.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 231.—MARCH, 1915. 20

from chloride and sulphate, but held a very little ammonia and considerable carbon dioxide. Iowitschitsch\* found that chromium hydroxide absorbs the latter from the air. All attempts to dehydrate chromium hydroxide below temperatures at which it would glow or change to the stable oxide failed to expel all of the water or carbon dioxide. One portion of chromium hydroxide was heated for a day at 320° while the vapor and gas were pumped off. The product contained 92 per cent of Cr.O.. After heating at common pressure to about 420° for three hours in a current of hydrogen to prevent oxidation, it had 94.1 per cent. This product is designated as A. Another portion of chromium hydroxide which was heated in hydrogen for a day at about 420° (the temperature may have been higher at times) still retained 3.4 per cent of water and carbon dioxide. This preparation (B) was a dark olive green. Both A and B glowed when heated in a closed tube, but the glow did not extend through the mass when the end of it only was heated unless the whole was moderately hot. B at a temperature below that required to make it glow became red hot when a rapid current of oxygen was passed into the tube containing it. The heat of the oxidation was sufficient to change the unstable olive green substance to the stable green oxide, the higher oxide first formed giving up oxygen. Another portion of chromium hydroxide was heated two days as just described and gave a product (C) like B. It lost 3.4 per cent on ignition. Part of C was next heated another day to approximately 400° in hydrogen. The temperature of the electric furnace used may have been somewhat higher at night. The olive green oxide was changed to bright green. It did not oxidize or glow on heating and lost 1.3 per cent on intense ignition. One gram of it gave when fused with sodium peroxide 687° cal. This is approximately the heat effect of ignited Cr.O.. Apparently long heating of the unstable oxide at a temperature below that at which it glows changes it to the stable oxide. The following experiments confirm this supposition. A portion of C was placed in a bulb with a capillary neck and gradually heated in an air bath to above 500° in a glass vessel. No glowing was observed and the oxide became bright green. It was also found that C did not glow when dropped into a platinum crucible below a faint red heat but oxidized and became black.

Preparation A was used for experiment 2, Table I, B for 3 and 4, and C for 5.<sup>+</sup> All contained water and carbon dioxide,

\*C. R. clviii, 872, Chem. Zentralblatt, 1914, I, 1635.

+ The lampblack used in the experiments was nearly free from ash. It was heated for three hours to about 1100°. Each portion used in a calorimetric experiment was heated to a faint red and left to cool in a desiccator. Determinations of the heat effect of the lampblack in fusions with sodium peroxide gave 10638, 10636 and 10635; mean 10636 cal. for 1 gram of lampblack. The oxidation of the lampblack was complete.

which added to the heat of the fusions. The effect of combined water, for example, is that of free water less the heat of combination of water with chromium sesquioxide. In fusions with sodium peroxide water combines with the sodium oxide formed. For 18 grams of free water the effect is 36,000 cal. or 2,000 cal. per gram. Likewise for one gram of carbon dioxide it is 1700 cal. The effect of the two in combination with chromium sesquioxide is unknown but less. It is assumed to be 1500 cal. Since the chromium sesquioxide contained

m r

5
7.009
0.043
6.966
0.471
21.
4132
2.694
11132
-5010
-20
6102
876

only small quantities of water and carbon dioxide, the error in the assumed heat effect of these will make but little difference in the value found for chromium sesquioxide. One gram of substance used in Exp. 2 contained 0.059 gram of water and carbon dioxide, and  $1500^{\circ} \times 0.059 = 88$ . The observed heat effect of the substance is  $922^{\circ}$ , and  $922 - 88 \div 0.941 = 886$ . From 865 cal., the mean of experiments 3, 4 and 5, 843 cal., is derived. The average of 886 and 843 is 865 cal. for the heat of the reaction of one gram of unstable chromium sesquioxide with sodium peroxide. This is an approximate value, very likely low since the oxide used may have contained some of the stable oxide. In the former paper 52.1 was taken for the

297

					TABLE	III.				
			1	ŝ	ଦ୍ୱ	4	5	9	č*	80
11203	amor.	(1	5.102	5.147	5.287	5.243	5.330			Grams
l <sup>2</sup> O <sup>3</sup>	crys.)							5.222		
1 <sup>3</sup> O <sup>3</sup> (	1.7%]	H <sub>3</sub> O)							5.125	4.998
l <sub>2</sub> O <sub>3</sub> t	incom	bined in fusion	0.0	0.080	0.100	0.153	670.0	1.984	0.058	0.008
Al <sub>3</sub> O <sub>3</sub> c	ombin	ned in fusion	5.102	5.067	5.187	5.09	5.257	3.238	2.067	4.99
8 8 8 8	1					2.000	2.000	2.000		
(Lan	npblac	ik)	1.275	1.251	1.264				1.328	1.297
[a,0,.	8		25.	29.	28.	29.	$26^{\circ}$	24.	30.	24.
Vater	equiv	. of system	4215	4204	4174	4168	4184	4155	4155	4179
empe	rature	interval	3.717	3.714	3.764	3.128	3.109	2.913	3.988	3-900°
										cal.
leat ei	fect.		15664	15614	15711	13038	13008	12104	16571	16298
22	0 ,,	f S or C	-13562	-13306	-13444	-10520	-10520	-10520	-14125	-13795
33	3 33	· Fe	40	-40	-40	-40	30	-50	-40	-40
<b>33</b>	y yy	' O <sub>2</sub> evolved	+575	+631	+647	+238	+278	0	+614	+493
"	, ,,	· Al <sub>2</sub> O <sub>3</sub>	2637	2899	2874	2716	2736	1534	3020	2956
,,	, ,,	(1  gm. of Al, 0)	517	572	554	534	520	474	596	592

298

Mixter-Unstable Chromium Sesquioxide.
atomic weight of chromium while 52.0 is used in deriving the following values:

 $2Cr + 3O = Cr_2O_3$  (crystalline) + 267 Cal.  $2Cr + 3O = Cr_2O_3$  (stable, amor. ?) + 266.  $2Cr + 3O = Cr_2O_3$  (unstable) + 243, approx.

New determinations have been made of the heat effect of alumina in fusions with sodium peroxide with higher results than were obtained six years ago.\* The difference, roughly speaking, in the two sets of experiments is in the oxygen, given off from the fusions. In the first experiments little or none was observed, while in the recent work the heat equivalent of oxygen set free is in some of the experiments over 100 cal. per gram of alumina. It is probable that in the previous work oxygen was also set free, for in only one of the five experiments was the pressure in the bomb taken after a combustion and in that the increase was small. Very likely the bomb had leaked under pressure. In the recent experiments the bomb was connected with an inverted flask filled with water into which the gas passed as evolved. Anhydrous alumina was made by heating the hydroxide 15 minutes over the blast lamp. Alumina containing 1.7 per cent water was made by heating the hydroxide for 24 hours at approximately 500°. The preparation lost 1.7 per cent over the blast lamp and the loss is called water. The crystalline alumina was corundum. The experimental data are in Table II.

The average of the experiments 1 to 5 inclusive for amorphous alumina is 539 cal. and 55.1 Cal. for one gram molecule combining with sodium oxide. This should be regarded as an approximate value since the results from which it is derived vary widely. As ortho- and meta-aluminates exit, it may be that the products were not the same in the different combustions. One determination with corundum gave 48.0 Cal. The average of experiments 7 and 8 is 594 cal. without correction for 1.7 per cent of water. This value indicates that alumina which has been nearly dehydrated at 500° polymerizes at higher temperatures.

\* Loc. cit.

#### ART. XX.—Note on the Shape of Pebbles; by HERBERT E. GREGORY.

ATTEMPTS to establish criteria for distinguishing beach pebbles from those formed by rivers, glaciers, or wind, or resulting from weathering in place, have led to unsatisfactory results. The summary classification of Mansfield:\* marine pebbles, "fairly uniform in size, well rounded"; fluviatile pebbles, "all sizes, generally subangular"; glacial pebbles, "faceted, rounded edges, snubbed ends, polished and striated"; is better adapted for use in the classroom than in the field. With respect to shape and distribution of pebbles, the same may be said of the criteria established by Trowbridge.† The distinctions drawn by Suess and Hoernes,‡ that marine and lacustrine pebbles are round and oval or roller-shaped, but not wedge-shaped; that fluviatile pebbles are flat and wedgeshaped; are not applicable to shores and streams which have come under my observation.

The assumption that flat pebbles are characteristic of river deposits is usually accompanied by the explanation emphasized by Liburnau, § that horizontal rotation rather than rolling is the normal method of attrition for river pebbles. Field observations show that this process of shaping is of local significance. Vertical and horizontal rotation, saltation, rolling and sliding, are effective at the same time, or at different times, in all moving water. Snubbed slabs, blunt wedges and disks may be collected from lake and ocean shores, and where conditions are favorable—as along shale cliffs—the beach gravel may consist in large part of these. Strong waves overturn and vigorously roll pebbles, while weak waves may shove pebbles of suitable shape and size or may not disturb them at all. On a shore fretted by waves of slight power the only modification in shape may be that due to the wearing accomplished by streams of sand which pass to and fro. Along a coastal belt whose shore line is rapidly migrating landward, and especially if the coast is low and the waves are weak, pebbles may be preserved by burial or drowning without much change in orig-

\* The characteristics of various types of conglomerates, Jour. Geol., xv, pp. 550-555, 1907.

<sup>†</sup> A classification of common sediments and some criteria for identification of the various classes, Jour. Geol., xxii, pp. 420–436, 1914.

<sup>†</sup>Suess : Der Boden der Stadt Wien, 1882<sup>°</sup>; quoted by Grabau, Stratigraphy, p. 595.

Hoernes : Gerölle und Geschiebe, Verhandl K.-K. geol. Reichsanstalt, No. 12, 1911.

§ Die geologischen Verhältnisse von Grund und Boden, 1888.

inal form. Likewise a retreating shore line may strand gravels which have not been completely reshaped. Material furnished to waves is quarried from coasts composed of all sorts of material, both consolidated and unconsolidated. Glacial and riverborne pebbles and bowlders, as well as joint-bounded and irregular fragments of rock, find their way to the beach, and the shape which they assume at various stages of their life history on the shore is believed to be predominantly controlled by their original form. Round and oval fragments tend to retain those shapes; blocks with rectangular and square cross sections develop elliptical or circular cross sections; flat fragments tend to remain flat or to become discoid. If the material supplied to waves consisted of silver dollars and marbles, it is difficult to imagine how any pebbles other than flat and round could result from the most vigorous and long-lived wave abrasion. It may be noted also that for stratigraphic purposes lacustrine and delta gravels are to be included with marine sediments, although their constituent pebbles are obviously of sub-aërial origin.

That pebbles may be well rounded by streams is proven by direct observation and by experimentation. As pointed out by Bonney,\* the results of Daubrèe's well known studies are not of general application, since the only phase of river work comparable with travel of irregular blocks in revolving cylinders is the attrition of pebbles in potholes. Omitting the time factor, the conditions surrounding Daubrèe's experiments may be approached and a high degree of sphericity of pebbles be attained in cases where irregular blocks, unmixed with much finer stuff, are carried en masse. Under such circumstances the pebbles experience a continuous direct bombardment among themselves. As bearing on this point, it was noted that gravel bars on the Navajo Reservation shift their position from year to year and even during sudden floods. A deposit composed of about 80 per cent of coarse gravel on Bonito Creek, Arizona, moved bodily down stream between 1910 and 1913, for a distance of about 300 feet, without apparent change in texture or composition. It was also observed at several localities that the pebbles on bars and terraces exposed between floods have a distinctly higher degree of rotundity where the mass is composed almost wholly of pebbles one-half inch to three inches in diameter, than where composed of sand, adobe, and pebbles. In studying these deposits it was noted that highly angular pebbles, and even blocks one foot in diameter, have been carried for distances exceeding 30 miles. In the lower Chinli valley a block of monzonite 5 inches in diameter, after a journey of 40 miles, has a form almost identical with that of talus

\* Geol. Mag., v, pp. 54-61, 1888.

blocks on Carrizo Mountain, from which it was derived. It would appear that such pebbles and bowlders had made their journey without the companionship of fragments of similar The slowness with which pebbles are rounded where size. they constitute a minor portion of the transported materials is a matter of everyday observation in the Colorado Plateau Province. In humid regions characterized by continuous stream flow, and where the sediment is largely supplied by surface run-off, the finer materials are strained out by running In regions where dry and wet seasons alternate and water. where wind is effective, the proportionate amount of finer stuff is greatly increased. Dunes strewn along valley bottoms, and formed of material carried from inter-stream areas, are abundant in arid regions. Following sudden showers, resulting in concentrated run-off, this material is swept into streams in enormous quantities. In 1914 Black Falls, 10 feet high, on the Little Colorado River, became obliterated, between two periods of stream flow, by a deposit of 36,000 cubic yards of wind-blown sand. So much sand is supplied along the middle portions of the Little Colorado that pebbles and bowlders, though large in number, have little chance to be abraded on rock bottoms or by grinding against each other. Such blocks may exist without change throughout an entire physiographic cycle, for during the time of the stream's greatest erosive power they may remain embedded in finer materials. Alternate wet and dry seasons would appear to favor subangularity of pebbles regardless of distance.

In regions characterized by intermittent stream flow it may be observed that the abrasive power of sand streaming past and over bowlders on a river bed is an important factor in determining form. For stretches of hundreds of feet in certain streams on the Navajo Reservation the upstream sides of bowlders are polished and worn and rounded, even faceted and etched, while the downstream sides are essentially unmodified. In places working up-valley across huge bowlders involves climbing precipitous faces and descending slopes, like travel over miniature cuestas. To obtain a quantitative estimate of erosion by this process, holes one incli deep were drilled in opposite faces of sandstone bowlders at eight localities. On visiting two of these localities a year later (in 1910) it was observed that in the case of three bowlders abrasion had reduced the depth of the upstream holes .03, .06 and .06 inches respectively. Five localities, including the two mentioned, were re-visited in 1914, at which time the deepest hole was 0.4 inch and at one locality no trace of the drilling remained. A hammer scar, made by clipping sandstone rock, exhibited fairly well-rounded edges after the passage of a single heavy flood. On the downstream side of the same bowlder, a blue

pencil mark had not been erased. Of the holes made in 1909 on the downstream side of the bowlders, none had been perceptibly modified. On quartzite and limestone bowlders the abrasion during four years amounted to less than '01 of an inch. That this process is continuous is shown by the presence of percussion marks on upstream faces of bowlders and their absence on the opposite side. In torrential streams of Connecticut the upstream faces of many bowlders are perceptibly worn, while lichens cover their downstream sides. On those portions of the Connecticut shore where current action prevails over wave work, comparable illustrations may be found.

In streams of semi-desert regions the rate of transportation appears to have high value in shaping pebbles, regardless of distance traveled, and to a lesser degree, of hardness and specific gravity. Pebbles in "washes" are prevailingly angular, but are less uniformly so in their torrential portions. At the base of steep slopes, approaching the perpendicular, such as exist on Navajo Mountain and the edges of Black Mesa, pebbles appear to be somewhat better rounded than along the Puerco, the Moencopi and the Kayenta valleys after traveling many times as far.

Moreover, many pebbles in fluviatile gravel bars are decomposed, and may be crushed in the hand, although retaining their form. It appears that the conditions surrounding such pebbles particularly favor chemical action, and that ancient river gravels may not in all cases be distinguishable from residual deposits resulting directly from weathering.

Wind-made pebbles when maturely developed and fresh are characteristic, but until faceting is far advanced and also after decomposition has modified their shape, may not be unlike certain classes of river and glacial pebbles.

At first sight it appears that pebbles resulting from glaciation could readily be distinguished, and the geologic literature is characterized by the assumption that the presence of "soled," striated, faceted, or polished pebbles demonstrates glaciation. That this criterion should be used with great caution is evident from the fact that "typical" glacial pebbles and bowlders are rare. Fluvio-glacial drift together with surficial and terminal moraines is many times more abundant than ground moraine, and is prevailingly lacking in striated and polished pebbles. The exceeding rarity of such pebbles about the existing glaciers in Switzerland, Peru and California is a matter worthy of comment. In the terminal moraines of Long Island striated and polished pebbles must be sought for with care; and in the "stony till" of Connecticut, even in well-exposed sections, an hour's search may be rewarded by the discovery of one "characteristic" glacial pebble. From a study of a number of deposits including drumlins and recessional remains, it appears that pebbles and bowlders which may be unqualifiedly assigned to ice work do not exceed one in a thousand for the Connecticut glacial deposits.

Pebbles with "characteristic glacial forms and markings" produced by processes other than glacial have been described from various parts of the world, and the presence of "impressed" pebbles in conglomerates implies pressure and differential motion more than sufficient for the production of striæ. Even from dikes, "glacial" pebbles suitable for classroom demonstration have been collected.

Of the many factors whose evaluation is essential in establishing distinctions between various modes of origin of conglomerate, that of shape of pebbles has perhaps the least significance. No constant difference between the constituents of marine, lacustrine and river gravel is likely to be established. Polished, striated, and soled pebbles are not of diagnostic rank, and their absence does not imply the absence of glaciation. In well-exposed and widely extended outcrops, or where proof of origin rests on other grounds, pebble form may have supplementary value; under other circumstances this criterion should be applied with extreme caution.

Yale University, New Haven, Conn.

#### ART. XXI.—Relation of the Late Tertiary Faunas of the Yorktown and Duplin Formations; by JULIA A. GARDNER.

CONTRIBUTIONS to the geology and paleontology of the Virginia and North Carolina Tertiaries have appeared from time to time since the days of Maclure and Say, but no monographic work was attempted until the recent cooperative study of the coastal plain formations under the auspices of the United States Geological Survey, and the Surveys of Virginia and North Carolina. Reports upon the stratigraphy have already been issued by the respective state surveys,\* but those upon the paleontology are not yet published.

The following formational units have been recognized in the Middle Atlantic Coastal Plain:

	Virginia	North Carolina
Pliocene		Waccamaw
	Yorktown	Yorktown, Duplin
Miocene	St. Mary's	St. Mary's
	Carvert	

The Calvert and St. Mary's have been traced southward from the Maryland region, where they were first differentiated and are best developed. The type locality of the Yorktown, how-ever, is at Yorktown in southeastern Virginia, that of the Duplin at the Natural Well in the environs of Magnolia, Duplin County, North Carolina, and that of the Waccamaw along the Waccamaw River in northeastern South Carolina. The present areal extent of the three last mentioned is shown in fig. 1.

All of the formations contain prolific molluscan faunas and very extensive collections have been available for study.<sup>+</sup> The shells are exceptionally well preserved, so perfectly, indeed, that many individuals still retain the enamel and traces of the color pattern. The fauna is exceedingly interesting, not only because of its diversity and the remarkable development of certain groups, but especially because it so fully confirms the opinion of Shaler, # Glenn, & Dall, and others, that the vicinity of the Hatteras axis was, in Tertiary times, as it is in Recent, a critical area in the distribution of the marine life, and that,

\* N. C. Geol. Surv., vol. iii, 1912. Va. Geol. Surv., Bull. iv, 1912.
† Collected by Stephenson, Miller, Twitchell, Bassler, and Berry.
‡ Shaler, 1871, Proc. Boston Soc. Nat. Hist., vol. xiv, pp. 110-123.
§ Glenn, 1899, American Geologist, vol. xxiii, pp. 375-379.
‡ Dall, 1903, Trans. Wagner Free Inst. Sci., Philadelphia, vol. iii, pt. vi, p. 1598.

306 Gardner-Relation of the Late Tertiary Faunas

in a general way, it has marked for geological epochs the southernmost extension of the northern forms and the northernmost extension of the southern.

The *tout ensemble* of the late Tertiary faunas is very similar to that of the existing fauna of the east coast of the



FIG. 1.

FIG. 1. Map showing areal distribution of Late Tertiary of Virginia and North Carolina.

Horizontal lines = Yorktown Formation. Vertical lines = Duplin '' Solid block = Waccamaw ''

United States. The Pelecypoda, although much more prolific in individuals, are exceeded in the number of species and subspecies by the Gastropoda, the former numbering only 363, or 45.2 per cent of the whole, while the latter number 430, or 53.5 per cent; the nine species of Scaphopoda and the single chiton (Amphineura) bringing the total up to 802 forms. One hundred and eighty-nine, or 23.6 per cent, of these are new to the literature.

The species persisting to the Recent fauna and upon which the deductions concerning the environmental conditions are chiefly based, number one hundred and eighty-five, of which 62.5 per cent are univalves and 36.4 per cent bivalves. The larger percentage of Gastropoda is possibly due to the more uniformly arenaceous character of the deposits of the Waccamaw and Duplin, the formations from which the most prolific faunas have been derived and which were laid down, apparently, under conditions more favorable to the univalve than to the mud-loving bivalve.

Of the one hundred and eighty-five species and subspecies of Tertiary mollusca represented in the recent seas, fifty-six, according to the latest check-lists, which are, of course, nothing more than the latest approximations to the truth, range both to the northward and the southward of the Virginia-North Carolina coast; eighty-four from North Carolina, southward; nine from Virginia, northward; while thirty-six have not been reported north of Florida. It is very possible, however, that some of these extra-limital species did not inhabit the area in which their shells were buried. Most of them are very small, and represented, in many cases, by a single individual, which may easily have furnished food for a Tertiary fish in the Antillean region, and later been disgorged in his journey up the Gulf Stream. In fact, Conus proteus Hwass and Petaloconchus nigracans Dall are the only forms not occurring off the Virginia and North Carolina coast to-day which are not rare in the late Tertiary faunas. Then, too, the northern limit of extension of a fauna is much less sharply defined than the southern, since forms which push southward can often reproduce under the new conditions while the larvæ of a form which has extended its range to the northward are frequently exterminated by a drop of only a couple of degrees in temperature.

The relative abundance of a race is, within certain limits, a much surer guide to the conditions under which it existed than a check-list of the species occurring within that area. Thus in the Yorktown formation, the Nuculas, Ledas, and Yoldias, all of them genera which flourish in the cooler waters, are very abundant; *Glycimeris americana* deFrance and *Glycimeris pectinata* Gmelin, species which range to-day from Hatteras southward throughout the West Indies, although listed in the Yorktown faunas are inconspicuous elements, while in the faunas south of Hatteras they occupy a major position. The distribution of the Pectens and the distribution and abundance of the Astartes

#### 308 Gardner-Relation of the Late Tertiary Faunas

in Virginia and North Carolina was probably governed more by temperature than by time, although the recent representatives are too distantly related to offer any definite proof. *Thracia conradi* Couthouy, ranging on the east coast from Labrador to Hatteras, is well known in the Yorktown, while its presence south of that region, either in Tertiary or Recent times, is exceedingly doubtful. The Venericardias are prolific throughout the Miocene and early Pliocene, but the more northern race, *Venericardia granulata* Say, which is present in the Recent seas from Hudson Straits to Hatteras, dominates in the Yorktown, which V. tridentata Say and V. perplana Conrad, both of them denizens of the waters between Hatteras and Charlotte Harbor, Florida, equal or exceed the northern species in abundance during the Duplin and Waccamaw.

The absence of any representative of the genus *Echinochama* is probably due to latitude rather than time, since a species very closely allied to E. arcinella is abundant in the Oligocene (Bowden beds) of Jamaica. Arca (Fossularca) adamsi Smith, which is well represented in the warm water faunas from the late Oligocene on through the Duplin and the Waccamaw to the Recent, is absent in the Yorktown. The very marked dissimilarity between the Cardiums north and south of the Hatteras axis is probably due, in large part, to differences in temperature since two of the three Yorktown species have a meagre representation in the Duplin, while the more ornate southern races are unknown in the Yorktown. Dosinia elegans Conrad, a species ranging from Hatteras to Aspinwall, is present in the Miocene at Alum Bluff, and was quite abundant during the Duplin, although it was unable, apparently, to extend its range northward into the cooler waters of the Yorktown basin. In most of the Veneracea, however, and in the Tellinacea, the cleavage in species seems to be along formational lines rather than climatic, in spite of the fact that the majority of the species are denizens of the between tides or littoral zone, and so would be exposed to climatic conditions more than those forms which dwell in a more stable habitat.

The gastropod fauna of the Virginia and northern North Carolina Miocene is, on the whole, much less prolific than the pelecypod, and much less evenly developed. The Terebras, the Cones, and the Pleurotomids, all of them prolific south of Hatteras, even in the Oak Grove sand member of Alum Bluff formation of Florida and the Bowden marks of Jamaica, have an exceedingly meager representation, both in species and individuals, north of Hatteras. The Marginellas, on the other hand, a cooler water group, are much more abundant in individuals north of Hatteras than they are south of it. *Fasciolaria*, represented in the Duplin by five species, two of which are present in the Alum Bluff formation of Florida, is unknown in the Yorktown. Purula and three species of Cypraeidae, all of them present in the Bowden marls as well as in the Duplin and Waccamaw. have no representatives north of Hatteras. Of the seven Recent species of *Muricidae* represented in the Tertiary, the only one present in the Yorktown is Eupleura caudata Say, a form which ranges in the Recent seas from Cape Cod to Charlotte Harbor and the West Indies, while of the remaining six Muricidae, half of them range from southern North Carolina southward, while the other half have not been recorded north of Florida. The group of *Triforis nigrocincta* and of Cerithiopsis subulata exhibit in their Tertiary range from Virginia to Florida the same line of variation as do the Recent representatives. The distribution of the Tertiary Naticidae is obviously governed by latitude. The two Recent species which range from New England to the Gulf or the West Indies, Natica pusilla Say and Polynices duplicatus (Say). are present in both the Yorktown and the Duplin fannas. Natica canrena Linné, which has been reported from Hatteras to Carthagena, and is very abundant in the Bowden beds, is unknown in the Yorktown, while Polynices heros (Say), which ranges from Labrador to Hogg Island, Virginia, is well represented in Virginia and northern North Carolina, but exceedingly rare in the Duplin, and altogether absent in the Waccamaw.

The dissimilarity between the Duplin and Waccamaw faunas is governed by time rather than place. Both contain a larger percentage of Floridian species than does the Recent North Carolina fauna, and while the danger of exaggerating the importance of the occurrence of a single individual of a characteristic Floridian species must be avoided, the occurrence of thirty-six such species, against six in the Yorktown, cannot but carry a considerable significance. The influence of ocean currents on the distribution of marine life, which has been so strongly emphasized by Dr. Bartsch in his study of the west coast Pyramidellidæ, and other groups of small univalves, was doubtless potent in Tertiary times. Dr. Dall, in his discussion of Tertiary conditions along the east coast, suggested the elimination of the cool inshore current, of the earlier Miocene, and the reëstablishment of a Tertiary Gulf Stream as the probable cause of the sub-tropical aspect of the Duplin fauna,\* and later investigations have done much to substantiate this theory. It seems probable, however, that this late Miocene Gulf Stream hugged the North Carolina shore even

\* Dall, 1903, Trans. Wagner Free Inst. Sci., Philadelphia, vol. iii, pt. vi, pp. 1598-1599.

#### 310 Gardner-Relation of the Late Tertiary Faunas.

more closely than does the present Gulf Stream, but swung off into the open sea in the vicinity of Hatteras so that its influence upon the Yorktown fauna was almost negligible.

Differences in depth of water in the areas of the late Miocene and early Pliocene that are now available for study were doubtless very slight, so slight that it is very hazardous to attempt to differentiate their effects upon the faunas. It seems highly probable that the Yorktown, the Duplin, and the Waccamaw, were all of them laid down in water, rarely, if ever, exceeding fifty fathoms in depth, and that the bathymetric variations were as great within the formations as they were between them. The sea floor was rather certainly more sandy during the Duplin and Waccamaw than it was during the St. Marys and Yorktown, the conspicuous abundance in Virginia and northern North Carolina of such a form as Mulinia congesta Conrad indicating dominantly muddy bottoms in some portions, at least, of the Chesapeake, while the profuseness of Oliva litterata Lam. and Olivella mutica Say give evidence of extensive sand flats during the Duplin and Waccamaw.

There is, then, every reason to believe that already in the late Tertiary, present-day conditions had been approximated along the east coast. The faunas of Virginia and North Carolina flourished in rather shallow, inshore waters, into which mud and sand were being freely carried, the waters of the Yorktown basin being slightly but not much warmer than those off the Virginia coast to-day, while the Duplin and Waccamaw faunas were obviously in more direct communications with the Floridian life than are the present faunas off Hatteras and Cape Fear and indicate slightly warmer climatic conditions than do those of the Yorktown.

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#### SCIENTIFIC INTELLIGENCE.

#### I. CHEMISTRY AND PHYSICS.

The Determination of Cuprous and Cupric Sulphides in 1. Mixtures of the Two.-In the course of an investigation on copper sulphide minerals, EUGEN POSNJAK, having had occasion to determine the two copper sulphides when mixed together, has worked out an interesting method for this purpose. The reaction between cuprous sulphide and silver salts was known from the results of several investigators to proceed according to the equation  $Cu_sS + 4AgNO_s = Ag_sS + 2Ag + 2Cu(NO_s)_s$ . In regard to the reaction between cupric sulphide and silver salts there were conflicting statements, so that this point was settled experimentally by the use of very pure natural cupric sulphide (the mineral covellite) and the synthetic compound. It was thus found that the reaction is represented by the following equation:  $CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$ . It was then found that a 6 per cent solution of ferric nitrate acting at 70° upon mixtures of silver sulphide and metallic silver showed practically no action upon the sulphide, while it dissolved the metal according to the following equation:  $Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_3$ . As many as 10 known mixtures of the two sulphides of copper were treated with 5 per cent solution of silver nitrate, at first while cold, then for three hours on the water bath, the residues were thoroughly washed, then extracted two or three times with the ferric nitrate solution. From the amounts of silver thus dissolved and remaining as sulphide the quantities of original cuprous and cupric sulphides were calculated, and the results showed very satisfactory agreements with the known composition of the mixtures.-Jour. Amer. Chem. Soc., xxxvi, 2475.

H. L. W.

2. Feldspar as a Possible Source of Potash.—A. S. CUSHMAN and G. W. Coggeshall have carried out experiments on a rather large scale, following the principle of the well-known analytical process of J. Lawrence Smith. The ground feldspar is mixed with a small proportion of burnt lime, then moistened with water containing about the theoretical amount of calcium chloride required to convert the potassium of the feldspar into chloride. This moistening causes the mixture to collect into small lumps. The product after drying is burnt in a long rotary furnace of the cement-kiln type by the use of powdered coal and an air blast. The nodules retain their form during the burning and are delivered while hot into water in order that the potassium chloride may be leached out. It is claimed that in this way more than 80 per cent of the potassium of the feldspar may be extracted, and that feldspar rock containing 10 per cent of potassium oxide may be readily obtained on the large scale. The authors have made careful estimates of the cost of this operation on a commercial

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, NO. 231.—MARCH, 1915.

scale and conclude that a product corresponding to the "80 per cent muriate" could be made for about \$31 per ton. This has previously cost about \$37.50 per ton as imported from Germany, and recently, owing to European conditions, a price of about \$100 per ton has been quoted. It appears that, if the calculations are accurate, the employment of feldspar as a source of potash is promising. The demand for potash salts in this country is very large, particularly for use as a fertilizer.—Jour. Indust. and Eng. Chem., vii, 145. H. L. W.

3. A Qualitative Test for Water.-E. R. WEAVER has devised a method for detecting very minute amounts of water in organic substances. It is sensitive to less than 0.1 mg. of water, and it depends upon placing the substance to be tested in contact with calcium carbide in the presence of a perfectly anhydrous solvent for acetylene. Any acetylene formed by the action of water is detected by adding the resulting solution to an ammoniacal solution of cuprous chloride. Nearly all the common organic liquids are suitable for the purpose of the solvent if carefully dried. The calcium carbide employed must be completely freed from adhering acetylene by adding to it some of the anhydrous solvent to be used and boiling the latter off completely. The test may be carried out by bringing the substance to be tested, the dry solvent and a few pieces of boiled out calcium carbide into a test tube. The tube is closed by a dry stopper and shaken occasionally for two or three minutes, without allowing the liquid to touch the stopper. The carbide is allowed to settle completely and the clear solvent is decanted into an ammoniacal cuprous chloride solution and vigorously shaken, when the red copper carbide shows that water was present. Of course very careful blank tests must be made with the reagents and apparatus used.-Jour. Amer. Chem. Soc., xxxvi, 2462. H. L. W.

4. The Rare Earths; by S. I. LEVY. 8vo, pp. 345. New York, 1915 (Longmans, Green and Co. Price \$3.00 net).-This book, which is of English origin, deals in a very satisfactory way with the occurrence, chemistry, and technology of this very mysterious group of elements. Much dignity is given to the work by a short but extremely interesting introduction by Sir William Crookes, who has made very extensive and valuable investigations in the field of the substances that are here discussed. He says that the rare earths constitute the most striking example of the association of chemical substances with others which are closely allied to themselves, and from which they are separated only with extreme difficulty; that they form a group to themselves, sharply demarcated from the other elements, and that it is his belief that by following the study of them to the utmost limits we may arrive at the explanation of what the elements really are and how they originated, and discover the reasons for their properties and mutual relations. He says, further, that there has long been a need for a work in the English language dealing historically and descriptively with these substances, and that Mr. Levy's book is well fitted to fill the gap.

In accordance with general usage the author has included the elements zirconium and thorium in his treatment, although they appear to fall outside the limits of the rare earth group proper. He has also included titanium chiefly on account of its general occurrence in the rare earth minerals and its relation in the periodic system to zirconium, cerium and thorium. The book is divided into three parts, the first of which deals with the occurrence of the rare earths, and is largely devoted to the minerals in which these earths occur. The second part, comprising about 250 pages, discusses the chemistry of the group, while the third part gives the technology of the elements and includes an interesting account of their applications in the lighting industry. H. L. W.

5. Ampère Molecular Currents.—It has been known for a long time that the electrical resistance of metals decreases in an approximately linear manner as the temperature is lowered, so that, if the straight line law continues to hold down to the absolute zero, the resistance should practically vanish in the vicinity of  $-273^{\circ}$  C. That this inference is correct has been shown by the experimental investigations of H. KAMERLINGH ONNES of Leyden. The observations made with a closed coil of lead wire are very striking and instructive, and a brief account of them will now be given.

The coil consisted of 1000 turns of wire, 1/70 mm. in diameter, wound on a brass-bobbin. The resistance of the coil at ordinary room temperature was 734 ohms, and it was calculated that the induced current would last for only 1/70,000 sec. after removal of the electromotive force. At 1.8° K., however, the "relaxation time," deduced from earlier determinations of the resistance, should be a matter of days. Theoretical considerations also led to the conclusion that the limiting value to which the current might be raised before the ordinary resistance would suddenly make its appearance was 0.8 ampere at 1.8° K. The coil, surrounded by a Dewar flask, was first placed between the poles of a large, excited electromagnet and then liquid helium was poured into the flask. After the coil had cooled down to about the boiling-point of helium at very low pressure (1.8° K.) the circuit of the electromagnet was broken in order to induce an electromotive force in the lead coil. The unexcited magnet was next removed and the presence in the lead coil of a current of about 0.6 ampere was shown by means of a suitable magnetometer system. No decrease in the magnetic moment caused by the induced current could be detected in the course of an hour, notwithstanding the fact that the temperature had risen to that of the boilingpoint of helium under ordinary atmospheric pressure, namely, 4.26° K. When the coil was removed from the bath the current ceased as soon as the temperature exceeded 6° K., which is the "vanishing point" of the electrical resistance of lead,

As a check on the preceding results the following experiments were performed. The observations were repeated with the plane of the lead coil parallel to the magnetic field, in order to test the

hypothesis that the magnetometer deflections noted in the preceding case (coil perpendicular to magnet's field) might have been due to some magnetic property of the wire or bobbin which existed only at very low temperatures. The very small deflections obtained could be fully accounted for as arising from slight asymmetry in the coil, hence the hypothesis just mentioned is untenable. "Other experiments finally disposed of all idea of direct magnetic action, and the actual presence of a continuing current was proved independently by attaching galvanometer leads to the points on the coil, and suddenly cutting the wire between them under the helium, when a swing of the galvanometer needle was observed, while the magnetometer immediately went to zero." It is thus seen that currents analogous to the molecular currents imagined by Ampère have been realized experimentally.-Nature, xciii, p. 481, July 9, 1914. H. S. U.

6. The Elements of Electricity and Magnetism; by WM. S. FRANKLIN and BARRY MACNUTT. Pp. viii, 351, with about 260 figures. New York, 1913 (The Macmillan Co.).-"The elementary theory of electricity and magnetism is essentially an extension of the science of mechanics, and the purpose of this book is to develop the science of electricity and magnetism from this point of view." Since the sequence of subjects differs from that followed in many other text-books of the same grade it may not be superfluous to enumerate the titles of the chapters, which are : "I The Electric Current. Its Chemical Effect. II Resistance and Electromotive Force. III The Magnetism of Iron. IV Magnetic Effect of the Electric Current. V Induced Electromotive Force. VI Electric Momentum. Inductance. VII Elec-The Condenser. VIII Phenomena of Electrostatics. tric Charge. IX Electric Oscillations and Electric Waves, and X Electrical Measurements."

The material selected seems to be presented in a manner preëminently adapted to attract and hold the attention of the student. Some of the features which combine to produce this impression may be briefly summarized as follows. The diagrams are large, clean-cut, and practical. Important facts, principles, and theorems are emphasized by italics. Mechanical analogies are stated and formulated in columns parallel to the corresponding electrical relations. 158 wholesome problems (with answers) are distributed through the volume. The appendices deal with terrestrial magnetism, ship's magnetism, and the compensation of the compass, miscellaneous phenomena (thermo-electricity, Zeeman effect, etc.), and miscellaneous practical applications (quadruplex and wireless telegraphy, etc.). Unfortunately the present volume does not differ in the minutest detail (save the date) from the edition published in July, 1908, and hence all of the typographical and other errors have been retained. H. S. U.

7. Molecular Physics; by JAMES ARNOLD CROWTHER. Pp. viii, 167, with 29 figures. Philadelphia, 1914 (P. Blakiston's Son and Co.).—A fair idea of the nature and scope of the text may be

obtained from the following list of the titles of the successive chapters, namely : "The Physics of the Electron, The Positive Particle, The New Method of Analysis, The Nature and Size of an Electron, The Chemistry of the Model Atom, The Atom in Vibration, The Molecular Theory of Matter, and The Atom in Dissolution." Elementary proofs of certain mathematical formulæ and a table of atomic data are given in three appendices. The volume closes with a short bibliography of the most important books and memoirs pertaining to its special field. The semipopular manner of presentation and the brevity of the text may furnish sufficient reasons for the absence of an index.

Of the several elementary books on the subject which have come to our notice the present one contains the most interesting and reliable account. This is due, in part at least, to the fact that the author spent eight years in the Cavendish Laboratory during the period when the brilliant researches of J. J. Thomson were in progress. The typographical errors are fairly numerous, but of such a nature, in general, as to admit of obvious correction.

H. S. U.

8. General Physics: Electricity, Electromagnetic Waves and Sound ; by J. A. CULLER. Pp. x, 321, with 224 figures. Philadelphia, 1914 (J. B. Lippincott Co.) .- This is a companion volume to the author's "Mechanics and Heat" (see vol. xxviii, page The endeavor has been made "(1) To make the descrip-557). tions, proofs, statements, and illustrations clear to the average student. (2) To emphasize the physical side of physics, point out its applications in the commercial world, and give more than an outline in the development of a topic. (3) To incorporate in the body of the discussions and in their proper place the electronic and electromagnetic theories now so well established." The third aim, namely, the explanation of electrical phenomena in terms of the electron, is the most novel feature of the text. Another salient point is the treatment of the entire subject of light in the chapter on electromagnetic waves. The discussion of optical apparatus is enhanced by the use of the curvature of wave-surfaces, sagittas, etc. The subject of sound is wisely condensed into one chapter (pages 270-293). Most of the figures are satisfactory diagrams, and four are excellent half-tones. Whenever feasible the chapters close with lists of problems (100 in all) with numerical answers. The appendix contains certain proofs which involve the calculus, special topics, and tables of physical and mathematical constants.

In spite of the fact that the book has many admirable features it is but fair to state that the information imparted is not unqualifieldy up to date. For example, on page 247 may be found the statement that "X-rays, however, cannot be reflected, refracted, or diffracted, and hence no way is known by which their wave-length can be determined." As a matter of fact, the determination of the wave-lengths of Röntgen rays is now an everyday occurrence, the field having been opened up by the work of Friedrich, Knipping, and Laue, whose first paper appeared about June, 1912 (see vol. xxxv, page 454). H. s. U.

#### II. GEOLOGY.

Thirty-fifth Annual Report of the Director of the U.S. 1. Geological Survey, GEORGE OTIS SMITH, Director, for the fiscal year ended June 30, 1914. Pp. 163, plates I and II. Washington, 1914.-Of a total expenditure of \$1,462,000 for the year 1913-14, \$575,000 of the Geological Survey funds were devoted to researches which may properly be classed as geologic, including mineral resources, geologic surveys, water resources and chemical and physical investigations; \$425,000 were expended for mapping. The Survey staff enrolls 891 persons holding appointments of the Secretary of the Interior, and the total amount paid in salaries and wages was \$1,077,000. The nationwide activities of the Survey are indicated by the fact that geologic investigations were carried on in 47 states, Alaska, Hawaii, and the Canal Zone, covering an area of 75,000 square miles. The topographers mapped 25,000 square miles, an area nine-tenths the size of the United Kingdom. The number of the various publications distributed was 1,105,711, a figure much in excess of that of previous years, and one which indicates a growing appreciation, on the part of the public, of the scientific investigations of this branch. Aside from published material, the extent to which the Survey is utilized is indicated in some degree by the increasing amount of mail handled. During the year 255,502 pieces of mail matter were received by the executive division, and 365,090 pieces of letter mail were dispatched, an increase of 20 per cent.

One of the most valuable features of the Survey policy is the coöperative agreements for investigations in the individual states, and with other departments of the Government. Coöperative geologic researches are now being undertaken in fourteen states, examination of mineral resources in eighteen states, topographic surveys in nineteen states. Coöperation is also effective with the Land Office, the Indian Office, the Bureau of Mines, the Bureau of Standards, the Department of Justice, the Office of Public Roads, the Smithsonian Institution, the Isthmian Canal Commission, the Geophysical Laboratory, and the Marine Biological Station. In the Land Classification Board the Government has now expert scientific advice regarding the disposition of public lands. H. E. G.

2. Publications of the United States Geological Survey.—Recent publications of the U. S. Geological Survey are noted in the following list (continued from vol. xxxviii, pp. 484-487):

Thirty-fifth Annual Report of the Director, GEORGE OTIS SMITH.—See above.

PROFESSIONAL PAPERS.—No. 90. Shorter Contributions to General Geology. F. A Reconnaissance in the Canyon Range, West-Central Utah; by G. F. LOUGHLIN. Pp. 51-60; 1 pl., 5 figs. G. The Montana Group of Northwestern Montana; by EUGENE STEBINGER. Pp. 61-68; 1 fig. H. A Deep Well at Charleston, South Carolina; by LLOYD W. STEPHENSON, with a report on the mineralogy of the water; by CHASE PALMER. Pp. 69-94; 3 figs.

GEOLOGICAL ATLAS, FOLIOS.—No. 191. Raritan Folio, New Jersey; by W. S. BAYLEY, R. D. SALISBURY and H. B. KÜMMEL. Pp. 32; 5 maps and columnar sections.

No. 192. Eastport Folio, Maine; by E. S. BASTIN and H. S. WILLIAMS. Pp. 15; 4 maps, 23 pls.

No. 193. San Francisco Folio (Tamalpais, San Francisco, Concord, San Mateo and Haywards Quadrangles), California; by A. C. LAWSON. Pp. 24; 15 maps, columnar sections, 10 pls.

No. 194. Van Horn Folio, Texas; by G. B. RICHARDSON. Pp. 9; 3 maps, 9 pls.

MINERAL RESOURCES of the United States. Calendar Year 1913—Part I. Mineral Products of the United States: Review of conditions and output in 1912 and 1913; by EDWARD W. PARKER. With a summary of Mineral Production in 1913: compiled by W. T. THOM. Pp. vii-clxix; 1 fig. and map in pocket. Also numerous advance chapters of the final report upon special subjects, chiefly the metals, gold, silver, copper, etc.

BULLETINS.—No. 541. Contributions to Economic Geology (short papers and preliminary reports), 1912. Part II. Mineral Fuels. MARIUS R. CAMPBELL, Geologist in Charge. Pp. 532; 29 pls., 17 figs.

No. 561, 562, 570, 572. Results of Spirit Leveling. R. B. MARSHALL, Chief Geographer. No. 561, Hawaii, 1910–1913. Pp. 42; 1 pl. No. 562, Virginia, 1900–1913. Pp. 68; 1 pl. No. 570. Wisconsin, 1897–1914. Pp. 86; 1 pl. No. 572. Nebraska, 1896– 1913. Pp. 57; 1 pl.

No. 576. Geology of the Hanagita-Bremner Region, Alaska; by FRED H. MOFFIT. Pp. 56; 6 pls. (2 maps in pocket), 6 figs.

No. 580. Contributions to Economic Geology, 1913. Part I. M. The Rochester Mining District, Nevada; by FRANK C. SCHRADER. Pp. 325-372; 1 pl., 4 figs. N. The Elliston Phosphate Field, Montana; by R. W. STONE and C. A. BONINE. Pp. 373-383; 1 pl. O. The Rutile Deposits of the Eastern United States; by THOMAS L. WATSON. Pp. 383-412; 5 figs.

No. 581. Contributions to Economic Geology, 1913, Part II. C. The Moorcroft Oil Field and the Big Muddy Dome, Wyoming. Papers by V. H. BARNETT. Pp. 83-116; 2 pls., 1 fig. D. Geology and Oil Prospects in Waltham, Priest, Bitterwater, and Peachtree Valleys, California, with notes on Coal; by ROBERT W. PACK and WALTER A. ENGLISH. Pp. 119-160; 1 pl., 4 figs.

No. 590. Reconnaissance of the Geology and Oil Prospects of Northwestern Oregon; by CHESTER W. WASHBURNE. Pp. 111; 1 pl.

No. 600. The Glacier National Park. A Popular Guide to its Geology and Scenery; by MARIUS R. CAMPBELL. Pp. 53; 13 pls. (map in pocket), 3 figs.

WATER SUPPLY PAPERS.—No. 326, 329, 330. Surface Water Supply of the United States, 1912. Part VI. Missouri River Basin; by W. A. LAMB, ROBERT FOLLANSBEE, and H. D. PADGETT. Pp. 375; 2 pls. No. 329. Part IX. Colorado River Basin; by ROBERT FOLLANSBEE, E. A. PORTER, and H. D. PADGETT. Pp. 238; 2 pls. No. 330. Part X. The Great Basin; by F. F. HENSHAW, E. A. PORTER and G. C. STEVENS. Pp. 275; 3 pls.

No. 335. Geology and Underground Waters of the Southeastern Part of the Texas Coastal Plain; by ALEXANDER DEUSSEN. Pp. 365; 9 pls., 17 figs.

No. 340. Stream-Gaging Stations, etc., 1885–1913 (compiled by B. D. WOOD). D. Part IV. St. Lawrence River Basin. Pp. xx. E. Part V. Hudson Bay and Upper Mississippi River Drainage Basins. Pp. xxi.

No. 344. Deschutes River, Oregon and its Utilization; by F. F. HENSHAW, JOHN H. LEWIS, and E. J. MCCAUSTLAND. Prepared in coöperation with the State of Oregon, JOHN H. LEWIS, State Engineer. Pp. 200; 28 pls., 8 figs.

No. 345. Hydrology of the United States, 1914. G. The Water Resources of Butte, Montana; by O. E. MEINZER. Pp. 79-125; 3 pls., 4 figs.

No. 347, 348, 366. Profile Surveys prepared under the direction of R. B. MARSHALL, Chief Geographer. No. 347. Snake River Basin, Idaho. Pp. 12; 3 pls. No. 348. Hood and Sandy River Basins, Oregon. Pp. 8; 2 pls. No. 366. Snoqualmie, Sultan and Skykomish Rivers, Washington. Pp. 7, 3 pls.

3. Sixth Biennial Report of the Commissioners of the State Geological and Natural History Survey of Connecticut for 1913-14. Bulletin No. 25, 1915. Pp. 24.—Since its organization in 1903, the Connecticut Survey has received an annual appropriation of \$1500. With this insignificant sum at his disposal the Director has secured remarkable results. Twenty-one bulletins have been published, covering the fields of geology, zoology and botany, three bulletins are in press, and five more are represented by completed manuscripts. According to a coöperative agreement with the United States Geological Survey, effective in 1913, \$2000 per year has been allotted to investigation of water resources and plans for the next biennial report involve the continuation of this work. H. E. G.

4. Topographic and Geologic Survey of Pennsylvania, RICHARD R. HICE, State Geologist. Report No. 9, Minerals of Pennsylvania; by AMOS P. BROWN and FREDERICK EHRENFELD. 1913. Pp. 160, pls. I-X, 1 fig. Harrisburg, 1913.—Pennsylvania ranks first among the states as a producer of coal and coke, pig iron, lime, mineral paints, sand, gravel, and building stone, and a mineralogical collection suitable for museums may be obtained within the borders of the state. The report by Brown and Ehrenfield is a sort of elementary text-book which should find a place in schools as well as in the libraries of the miner and prospector. H. E. G.

5. The Problem of Volcanism; by JOSEPH P. IDDINGS. Pp. 273, 8vo, 86 pls. and chart. New Haven, 1914 (Yale Univerity Press).—This volume contains in printed form the lectures delivered by Prof. Iddings on the Silliman foundation at Yale Uni-

#### Geology.

versity in the spring of 1914. The work contains eight chapters, corresponding to the number of lectures given. It should be stated at the outset that the author uses the term "volcanism" in its broadest sense to include the varied forms in which the igneous activity of the earth manifests itself. His purpose has been to present the problem of volcanism in this sense, rather than a theory or a supposed explanation of it. And since any conception of the problem must be modified, not only by our knowledge of the physical properties of the earth as a whole, but by its origin and astronomical relations, these phases of the subject are also treated.

The first chapter undertakes a brief review of the material for discussion: various types of volcanic activity, both extrusive and intrusive, are described with mention of their geographical distribution; and in this way the problem which is to be treated is laid briefly before the reader.

In the second chapter the author takes up the nebular hypothesis for the origin of the earth, and reviews it historically, commencing with Buffon and Kant. He shows that the conceptions of Laplace, in the general form postulated by him, are still applicable, though the particular hypothesis in which it has been restated by geologists under his name may be no longer tenable. He shows how the idea of the nebular origin of the planetary system has grown and how greater knowledge of nebulæ has affected it; carrying the discussion down to the conceptions of Chamberlin and Moulton, who have treated it from mathematical and physical standpoints. The author concludes with the statement that "It seems reasonable to assume that nebulæ are not highly heated; that exploding and expanding matter, if finely divided and distributed through an enormous space, would cool far below its former temperature, if derived from a disrupted sun ; that subsequent aggregation would be a very gradual process, and that whatever heat were generated by impact would be dissipated without considerable rise in temperature; that the heat of condensation might be a principal source of internal heat in a globe so formed, but that its amount would be greatly modified by the size and mass of the aggregation, the physical character of its components, and by the time occupied in its growth."

In the next chapter the general physical characters of the earth as a whole are considered; its relief, variations of gravity, nature of its outer shell, etc., and the conclusion is reached that the earth is a heterogeneous elastic solid, subject to accumulating stresses that periodically exceed the limit of elasticity and cohesion. This chapter is followed by one dealing in a general way with the more important petrological features of the rocks composing the earth's outer shell; and is succeeded by the fifth one, treating of the dynamical status of the earth, in which conceptions as to its possible interior constitution and physical and chemical properties are advanced, postulated on an origin from a nebular condition in agreement with the author's viewpoint.

The next two chapters, VI and VII, will be, perhaps, the most important and interesting of the work to geologists. They present the author's conception of the nature of magma, beginning with it in its original seat, and following it upward until it appears in various forms of intrusion in the upper lithosphere or, as in the last one, VIII, in extrusions of lava upon the earth's surface. In accordance with the conditions imposed by astronomical considerations, and shown to exist, by seismical investigations, with respect to the physical status of the earth, magma in its original place toward the base of the lithosphere must be conceived as a condition of a zone of the latter, not as any mass of a liquid nature. Although highly heated, it is rigid, but potentially mobile, and may shift its position slowly as adjustments of the lithosphere cause differential changes in pressure. In the beginning it can have no definite boundary, but as it moves upward its viscosity diminishes with lessening pressure, and it enters the zone of intrusions. The possible cases of such intrusions are fully discussed; thus the bathylith is conceived by the author as a broad flattened body in nearly horizontal position, where magma has entered the fractured lithosphere in regions of major thrusting, as on the Pacific border. It is when the magma leaves what we may term the zone of speculation and enters that one where observation is possible that the ideas of the writer will be especially open to testing by other geologists. His conceptions seem logical, and are based upon geological observations and buttressed by reference to the known laws of physics and chemistry, but some of them will probably not be accepted without discussion. Thus, while it would seem as if Prof. Iddings had presented powerful arguments against the hypothesis of the upward movement of magma into the outer lithosphere on a large scale by the sinking and assimilation of crust blocks in the depths, his view that spalling and sinking of blocks cannot probably occur at all (p. 210) on account of the viscosity and pressure of the magma, places one on the horns of a dilemma. For if the magma were always of this nature it is difficult to see how differentiation, under any terms of that process, could take place. It would seem to the reviewer as if only highly siliceous, and, therefore, viscous magmas, were in the author's mind, but in the less siliceous ones greater fluidity might be expected, which would give opportunities for differentiation, and in these at times, under suitable conditions, the sinking of crust blocks might be expected to a limited extent.

The volume is a most important contribution to the theoretical side of geology; it is very stimulating and should be read by every worker in the physical fields of this science. It is handsomely printed and abundantly illustrated with halftone plates and fine photogravures of nebulæ. L. V. P.

6. Pleistocene Mammals of Iowa; by OLIVER P. HAY. Annual Report, Iowa Geological Survey, for 1912, 1914, pp. 1-499, pls. I-LXXV, 142 text figs.—This important contribution by the well-

#### Geology.

known paleontologist of the Carnegie Institution of Washington constitutes almost the entire volume. In it Doctor Hay treats exhaustively not only all Pleistocene mammals which have been found within the limits of Iowa, but those which from their known distribution may be expected to be found. He also discusses in detail the skeletons and measurements of certain existing types to enable the future discoverer of Iowa fossils more readily to identify his material. Doctor Hay has already done valuable service in his recognition of the various Pleistocene faunas, of which little was clearly known before he began his studies, and the present work furthers our knowledge of Quaternary animals very materially.

The Iowa Pleistocene contains a very large fauna, as its central position and abundance of fossil-bearing localities would lead one to expect, and this is discussed in much detail. Preliminary to such description, however, the following topics are treated : Definition of the Pleistocene, division of the Pleistocene into its five glacial and five interglacial periods, and a study of these times in detail. The author next describes the loess, which covers practically the whole state except that part which is overlain by the Des Moines lobe of the Wisconsin drift and some counties along the southern border. Loess rarely overlies the Wisconsin drift. Another section describes the localities in Iowa where Pleistocene vertebrates have been found, and this subject is further elucidated by a map. A bibliography follows.

The second part of the work is entitled "The mammals of the Pleistocene," and herein the paleontological discussion is found. To enumerate the former briefly, there have been discovered :

Of the ground sloths, two, *Mylodon* and *Megalonyx*; five horses, four of the genus *Equus* and one three-toed *Neohipparion* doubtfully reported from the Aftonian; no tapirs or rhinoceroses, as the latter had become extinct, and the range of the former was farther south. The artiodactyles are represented by at least three pig-like animals related to the modern peccary, one camel, and several deer, representing at least five genera, *Odocoileus, Cervus, Cervalces, Alces* and *Rangifer.* In addition, there were the prongbuck, a new goat, musk oxen, and bison, including at least four and probably six species, two of which are as yet undiscovered within the limits of the state.

Proboscidea were an abundant and conspicuous element in the Iowa Pleistocene, including two genera of mastodons, Mammut and Rhabdobunus, the latter being a new name to take the place of Dibelodon, which may prove a synonym. Of Mammut, Hay recognizes two species : the common mastodon, M. americanum, and a new form with large persistent lower incisors which he calls M. progenium. The true elephants are represented by all three American species, Elephas primigenius, E. columbi, and the majestic E. imperator.

Rodents must have swarmed over the state, but the only ones which seem to be actually recorded from the Pleistocene are the living cottontail rabbit, the existing Canadian beaver, and the giant beaver, *Castoroides*, with a length of 8 or 9 feet and eight times the bulk of its living relative. Carnivora are represented by the brown bear, common skunk, prairie wolf, and the extinct *Canis mississippiensis*, allied to the timber wolf of to-day.

It is to be regretted that in his extended analysis Doctor Hay did not give revised lists of each of the successive faunas. The few which are given, like the Aftonian fauna, seem to include questionable forms.

The figures are well drawn, and there is an abundance of wellchosen photographs reproduced in the plates. The latter are for the most part, however, very poor half-tone prints, which lack clarity of detail and mar the appearance of the work.

Doctor Hay's work is highly important, and it is hoped that so well-equipped an authority may be able to extend his studies to include the Quaternary of the entire continent. R. s. L.

7. Notes on Agelacrinidæ and Lepudocystinæ, with descriptions of Thresherodiscus and Brockocystis; by AUG. F. FOERSTE. Bull. Sci. Lab. Denison Univ., vol. 17, pp. 399-487, pls. 1-6, 8 text figs., 1914.—The author here describes the detail of the forms cited in the title, along with some new species and the new genera Thresherodiscus and Brockocystis. C. s.

8. An Introduction to the Study of Fossils (Plants and Animals); by HERVEY WOODBURN SHIMER. New York 1914 (The Macmillan Company).—Professor Shimer presents in this new book an introduction to the various types of organisms found fossil, treated by way of their living representatives. The first 82 pages are devoted to plants, followed by 238 pages treating of invertebrates, and 82 pages describing vertebrates. The subject matter is handled in a broad and general way, as for instance among the brachiopods (25 pages), where 12 pages are devoted to general characteristics and the remainder to 11 genera representative of this class of organisms, illustrated by 43 figures. To fasten the information in the student's mind and to facilitate laboratory work, 57 questions are a-ked in 12 different places.

This is a good elementary book with which to begin the study of paleontology, and if the subject is pursued along with the laboratory studies as designed by the author, the illustrations are sufficient. The best part of the book is that relating to the invertebrates; while the other two divisions are adequate for general information, they are yet not detailed enough for students intending to pursue paleobotany or vertebrate paleontology. C. S.

9. Notes on the Paleontology of Preston County : Fossil fauna of the Conemaugh rocks; by W. ARMSTRONG PRICE. West Virginia Geol. Surv., Preston County Rept., pp. 472-553, pls. 42, 43, 1914.—The author describes the entire fauna known from the Conemaugh division of the Pennsylvanian of Preston County, West Virginia. There are 71 named forms (3 new), all invertebrates, and carefully identified with authentic material. Of these 15 are brachiopods, 31 bivalves, and 17 gastropods. C. S. 10. A Beatricea-like organism from the Middle Ordovician; by PERCY E. RAYMOND. Geol. Surv. Canada, Museum Bull. No. 5, 1914, pp. 1-19, pls. 1-4.—This excellent paper describes in detail the form and internal structure of the oldest known form of Beatricea under the name of Cryptophragmus antiquatus, n. gen. n. sp. It is found just below the Lowville in the Pamelia formation (Ordovician) of Ontario and New York. The internal structure shows it to be the cylindrical base of a vertically growing hydroid closely related to the stromatoporids.

In a paper just published by M. Heinrich (Centralbl. f. Min., etc., 1914, No. 23, pp. 732-736), the families Labechidæ and Idiostromidæ, one of which includes *Beatricea*, are removed from the order Stromatoporoidea. As this paper is of importance to American paleontology, a translation of it will be presented later in this Journal. c. s.

11. The Middle Triassic marine invertebrate faunas of North America; by JAMES PERRIN SMITH. U. S. Geol. Surv., Prof. Paper 83, 1914, pp. 254, pls. 99.—This abundantly illustrated and valuable monograph of the Middle Triassic invertebrate faunas of the western United States describes 153 species, and lists 7 vertebrates. Of the invertebrates, 124 are ammonids (in 36 genera), 6 belemnids, 5 nautilids, 11 bivalves, 6 brachiopods, and 1 Pentacrinus. These faunas are in part of northern Pacific-Asiatic origin, but mainly of Euro-Tethyian derivation, apparently by way of Gondwana and northern Mexico. A large and detailed interregional correlation table of all Triassic time faces page 4.

C. S.

12. New Miocene Coleoptera from Florissant; by H. F. WICK-HAM. Bull. Mus. Comp. Zoöl., vol. lviii, No. 11, 1914, pp. 423-494, pls. 1-16.—The author here describes 86 new forms of Coleoptera, and these, together with those taken up in another paper in press, raise the total number of species of this order found in the Florissant shales to 494. About 80 additional forms still await description. Wickham concludes : "From these considerations we are justified in believing that the proportional development of the various coleopterous families during the Miocene times differed, sometimes very decidedly, from that obtaining to-day. Consequently we should be conservative in using data derived from comparison of these lists with recent ones as bases of conclusions as to probable climatic conditions." c. s.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Insects Injurious to the Household; by GLENN W. HER-RICK. Pp. xvii, 470, with 152 figures and 8 plates. New York, 1914 (The Macmillan Co.).—This volume of the Rural Science Series contains a general account of the insects and related animals, such as spiders, ticks, and mites, which are in any way harmful or annoying to man, and which are likely to invade the dwelling. The manner in which flies, mosquitoes, fleas, and other unwelcome visitors to the household bring with them the germs of some of our most dreaded diseases is clearly pointed out, and simple directions are given for the extermination and exclusion of these pests. Of the other insects which destroy the furnishings of the home and the food and clothing of its members, the book contains the necessary descriptions of the appearance and habits of each species and of the means of preventing injury. There are also included such insects as are annoying by their bites or stings, those which are reputed to be poisonous, and those which are parasitic upon the human body. The descriptions are free from technical terms, and the numerous figures will aid in the identification of the species.

Of all branches of human knowledge, that pertaining to the health and prosperity of the community is perhaps the most important, and is in no small measure dependent upon a knowledge of just such facts as are so clearly stated in this book. An enlightened community may therefore reasonably expect of every citizen some knowledge of the insects which endanger the home and of the means by which they may be destroyed. W. R. C.

2. The Germ-cell Cycle in Animals; by ROBERT W. HEGNER. Pp. x, 346, with 84 figures and an extended list of references to literature. New York, 1914 (The Macmillan Company).—The author traces the history of the germ-cells from one generation to the next in nearly all the species of animals in which this history has been discovered. The account is based largely on the author's own investigations in this comparatively new field of study and shows how the germ-cells, which are reserved for the perpetuation of the species, are very early in embryonic life completely differentiated from those that are to form the body itself. Although necessarily somewhat technical in nature, no other treatise presents the subject so logically, clearly, and exhaustively. The work is well illustrated, and the facts presented will have an important influence on the modern conceptions of the mechanism of inheritance. W. R. C.

3. Dynamic Evolution: A Study of the Causes of Evolution and Degeneracy; by CASPER L. REDFIELD. Pp. xi, 210. New York and London, 1914 (G. P. Putnam's Sons).—The author attempts to prove from an extensive study of the pedigree records of trotting horses, and of cattle, dogs, and men, that the characters transmitted to the offspring of any individual are dependent in large measure on the reserve supply of energy which the individual possesses at the time of reproduction. The theory thus supports the formerly widely accepted Lamarckian doctrine that the effects of use and disuse are heritable, but this view is quite at variance with recent experience in experimental breeding. W. R. C.

4. Physikalische Chemie der Zelle und der Gewebe; von Prof. Dr. RUDOLF HÖBER. Privatdozent der Physiologie an der Universität Kiel. 4te Auflage. Pp. xvii, 808. Leipzig und Berlin, 1914 (Wilhelm Engelmann).—To reflect properly the advances of any rapidly growing branch of science in the form of a textbook requires an adequate appreciation of the progress initiated and a frequent revision to keep it up to date. The fact that Höber's book has attained sufficient popularity to encourage four editions, each an improvement on its predecessor, since 1902, is of itself evidence that this presentation of the interrelations of physical chemistry and physiology is helpful. During this period the physico-chemical viewpoint has indeed become essential for any broad consideration of biological problems. Each successive edition of Höber has maintained its leadership as an authoritative guide in the new field which it covers. A book which has become an almost indispensable work of reference in every laboratory where biological problems are dealt with requires no further review here. L. B. M.

5. Infection and Resistance, by HANS ZINSSER. Pp. xiii, 546. New York, 1914 (The Macmillan Co.) .- In this book an American student of the phenomena of infection, i. e. "the reaction which takes place between invading micro-organisms and their products, on the one hand, and the cells and fluids of the animal's body on the other," has summarized the current knowledge of the subject. The volume gives evidence of familiar laboratory acquaintance with the biological features involved along with an extensive study of the literature of infectious disease. Professor S. W. Young has appended a chapter dealing with colloids and the colloidal reactions lately drawn into account in the interpretation of the reactions of immunochemistry. It is gratifying to find in the volume appreciation everywhere of the contributions of American workers in this field. As may be expected in the case of a comparatively new and rapidly growing subject, Dr. Zinsser's chapters deal with much that is problematical and debated; but there is no serious difficulty in distin-guishing between fact and fancy in his presentation of such topics as antitoxins, opsonins, agglutination, phagocytosis, complement fixation, anaphylaxis, and the numerous others which belong to the young science of immunity. L. B. M.

6. British Museum Publications.—The following Catalogues and Memoirs have been recently issued by the British Museum:

Catalogue of the Ungulate Mammals in the British Museum (Natural History). Vol. III. Artiodactyla, Families Bovidæ, Subfamilies Æpycerotinæ to Tragelaphinæ (Pala, Saiga, Gazelles, Oryx Group, Bushbucks, Kudus, Elands, etc.) Antilocapridæ (Prongbuck), and Giraffidæ (Giraffes and Okapi); by R. LYDEK-KER, assisted by GILBERT BLAINE. Pp. xv, 283; 50 figures. The title above quoted gives the scope of this third volume of the British Museum Catalogue of Ungulate Mammals. The fourth volume is in preparation and will include the remainder of the Artiodactyla.

A Revision of the Ichneumonidæ: based on the Collection in the British Museum (Natural History). Part III. Tribes Pimplides and Bassides; by CLAUDE MORLEY. Pp. ix, 148. The second part of this revision of the Ichneumonidæ by Mr. Morley was published in 1913. The present Part includes two additional tribes, and is illustrated by a plate in color by Mr. Rupert Stenton.

A Monograph of the Genus Sabicea; by HERBERT F. WERN-HAM. Pp. 82; 12 pls., and text-figs.—This is the first of a series of monographs planned as the result of a study of the family of Rubiaceæ by Mr. Wernham. It is based on a study of the collections of the Royal Gardens at Kew, and also the principal continental Herbaria.

Report on Cetacea stranded on the British Coasts during 1913; by S. F. HARMER. Pp. 12, with 1 text-figure and 3 maps.

Catalogue of the Lepidoptera Phalænæ in the British Museum. Supplement, Vol. I. Catalogue of the Amatidæ and Arctiadæ (Nolinæ and Lithosianæ); by GEORGE F. HAMPSON. Pp. xxviii, 858; 276 figs.—This Supplement contains descriptions of the large numbers of species in the families of this great work embraced in Vol. I, published in 1898 and Vol. II, 1900. The name Amatidæ is substituted, according to priority, for that of Syntomidæ. A Supplement to Vol. III is planned.

#### OBITUARY.

PROFESSOR ANDREW WHEELER PHILLIPS, for many years professor of mathematics in Yale University, and the author of numerous mathematical works, died at his home in New Haven on January 10, in his seventy-first year.

DR. CYRUS FOGG BRACKETT, professor emeritus of physics at Princeton University, died recently at the age of eighty-two.

DR. BENJAMIN SHARP, the zoologist, and formerly corresponding secretary of the Philadelphia Academy of Natural Sciences, died January 25 at Morehead, N. C.

VICE-ADMIRAL SIR GEORGE NARES, the Arctic explorer, who, in addition to his contributions to our knowledge of the aretic regions, was also prominent in connection with several scientific voyages, particularly some of the "Challenger Expeditions," died on January 15, at the age of eighty-four.

MR. J. S. HARDING, prominent among English meterologists, died on January 11 in his seventy-sixth year.

MR. F. W. RUDLER, curator of the Museum of Practical Geology in London and author of many papers on geology and chemistry, died on January 23 in his seventy-fifth year.

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#### CONTENTS.

ART. XVThe Salton Sea; by D. T. MACDOUGAL	Page 231
XVI.—Illustrations of the Stem Structure of Tietea Singu- laris; by O. A. DERBY	251
XVII.—Petrographic Evidence on the Origin of the Cata- houla Sandstone of Texas; by M. I. GOLDMAN	261-
XVIII.—Age of the Igneous Rocks of the Adirondack Region; by H. P. CUSHING	288
XIX.—Unstable Chromium Sesquioxide, and Corrections of Previous Work on the Heat Effect of Chromium and Aluminum Sesquioxides in Fusions with Sodium Per-	0.0 5
oxide; by W. G. MIXTER.	295 300
XXI.—Relation of the Late Tertiary Faunas of the York- town and Duplin Formations; by JULIA A. GARDNER	305

#### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Determination of Cuprous and Cupric Sulphides in Mixtures of the Two, E. POSNJAK: Feldspar as a Possible Source of Potash, A. S. CUSHMAN and G. W. COGGESHALL, 311.—Qualitative Test for Water, E. R. WEAVER: The Rare Earths, S. I. LEVY, 312.—Ampère Molecular Currents, H. K. ONNES, 313.—Elements of Electricity and Magnetism, W. S. FRANKLIN and B. MACNUTT: Molecular Physics, J. A. CROWTHER, 314.—General Physics; Electricity, Electromagnetic Waves and Sound, J. A. CULLER, 315.
- Geology—Thirty-fifth Annual Report of the Director of the U. S. Geological Survey, G. O. SMITH: Publications of the United States Geological Survey, 316.—Sixth Biennial Report of the Commissioners of the State Geological and Natural History Survey of Connecticut for 1913-14: Topographic and Geologic Survey of Pennsylvania, R. R. HICE: The Problem of Volcanism, J. P. IDDINGS, 318.—Pleistocene Mammals of Iowa, O. P. HAY, 320.—Notes on Agelacrinidæ and Lepadocystinæ, with descriptions of Thresherodiscus and Brockoeystis, A. F. FOERSTE: Introduction to the Study of Fossils (Plants and Animals), H. W. SHIMER: Paleontology of Preston County; Fossil fauna of the Conemaugh rocks, W. A. PRICE, 322. A Beatricea-like organism from the Middle Ordovician, P. E. RAYMOND: Middle Triassic marine invertebrate faunas of North America, J. P. SMITH: New Miocene Coleoptera from Florissant; H. F. WICKHAM, 323.
- Miscellaneous Scientific Intelligence-Insects Injurious to the Household, G. W. HERRICK, 323.-Germ-cell Cycle in Animals, R. W. HEGNER: Dynamic Evolution; A Study of the Causes of Evolution and Degeneracy, C. L. REDFIELD: Physikalische Chemie der Zelle und der Gewebe, R. HÖBER, 324 --Infection and Resistance, H. ZINSSER: British Museum Publications, 325.

Obituary-A. W. PHILLIPS: C. F. BRACKETT: B. SHARP: SIR G. NARES: J. S. HARDING: F. W. RUDLER, 326.

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If so, you will find my stock now richer than ever before in beautiful examples suitable for both jewelry and specimens. Among the synthetic gems in my stock, all of which are of the finest quality, I have the following: Rubies, pink, white, blue and yellow Sapphires, and the latest discovery, the alexandrite. I have an unusually large stock of common and rare Semi-Precious and Precious Stones, both cut and in the rough. I am able to supply any gem desired, in best quality and all sizes.

### New Minerals

HODGKINSONITE:—I have been fortunate enough to secure the best specimens of this very rare mineral. It is from the celebrated Franklin Furnace Mines and is a rare compound, the formula of which is  $Mn(Zn OH)_2SiO_4$ . It crystallizes under the monoclinic system and is pink in color, associated with barite. In a few specimens it is associated with the rare minerals pyrochroite and gageite. The whole makes a very pretty specimen.

BETAFITE: — A member of a group of cubic minerals, niobotantalotitanites of uranium, etc., including also blomstrandite (of G. Lindstrom 1874) and samiresite (q. v.); they are closely allied to pyrochlore and hatchettolite, but differ from the former in containing titanium. Betafite is a hydrated niobate and titanate of uranium and occurs in pegmatite near Betafe, Madagascar. Named after the locality.

. Any of the above which may be desired for selection I shall be glad to send on approval to patrons and customers. Information and prices of individual specimens cheerfully furnished upon request.

### ALBERT H. PETEREIT

81-83 Fulton St.,

New York City

#### THE

## AMERICAN JOURNAL OF SCIENCE

#### [FOURTH SERIES.]

ART. XXII.—A Pleistocene Ground Sloth, Mylodon harlani, from Rock Creek, Texas; by Richard Swann Lull.

[Contributions from the Marsh Publication Fund, Peabody Museum, Yale University.]

> Introductory Locality Associated fauna Geologic age Specific summary Morphology Axial skeleton Skull Mandible Vertebræ Pelvis Ribs Appendicular skeleton Scapulæ Fore limb Hind limb Taxonomic summarv Bionomy Relationships and distribution

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#### INTRODUCTORY.

Two years ago it was the writer's privilege to conduct an expedition to the Panhandle of Texas with the avowed and fulfilled purpose of obtaining for the Peabody Museum at Yale a mountable skeleton of a fossil horse, *Equus scotti*, to add to the classic series of equine remains assembled by Professor Othniel C. Marsh.

We went at once to the type locality near the head of Rock Creek, and reopening the old quarry explored by Mr. James W. Gidley in the interests of the American Museum of Natural History, soon secured the needed skeleton. In the meantime we were made aware of a hill farther up the canyon

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 232.—April, 1915. 22 which gave abundant evidence of containing a mine of paleontologic treasure. The excavation of this hill employed us for several weeks and resulted in the finding of quantities of bone, mostly fragmental, but giving a very important faunal summary of Lower Pleistocene time in that the remains were necessarily those of contemporaneous forms. This fauna has been discussed in detail by one of my associates in the work, Doctor Edward L. Troxell, who made the data thus obtained the subject-matter of the dissertation for his doctorate at Yale.

Among the other material were the remains of at least four, and possibly five, individuals of the great ground sloth *Mylodon*. These, taken collectively, may serve to amplify our knowledge of the American Mylodonts, as they give a more complete representation of the skeleton than any previous American discovery, except perhaps the skeletons exhumed from the asphalt deposits at Rancho La Brea, near Los Angeles, California.

Locality.— The exact locality of the quarry is near the head of Rock Creek in Briscoe County, Texas. Rock Creek is a tributary of the Red River, which has carved for itself the profound Palo Duro canyon to a depth of 1400 feet. The valley of Rock Creek opens into Palo Duro canyon from the south.

Associated fauna. — The associated fauna, according to Doctor Troxell,\* includes the following forms:

CLASS MAMMALIA

Family Equidæ Equus calobatus Troxell Equus sp.

Family Camelidæ Auchenia hesterna Leidy Eschatius conidens Cope ? E. macrocephalus (Cope)

Family Canidæ

Canis dirus Allen

C. texanus Troxell cf. mississippiensis Leidy

C. ? sævus Leidy

C. temerarius Leidy

Family Elephantidæ

Elephas columbi Falconer or young imperator

Family Suidæ

Platygonus compressus Le Conte

CLASS REPTILIA Family Testudinidæ Testudo campester Hay

\* An abstract of Doctor Troxell's dissertation on the Rock Creek fauna, containing the description of several new species, will appear in a later number of this Journal.

These, together with the Mylodon, make at least twelve associated species representing five families of mammals and one of reptiles.

Geologic age.—The age of the fauna has been set forth by Osborn.\* who thus speaks of the Rock Creek beds:

"These beds are extensively exposed in the Staked Plains of Texas along the south side of Tule Cañon. As described above (p. 362) they represent a Lower Pleistocene river channel cutting its way into an older Miocene horizon."

And on page 362 he says:

"A third period of river or flood-plain formation traversing the same Lower Miocene substratum [of northwestern Texas] occurred during the Pleistocene epoch, laying down the broad bands of the 'Rock Creek formation', also of fluviatile, alluvial, and æolian origin, composed of cross-bedded sands, gravels, and clays. The wind, carrying large quantities of fine dust and sand on the surrounding plains, may have played an important part in forming these deposits. The mammals represented consisted wholly of land forms, and some of the bones show weather-checking; they contain the characteristic Lower Pleistocene forms, Equus, Elephas imperator, and Platygonus."

Doctor Hay+ in 1912 says:

"In his Age of Mammals, 1910, Osborn adopts, in general, the views of Cope, recognizing, however, four faunas, which he named the fauna of the first or Equus-Mylodon zone; the fauna of the second, or Megalonyx zone; the fauna of the third, or Ovibos-Rangifer zone; and that of the fourth, or Cervus zone. The latter fauna is that which existed at the time of the discovery of the continent by Columbus.... Professor Osborn holds that the Equus-Mylodon fauna occupied the dry Plains regions, but also the coast of Florida (p. 452), while the Megalonyx fauna had possession of the forested regions of the eastern part of the United States and of the Pacific Coast (p. 467)...

"As to the time of the existence of the Equus-Mylodon and the Megalonyx faunas, Osborn (p. 454) is inclined to believe that they were to a great extent contemporary, but that probably early phases of the Equus-Mylodon fauna antedated the beginning of the Megalonyx fauna."

Thus the evidence points to the age of the species under consideration as early Pleistocene.

\*Osborn, H. F., The Age of Mammals, p. 458, 1910. + Hay, O. P., Smithson. Misc. Coll., vol. lix, No. 20, p. 3, 1912.

#### SPECIFIC SUMMARY.

The North American Mylodonts have been referred to two genera and six species, of which the list follows:

#### Mylodon Owen

Mylodon harlani Owen. Referred by Harlan to Megalonyx laqueatus. Type locality, Big Bone Lick, Kentucky.

M. sodalis Cope. Pliocene of Oregon.

M. renidens Cope. Petite Anse, Louisiana.

M. sulcidens Cope. Petite Anse, Louisiana.

M. garmani Allen. Near Hay Springs, Nebraska.

#### Paramylodon Brown

Near Hay Springs, Nebraska. P. nebrascensis Brown.

In addition to these a species of *Mylodon* has been described from Colorado by Professor Cockerell, and a paper upon the Mylodonts of the Rancho La Brea of California has been published by Mr. Chester Stock. To the form mentioned in the former publication no name has as yet been assigned, although the Cockerell skull has been referred to *M. harlani* by Doctor Allen. The Rancho La Brea skulls, however, which Stock also refers to *M. harlani*, exhibit characters which serve to link up the two genera Mylodon and Paramylodon, to the confusion of the latter.

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Much additional material from widely remote localities has been referred to *M. harlani* by various authors, but with a considerable element of doubt, as the portions represented are rarely anatomically comparable with the type.

#### Mylodon harlani Owen.

Originally described by Harlan<sup>\*</sup> and attributed to Megalonyx laqueatus; recognized by Owen<sup>+</sup> as pertaining to a new genus, Mylodon, and dedicated to the original discoverer. Owen's description follows:

"Subsequently to the discovery of these bones, and of those of the Megalonyx laqueatus above alluded to, the remains of another great Edentate animal were found in North America, and were deposited in the Lyceum at New York; among these is a portion of the lower jaw with the whole dental series of one side. It is thus described by Dr. Harlan:

"' The fragment I am now about to describe is a portion of the dexter lower jaw of the Megalonyx, containing four molar teeth; three of the crowns of these teeth are perfect, that of

\* Harlan, R., Monthly Amer. Jour. Geol. and Nat. Sci., vol. i, p. 74, pl. 3, figs. 1-3, 1831. † Owen, R., Zoology, Voyage H. M. S. Beagle, Pt. I, p. 67, 1840.
# Mylodon harlani, from Rock Creek, Texas.

the anterior one is imperfect. These teeth differ considerably from each other in shape, and increase in size from the front, the fourth and posterior tooth being double the size of the first, and more compressed laterally; it is also vertically concave on its external aspect, and vertically convex on its internal aspect; the interior or mesial surface is strongly fluted, and it has a deep longitudinal furrow on the dermal aspect, in which respect it differs from the tooth of the *M. laqueatus* previously described by me, of which the dermal aspect is uniform, but to which, in all other respects, it has a close resemblance. I suppose it therefore probable, that this last may have belonged to the upper jaw. The three anterior molars differ in shape and markings: they are vertically grooved, or fluted, on their interior and posterior aspects, a transverse section presenting an irregular cube. The length of the crown of the posterior molar is two inches: the breadth about five-tenths of an inch: the length of the tooth is three inches and sixtenths. The diameter of the penultimate molar is eight-tenths by seven-tenths of an inch. The length of this fragment of the jawbone is eight inches and four-tenths; the height three inches and six-tenths: the length of the space occupied by the alveolar sockets five inches and eight-tenths. The crown of the tooth presents no protuberances, but resembles that of the Sloth; the roots are hollow."\*

This fossil, as stated above, was referred by Doctor Harlan to his *Megalonyx laqueatus*. Owen secured from M. Laurillard of the Jardin des Plantes, Paris, a drawing of a cast of the type jaw which the Museum possessed. Basing his conclusion upon this drawing, Owen says further:

"I am disposed to regard the amount of difference recognizable in every tooth in the lower jaw in question (figs. 3 and 4) as compared with the molar tooth either of Meyalonyx Jeffersonii (fig. 1) or Megalonyx laqueatus (fig. 2) to be such as to justify its generic separation from Megalonyx on the same grounds as Megalonyx is distinguished from Megatherium, and for the subgenus of Megatherioid Edentata, thus indicated, I would propose the name of MYLODON. The species of which the fossil remains are described by Dr. Harlan may be dedicated to that indefatigable Naturalist who has contributed to natural science so much valuable information respecting the Zoology, both recent and fossil, of the North American continent."

Leidy in 1855 + redescribes and figures the type specimens of Mylodon harlani, after which he enumerates other material

\*Harlan, Medical and Physical Researches, p. 334, 1835.

<sup>+</sup> Leidy, J., Smithson. Contrib. Knowl., vol. vii, art. V, pp. 47-49, 58, pl. 14, figs. 1-3, pl. 16, figs. 19-20.

331

from various localities which he refers to this species. The list follows :

1. Two fragments of the last molar in Mammoth Ravine, Mississippi.

2. Tooth and humerus, found on the Willamette, or Multonah River, a tributary of the Columbia in Oregon, referred to M. harlani by Owen.

3. A number of bones and teeth found by Mr. Koch, in association with remains of mastodon, etc., in Benton County, Missouri. These Harlan called *Orycterotherium missouriense*. but Owen, who had an opportunity to see the specimens, referred them to *M. harlani*.

4. Humerus from Big Bone Lick, Kentucky, preserved in the cabinet of the Academy of Natural Sciences, Philadelphia, an adult agreeing pretty closely with *M. robustus*, and its measurements according with those of the Oregon specimen described by Perkins.

5. The collection of Dr. Dickeson, deposited in the Academy of Natural Sciences, contains a number of bones of a half grown *M. harlani* found in association with *Megalonyx*, in the vicinity of Natchez, Mississippi.

Leidy's description of *M. harlani* reads :

"The left half of the lower jaw preserved with all its teeth. The bone in its present condition measures ten inches from its posterior margin to the anterior mental foramen, which is placed an inch and a quarter in advance of the position of the first molar; and its depth below the third molar is about two and a half inches. Its form agrees with the corresponding portion of the jaw of *Mylodon robustus* but is more convex externally in accordance with its age. The teeth have the same form and proportions as those in the adult fragment of jaw above described, except that the first of the series in transverse section is more demi-oval than reniform, and the anterior side of the second tooth is a little convex instead of being a little concave.

"The malar bone of the left side. It presents the same trilobate appearance as in *Mylodon robustus*.

"Fourteen fragments of vertebræ.

"The scapula of the right side. Its glenoid articulation and coracoid process have the same mode of development indicated in the account of the corresponding bone of the young skeleton of the *Megalonyx jeffersonii*.

"Both humeral diaphyses. These are nine and a half inches long, by seven and a half inches in circumference at the middle. The deltoidal tract already presents a prominent outline.

"The right ulnar diaphysis, which is eight and a half inches long, and its lower third is six and a quarter inches in circumference. The coronoid process rises almost from its middle.

"Both radial diaphyses. These are five and a half inches long, and four and a half inches in circumference about the middle.

"One ilium, two ischia, and an os pubis. Both femoral diaphyses accompanied by the head of one. Length of the diaphyses eleven inches; circumference about the middle ten inches.

"A tibial and fibular diaphysis. The former measures four and three-quarter inches in length, and seven inches in circumference about the middle; and the latter is about the same length, and two and three-quarter inches in circumference at the middle."

Professor Cope<sup>\*</sup> has described two new species of Mylodonfrom Louisiana, referring the other material in the lot to M. hartani. Of this latter species, the collection contains the following teeth: a complete series of superior molars, all separate, the anterior internal lobe of the third broken off; the second, fourth and fifth of the superior series of the opposite side, all separate; the first, third and fourth of the inferior series, all separate; separate first and third inferior molars.

# Mylodon sodalis Cope.

Cope's original description<sup>+</sup> of this species is as follows:

"The occurrence of this genus of sloths in Oregon was pointed out some years ago by Professor Leidy, as indicated by a specimen preserved in the museum of the Smithsonian Institution, but the means of determining its specific relations to the other species of the genus were not at that time extant. A number of phalanges, including those of the ungues, contained in my collection, demonstrate that the species of Oregon was quite different from those of the eastern portion of North America.

"The ungual phalange selected for description has its basal sheath developed on one side only; its place is taken on the opposite side by a prominent rim, which is tuberculate and notched. The rim is low on the superior part of the proximal extremity, and is separated from the articular cotylus by a concave subvertical surface, wider than long. The basal tendinous insertion is subdiscoid and flat, with a lateral projecting rim, which is pierced at the base by the arterial foramina. The general form of the phalange is more compressed than in *Mylodon harlani*. Its superior middle line is

\*Cope, E. D., Proc. Amer. Philos. Soc., vol. xxxiv, p. 458, 1896.

† Cope, E. D., Bull. U. S. Geol. and Geog. Surv. Territories, vol. iv, p. 385, 1878.

broadly rounded, and continues nearly uniform to the apex. One side is subregularly convex; the other is divided into three planes. The middle one of these is flat, and terminates in a short lateral ridge which extends to the apex. The superior plane becomes somewhat concave near the apex, and the inferior gently convex.

"The proximal phalanges have the form usual in the genus. They are rather short, and with the trochlear tongues and grooves strongly marked. The proximal extremities are especially expanded in the vertical direction.

"In size, this species equalled the M. harlani or the Megalonyx jeffersonii.

"From the Pliocene of Oregon."

To this species Cope \* also refers provisionally a specimen from Rock Creek, Texas, as follows :

" Mylodon ? sodalis Cope.—The distal part of a femur, lacking part of the internal condyle and adjacent epicondyle, represents a gigantic species of Mylodon. At present it is not possible to determine exactly its specific relations, but its association with the species of the Equus fauna renders it possible that it is the animal which has been found associated with the same fauna in Oregon, and which I have named as above. The measurements of the part preserved are about equal to those of the M. robustus, Owen, from Argentina. The transverse extent of the condyle is about 210<sup>mm</sup> (restored), of which the popliteal fossa is about  $60^{\text{mm}}$ .

"Since the species was described. I have received from Mr. George Duncan, of Paisley, Oregon, an imperfect symphysis mandibuli from near the original source of the M. sodalis, which presents characters appropriate to that genus and species."

# Mylodon renidens Cope.

Cope's original description reads as follows:

"This species is founded on a right maxillary bone, which contains all but the first molar tooth. This tooth is represented by an alveolus broken anteriorly, and the free portions of the crowns of the second and third molars are broken off. The crowns of the fourth and fifth molars are perfect. Associated with this specimen are the following, which probably belong to the same species: The posterior three molar teeth of the inferior series; a superior first molar in place in the anterior part of a right maxillary bone.

"The superior and inferior series referred to are considerably smaller than the corresponding parts of the M. harlanii,

\*Cope, E. D., Geol. Surv. Texas, 4th Ann. Rept., p. 78, 1893. +Cope, E. D., Proc. Amer. Philos. Soc., vol. xxxiv, p. 460, pl. 10, fig. 3, pl. 11, figs. 5, 6, 1896.

and might be supposed to have belonged to young individuals. As these animals are, however, monophyodont, it is evident that the only way in which a permanent dentition could be adapted to a growing jaw is by the appearance of but a part of the dentition at a time, or by a conical form of tooth crown, which will permit of the expansion of each tooth at the base. This mode of enlargement does exist for a short time among the Bruta, and this is exhibited in the teeth of the species called Sphenodon by Lund, and Megalonyx sphenodon by myself. The wider base is visible in the inferior series of Mylodon renidens in this collection, but the largest dimensions thus obtained are much below those of the *M. harlanii*. The superior molars display little if any expansion at the basis of the roots. The The crowns of both superior and inferior molars are worn. presence of a third inferior molar of a species of much larger size, but of the same peculiar character as that of the smaller series, shows that the character is constant and significant.

"The typical specimen consists of almost the entire right maxillary bone, with the teeth in place as above described. The alveolus for the first molar indicates that the latter has a subcylindric shaft, curved slightly posteriorly at the extremities. The second molar has a rather narrowly oval section, with a very slight concavity on the inner side, the long axis directed a little inwards anteriorly if truly antero-posteriorly. Dentine equally thick all round. Extremities of section regularly rounded. This tooth is like the corresponding one of the M. harlanii, and with a greater antero-posterior diameter than in the M. robustus. The third molar is reniform in section, wider anteriorly than posteriorly, the long diameter directed a little outwards anteriorly from strictly longitudinal. The posterior lobe is narrower than the anterior measured transversely, and neither lobe is flattened or truncate at any point. There are two longitudinal shallow grooves of the shaft; one submedian interior, the other opposite to it, presenting outwards and backwards at an angle of  $45^{\circ}$  to the axis of the jaw. This tooth is quite different in form from the corresponding one in the M. robustus and M. harlanii, in its relatively much greater antero-posterior diameter, approaching in this respect the form of the second superior molar.

"Three inferior molars, which correspond in size with the M. renidens, are provisionally referred to it; especially as the third presents characters quite distinct from those of the M. harlanii. The first tooth is not preserved. The second is like the corresponding tooth in the two larger species. The section is trilobate, the narrowest and most distinct lobe directed posterointernally; the long axis of the two other lobes, which are less distinct from each other, at  $45^{\circ}$  with that

of the jaw. The grinding surface of the two anterior lobes is directed obliquely forwards, and that of the posterointernal lobe obliquely backwards, for contact with the second and third superior molars.

"The third inferior molar exhibits externally the outlines of a parallelogram with rounded angles, in its cross-section, as in the other species, but the inner extremity is different. The internal border is oblique, and not parallel to the external border, owing to the fact that the anterior internal angle is much exterior in position to the posterior internal angle, from which it is separated by a shallow concavity which presents forwards and inwards, as the section of a groove of the shaft, which is wanting in the two larger species. The anterior and posterior faces present each an open shallow median groove.

"The last inferior molar does not differ in form from that of the *M. harlanii* and *M. robustus.*"

# Mylodon sulcidens Cope.

This species was described by Cope\* at the same time as the preceding one, as follows:

"This species is represented by a penultimate inferior molar of a species of the size of the *M. harlanii*. Accompanying the remains of the two species are two penultimate superior molars of opposite sides, which I suspect to belong to the *M. sulcidens*, as they differ from the corresponding teeth of the *M. harlanii* in the same way as the penultimate inferior molar.

"The penultimate inferior molar resembles closely that of the *M. renidens*, but has the dimensions of the *M. harlanii*. The internal extremity of the crown is beveled on the posterior border, so that an obtuse ridge characterizes the posterior side of the crown, which is separated from the posterior border of the external face. The latter is subtruncate.

"The penultimate superior molars look as though they belonged to the same individual, they so exactly agree. Their long diameter is obliquely transverse to the maxillary bone, and the internal face is deeply grooved as in other species of the genus, the anterior ridge being much less prominent than the posterior. The character which distinguishes the tooth from that of the other species is that the external aspect instead of being regularly rounded is obliquely beveled posteriorly so as to produce an obtuse angle on the posterior side within the posterior margin. This is separated from the posterior internal rib by a shallow concavity. When the tooth is held obliquely, as it was in the jaw, the external bevel is parallel with a line connecting the two internal ribs or borders."

\* Cope, E. D., op. cit., p. 462, pl. 10, fig. 4, pl. 11, fig. 7.

# Mylodon garmani Allen.

This, the latest species of *Mylodon* to be differentiated, was described by Allen<sup>\*</sup> in 1913, as follows :

"*Type.*--Well preserved skull and parts of the skeleton, No. 8429 M.C.Z., from the Pleistocene of the Niobrara River, Nebraska. Samuel Garman, 1880.

"*Horizon.*—The locality is practically the same as that of the Hay Springs fauna, probably Mid Pleistocene, though precise details of the situation are lacking.

"General characters.—A large species about the size of *M. harlani*, from which it differs conspicuously in the conformation of the last molars, the fifth upper molar being in outline like a figure 8 with a constriction in the middle on either side; the fourth lower molar much elongated and laterally compressed, with the greater axes of the internal lobes nearly longitudinal instead of transverse. Skull high and much narrowed from side to side, with high sagittal crest; pterygoids deep and rounded in side view, palate long and narrow with a very deep and narrow interpterygoid fossa. Edentulous portion of the tip of the rami much contracted."

The remainder of the description is too full to be quoted in extenso.

#### Paramylodon Brown.

Brown<sup>+</sup> gives the following description of this genus :

"This genus is founded on a nearly perfect skull and lower jaw in the American Museum collections (No. 2780), with associated skeletal material including five cervical vertebræ, tibia, fibula, calcaneum, astragalus, lunar, middle digit of manus, and ribs, found by the Expedition of 1897 near Hay Spring, Nebraska...

"The following characters distinguish it from allied genera:

"Skull elongate; muzzle inflated; dentition  $\frac{4}{4}$ ; first upper molar the largest of the series; last lower molar trilobate; first lower molar without opposing tooth.

"Paramylodon seems to have been less specialized than Mylodon, retaining features of the older, more primitive sloths. From the long nasals it seems improbable that it had a proboscis, while the greatly inflated muzzle, and the large movable premaxillæ, indicate a large prehensile lip. The reduction of the twelfth nerve shows a less specialized tongue

\* Allen, G. M., Mem. Mus. Comp. Zoöl., vol. xl, No. 7, pp. 319-346, pls. 1-4, 1913.

<sup>†</sup>Brown, B., Bull. Amer. Mus. Nat. Hist., vol. xix, pp. 569-583, pls. 50, 51, 1903.

than in Mylodon. The rounded condyles, with the greater part of the articular area on the ventral surface, and the aspect of the foramen magnum, opening obliquely to the long axis of the skull instead of backward, show that the head was carried more at right angles to the vertebral column than in *Mylodon*. The long calcaneum with posterior end resting flat on the ground, and the astragalar facet looking forward, indicate a primitive foot more flexible at the ankle than in the contemporaneous Mylodon."

Of the type species of this genus, P. nebrascensis, Mr. Brown describes at some length the skull, jaws, and bones of the hind limb and the digits of the manus.

Doubt has been cast on the validity of the genus Paramylodon by Osborn,\* who says:

"Paramylodon is described as in some features more, in others less specialized than *Mylodon* and retaining features of the older, more primitive sloths. It differs from *Mylodon* in having but four upper teeth.... A second specimen has recently been found near Walsenburg, Colorado [that described by Cockerell, Univ. of Colorado Studies, vol. vi, pp. 309-312, 1909], which contains five upper teeth, and while exhibiting the elongate skull and inflated muzzle of the type of *Para*mylodon, it indicates that the generic distinction between these two forms may be insecurely founded. A fine specimen of a Mylodon, not distinguishable from the Walsenburg specimen, comprising most of the skeleton, was found in 1880 by Mr. S. Garman of a Harvard University expedition at Hay Springs [Mylodon garmani Allen type]."

Regarding the matter under consideration Allen<sup>+</sup> says:

"Concerning *Paramylodon*, as to the validity of which some doubt has been expressed, it seems that its claims to generic rank are well founded. Its reduced dentition and elongate rostrum, with other characters pointed out by Brown, seem sufficiently trenchant. The contiguity of the astragalar and tibial facets of the fibula, however, can not be considered of generic value, since this condition is also found in M. garmani."

In a paper by Mr. Chester Stock<sup>‡</sup> on the Rancho La Brea skulls, twenty-seven of which are now in the collection of the University of California, the author expresses the following opinion:

"The nineteen skulls from Rancho La Brea are similar to the Nebraska and Colorado specimens in the elongation of the

\* Osborn, H. F., The Age of Mammals, p. 457, 1910.

Allen, op. cit., p. 344.
 Stock, C., Science, new ser., vol. xxxix, p. 762, 1914.

head and the inflation of the muzzle. In several of the California specimens the teeth have fallen from the sockets, the study in such cases being restricted to the alveolar outlines. The series arranges itself as follows :

1. Four skulls with four teeth on both sides.

2. Six skulls with four teeth on one side and five teeth on the opposite side.

3. Nine skulls with five teeth on both sides.

"The superior dentition varies, therefore, from four to five teeth on each side; and this variation appears to be independent of the age of the individual. It follows from the variable presence of the first tooth, that it is the second superior tooth which is the largest of the series. Upon the presence of the first superior tooth depends, also, the nature of occlusion with the first inferior tooth.

"The fourth inferior tooth, in a series of five lower jaws, is most distinctly trilobed in an individual of the first group. The tooth appears slightly less trilobed in individuals of the second and third groups, and may be two-lobed in the last group.

"Judging from the variation in the large series from Rancho La Brea, the form described by Brown, as well as the remains from the asphalt deposits, should apparently be placed in the genus *Mylodon*."

Stock goes on to say that the inferior dental series of several mandibles from Rancho La Brea bears a close resemblance to the type specimen of M. harlani.

#### MORPHOLOGY.

The specimens under consideration represent three individuals of approximately equivalent size and a fourth much smaller animal. They are known respectively as catalogue numbers 10264–10267 of the Peabody Museum fossil vertebrate collection, of which 10266 is perhaps the largest and 10267 the smallest, but the reference of all the bones to their respective numbers, which is based alone upon difference of size, is not without question. The elements represented collectively are skull and jaw parts, about twenty-seven vertebræ, ribs, one complete pelvis, two more sacra, fragments of the ilia, three femora, one humerus, two tibiæ, three astragali, one calcaneum, one radius, two ulnæ, four scapulæ, carpal and foot bones, etc.

#### Axial Skeleton.

Skull.

The elements represented are the complete occiput with both condyles, the palate to the inner margins of the dental alveoli of the four posterior molars, part of the left squamosal, the left jugal, two portions of the right mandibular ramus, and the symphysis of the jaw, all of which because of size agreement have been referred to one specimen, No. 10264.

Of 10265, we possess two halves of the occiput lacking the basi-occipital element, the right squamosal with periotic, a portion of the right mandible, and the left side of the symphysis. No. 10266 represents a larger individual, of which only the



FIG. 1. Skull and jaw of *Mylodon harlani*. Shaded portion indicates the parts preserved in the Rock Creek, Texas, quarry. Drawn from skull No. 10205, Yale collection, from Rancho La Brea. One-fifth nat. size. *ef*, anterior condyloid foramen; *jug. f*, jugular foramen.

right squamosal, right periotic, and right exoccipital, with a nearly complete condyle, are preserved. Of 10267, the smallest animal, there is only a portion of the right ramus. In addition, several teeth are present, mainly inferior molars, and probably referable to No. 10264. There are also several skull fragments, and two more periotic bones, which I can not surely identify.

340

Through the courtesy of Professor J. C. Merriam of the University of California, I have been able to secure by exchange a fine skull of *Mylodon* from the Rancho La Brea asphalt deposits, with which to make a comparison. This skull, Cot. No. 10205, Yale Museum collection, while very complete, is that of an individual somewhat smaller than any under consideration except No. 10267. The asphalt specimen, except for its color, has all of the aspect of recent bone, in that the finest details of surface sculpture and relief are preserved. The Texas specimens, on the other hand, are partially mineralized and are somewhat abraded so as to lack this surficial detail.

Occiput.--The occipitals of the Texas form, in keeping with their greater size, are of proportionately heavier bone than those in the Rancho La Brea specimen. As preserved, the general outline of the bone is somewhat pentagonal, with a sharply incised lower border. The median occipital crest in the California specimen is here represented by a low rounded ridge in No. 10264, while in 10265 it is somewhat more prominent. The reduction of the crest in the former speciinen may in part be due to abrasion, but its condition is midway between that of the California type and M. robustus as figured by Owen. The Brea specimen also shows on each side the narrow and sharper ridge receding from the upper crest as it curves downward toward the condyle mentioned by Owen\* as true of Mylodon robustus. These crests are but faintly indicated in either Texan occiput. The shape of the foramen magnum differs materially in the California and Texas specimens, especially in its upper margin. In the latter there is a deep median notch on either side of which the margin rounds in a gentle curve to the occipital condyle. In the Brea skull the notch is rounded and is bounded on either side by a distinct lobe of bone, the outer margin of which rises to its junction with the condyle. In this regard the Texas form resembles M. robustus more nearly, as it also does in the reduction of the crest. The inferior margin of the foramen magnum is somewhat more acutely angled in the Texas specimens than in either the California type or in M. robustus, and the general proportions of the foramen differ in the two former types, the height of the aperture in the Texas individual, No. 10264, being 41.5<sup>mm</sup>, and the breadth, 41<sup>mm</sup>; while in the Rancho La Brea specimen the height is 32.5<sup>mm</sup>, and the breadth is 48.7<sup>mm</sup>, the ratio of width to height being markedly greater.

\* Owen, R., Description of the skeleton of an extinct gigantic sloth, Mylodon robustus, Owen, p. 28, 1842.

The occipital condyles in the three Texan specimens vary as much in shape and proportions as either does from the Brea type, and the slightly smaller anterior condyloid foramina, preserved only in No. 10264 of the Texan series, may also be merely an individual variation of no particular moment.

The inner aspect of the occiput gives an impression of certain elements of the brain. I have before me for comparison casts of the brains of the recent sloths *Cholæpus didactylus* and

FIG. 2.

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FIG. 2. Cast of the brain of Mylodon harlani, from the Rock Creek specimen No. 10264, Yale collection. and of the modern two-toed sloth, Cholæpus didactylus, drawn to scale. One-fourth nat. size. Compare fig. 15.

C. hoffmanni. That of Mylodon agrees in the superior aspect of the cerebellum with *didactylus* in the distinct three-lobed character of the surface, though in the fossil form the lobes were more sharply defined and more divergent from the rear forward. The lateral lobes are relatively larger in the recent The cerebral impression shows, on the contrary, a sometype. what greater agreement with C. hoffmanni in lacking the median longitudinal ridge shown in *didactylus* and exhibiting, on the contrary, the clear division of the hemispheres. Bloodvessels of the dura mater have impressed themselves deeply into the cranial roof and the convolutions are quite as clearly defined as in the C. hoffmanni brain. The proportions of the brain are much the same in both ancient and modern types, despite the difference in cranial proportions, the elongation of the skull in Mylodon including in general the portion anterior to the brain case—procerebral dolichocephaly.

Squamosals.—Three squamosal bones are preserved, two from the right side and a less complete one from the left. The right ones I have referred to Nos. 10265 and 10266 respectively. The latter is somewhat the larger and more robust, but the former yet bears the periotic firmly coossified in position. The left squamosal I have referred to 10264, but it may have been the opposite of the smaller right one, No. 10265.

The squamosal resembles that of the Brea specimen, differing from it mainly in that in the latter there is a distinct though low prominence opposite the glenoid fossa which is entirely lacking in the Texas type. This prominence is also present in *M. robustus* as figured by Lydekker,\* but is less conspicuous in the skull described by Owen. In the Texas form the glenoid fossa is deeply concave transversely, while in the Brea skull it is nearly flat. In No. 10265 there is a distinct circular facet in the fossa which I do not observe in any other specimen or figure. The interior of the bone is extremely cellular, so that the entire anterior limb of the squamosal as preserved is hollow.

A left jugal referred to No. 10264 is present, though lacking in the fine California skull. Anteriorly the bone is almost complete, showing a large part of the articular surface which must have had somewhat the same area as that indicated in the Brea skull. The bone resembles quite closely that figured by Allent as Mylodon garmani, but is more slender than in M. robustus. The superior margin of the bone is more abruptly curved than in M. robustus and a marked though obtuse angle limits the inferior margin of the orbit. This angle is represented in *robustus* by a gentle curve.

Palate.—The fused palatines and portions of the maxillæ are present, to which I have arbitrarily given the number 10264, though this reference is incapable of proof. The bone is very massive, which accounts in part for its preservation. Seen from the ventral aspect, it is extremely rugose, and while resembling that of the Brea skull in size, is from an older animal, as the median suture is completely obliterated. The Brea palate is characterized by a delicate median and two lateral ridges, the latter being separated from the alveolar margin on either side by an irregular longitudinal sulcus. In the Texas form these ridges are more pronounced, but the lateral sulci are not distinguishable. In this respect the palate under description resembles more nearly that of M. robustus, especially the so-called male skull figured by Lydekker.

The Texan palate shows upon the right side the inner walls of the third and fourth and a portion of the fifth dental alveoli, while, on the left, part of the second is also present. These

<sup>\*</sup>Lydekker, R., Anales del Museo de La Plata, Paleontologia Argentina, iii, pl. 49, 1894.
† Allen, G. M., op. cit., pl. 3. fig. 7.
‡ Lydekker, op. cit., pl. 49, fig. 1.

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, No. 232.-APRIL, 1915. 23

alveoli, in so far as they are preserved, would seem to indicate a dental series similar to that of the Brea skull in form and proportions.

Several other skull fragments are present which can not yet





FIG. 3. Jaws of *Mylodon harlani*, showing variation of tooth proportions. A, Rancho La Brea specimen No. 10205. B, Rock Creek specimen No. 10267. C, Rock Creek specimen No. 10264. All from Yale collection. D, cast of type, superior view. E, same from within. One-fourth nat. size.

be given their precise location in the cranium. They are characterized, however, by that remarkable development of cancellous tissues emphasized by Owen.\*

 $^{*}$  Owen, R., Description of the skeleton of an extinct gigantic sloth, p. 23, 1842.

# Mandible.

Portions of the lower jaws of at least three individuals are present, to which arbitrary numbers have been assigned as before, based largely upon distinctions of size. Of these at least three portions could have come from one jaw and represent an old animal of greater size and indicated jaw power than the Rancho La Brea specimen, the relative depth of the ramus at the hinder margin of the posterior alveolus being 108<sup>nm</sup> for the Texan form to 100.5<sup>mm</sup> for the Californian. Opposite the anterior limit of the third alveolus the disparity is still more apparent, the latter measuring 80<sup>mm</sup> and the former 99<sup>mm</sup>. The least thickness of the California mandible is  $33^{\text{mm}}$  and of the Texan  $43^{\text{mm}}$ . The antero-posterior diameter of the alveolus of the fourth tooth is 55.5<sup>mm</sup> for the first and 62<sup>mm</sup> for the second. The symphysis of the Texan form is much more robust, but the outline of the muzzle is not preserved, though that of the California type is slenderer than in M. robustus.

As a further distinction between the California and Texas forms the third alveolus shows a distinct ridge on its outer wall in the latter which is lacking in the former type, and that on the inner wall is more pronounced. The tooth of the Texas form, therefore, would be somewhat quatrefoil in section, that of the California jaw having but two columns, an outer and an inner one. The hinder wall of the posterior alveolus in the Texas form is nearly at right angles to the long axis of the jaw; in the California type it is more oblique. The trilobate character of the last lower molar which Brown\* makes a distinguishing feature of *Paramylodon* is very distinctly seen in the smaller ramus No. 10267, but very faintly indicated in the larger 10264. The ridge on the external wall of the penultimate alveolus is, on the contrary, absent in the smaller jaw. Otherwise, except for size, the two jaws approximately agree, the distinctions being mainly those of age.

A comparison with the California jaw and that of the type of *Paramylodon* shows a curious complex of agreement and disagreement.

The large Texan jaw has a penultimate tooth which is unique, while the ultimate one agrees with that from California. In the smaller Texan jaw both teeth are like those of *Paramylodon*, whereas the Californian jaw shows a *Paramylodon*-like penultimate tooth, while the hinder one resembles more nearly, except for its oblique hinder face, that of the larger Texan type.

I have before me for comparison also a cast of the type of *Mylodon harlani*, which is somewhat smaller than the larger

\* Brown, B., op. cit., p. 569.

#### R. S. Lull-Pleistocene Ground Sloth,

Texas specimen. Here the hinder tooth differs from any of the four jaws compared in the relatively smaller posterior lobe, and in having but the slightest trace or tendency to a three-lobed condition. *M. harlani* in this respect stands at one end of a series, with the *Paramylodon* tooth at the other. The California jaw is next to *harlani*, then comes the

	3d molar	4th molar
(10264	quatrefoil, unique	like California type
10267	like Paramylodon	like Paramylodon
Californian jaw	like Paramylodon	like 10264

larger Texan, the smaller Texan, and finally the *Paramylodon*, the last being the most complex.

With regard to the penultimate molars, the smaller Texan jaw has the simplest, *M. harlani* next, the California jaw next, with the tooth of the larger Texan jaw the most complex. Little can be learned from the jaw of *M. harlani*, as it has apparently been subject to abrasion, whether in the cast or in the original I do not know, which has destroyed most of the surface and probably altered its contour. As it is, it resembles the smaller Texan jaw in the smooth youthful roundness of the curves, but in weight and proportions it is nearest the larger Texan individual.

## Vertebræ.

The vertebral formula for Mylodon robustus given in Flower's Osteology is: cervicals 7, dorsals 15, lumbar-sacrals 10, candals 21; and the mounted or figured specimens known to me approximate this number. On the other hand, the mounted skeleton of Mylodon from the Rancho la Brea, now in the Museum of History, Science and Art in Los Angeles, exhibits at least twenty-three pairs of ribs, a number largely in excess of those in M. robustus. That there is a chance of error in a composite skeleton, however, must be admitted. The Texas material before me cannot settle this matter, as the vertebrae and ribs of at least three individuals may have been present and commingled. If all the bones present were of one animal, the result would be far more conservative than that of

#### Mylodon harlani, from Rock Creek, Texas.

the California mount. In all there are in the Texas collection five cervicals, one of which lacks the neural arch, while in another the centrum bears but one pedicel. Of the dorsals, approximately thirteen are present, represented by two practically complete vertebræ, one with half the arch preserved, six centra, and eight neural arches, not all of which could have belonged together. The one complete pelvis includes at least ten coössified sacral vertebræ, while the number of caudals



FIG. 4. Sixth cervical vertebra of Mylodon harlani, from Rock Creek, Texas. One-fourth nat. size. a, anterior aspect; p, posterior aspect; az, prezygapophysis; nc, neural canal; pz, postzygapophysis; vc, vertebrarterial canal.

FIG. 5. Seventh cervical vertebra of Mylodon harlani. One-fourth nat. size. rf, rib facet; other lettering as in fig. 4.

present is six and a half, all from the proximal portion of the tail.

Cervicals.—If one may judge from their color and general appearance, at least two, possibly three, animals are represented by the five cervicals which have been preserved. One of these, which may be regarded as the sixth, as it articulated fairly well with a typical seventh, has the following characteristics: The centrum presents a more or less pentagonal anterior face, while the posterior one is six-sided. The anterior face is distinctly convex, with a slight depression in the center, the posterior face being concave, with a well-marked convexity around the periphery. Dorsally two good-sized nutritive apertures are seen flanked by two much smaller ones, while ventrally there is a distinct keel-like prominence on the anterior half which broadens and flattens posteriorly to give the hexagonal outline to the hinder face of the centrum. The neural arch arises on two massive pedicels situated over the anterior two-thirds of the centrum on either side so as to give ample space for the intervertebral foramen. The neural canal is pentagonal in shape, with a rounded angle at the summit of the arch. Its height is a little less than its greatest width. The zygapophyses are well marked, the anterior ones presenting a transversely concave face, while in the postzygapophyses the reverse is true.

The vertebrarterial canal is large, bounded above by a robust transverse process, while below the bone forming the floor of the canal is thin, though wide in antero-posterior extent. The inferior lamella of the transverse process is broken away. The transverse process is deflected downward and backward.

#### Dimensions.

Centrum, antpost. diameter	$35^{\mathrm{mm}}$
$\operatorname{depth}$	43.5
width	66
Neural canal, height	40
width	44
Neural arch, antpost. diameter over zygapophyses.	49
width over prezygapophyses	109
pedicel, transverse diameter	22
antpost. diameter	21
Width over transverse processes	156

Seventh cervical.—This is a bone in fine preservation, except that it lacks the left moiety of the neural arch and the transverse process. It articulates approximately with the sixth cervical just described and resembles the latter in the general proportions of the centrum. In this regard the bone differs markedly from the dorsals. The centrum presents a somewhat pentagonal anterior aspect, while on the posterior one the presence of the facets for the first dorsal ribs serves to flat-ten the ventral margin. Ventrally the centrum bears a slight keel flanked by four nutritive foramina. The rib facet on the right side is well preserved and is a slightly oval, saucer-like depression backed by a conical mass of bone which arises from the body of the centrum. The neural arch is robust and springs from the anterior half of the centrum. It bears a strong transverse process which is directed obliquely outward, being deflected downward about 30° from the horizontal. Distally it terminates in a slight vertical expansion. The zygapophyses are similar to those of the sixth cervical, but are of somewhat greater extent and sharper curvature along their transverse axis.

The pedicel of the neural arch is strong, but dorsally the roof of the canal becomes thin and somewhat broadly expanded in the antero-posterior direction.

## Dimensions.

Centrum, length	$36^{\mathrm{mm}}$
depth	43
breadth	60
Neural canal, height (estimated)	14.5
width	53.5
Neural arch, antpost. diameter over zygapophyses	51.5
diameter of rib facet	21
width over prezygapophyses	117
pedicel, antpost. diameter	28.5
transverse diameter	24
Width over transverse processes	180
Summit of spinous process destroyed so that its height cannot be ascertained	

Dorsals.—Third dorsal.—A detached neural arch of what was apparently a third dorsal begins to exhibit the anteroposterior expansion of the dorsal wall of the neural cavity so characteristic of the later vertebræ of both ancient and modern sloths. The neural canal was almost triangular in section and nearly equilateral in the relative extent of its boundaries. The transverse processes are massive and exhibit a clearly defined facet for the tuberculum of the rib. This facet looks downward and slightly outward. The anterior zygapophyses are somewhat similar to those of the first dorsal, but the posterior ones lie entirely beneath the neural arch and present a flat rather than a curved facet. The facet looks downward and inward but only slightly backward.

## Dimensions.

Breadth	acros	ss pre	ezygaj	ophy	vses	 	 	$123.5^{\mathrm{mm}}$
66	over	trans	sverse	proc	esses	 	 	181
66	of ne	eural	canal			 	 	55
Height	66	""	66			 	 	45

Seventh? dorsal.—The probable seventh dorsal is a wellpreserved bone lacking only the epiphyses and the tip of the spinous process. It represents an individual not fully mature, though of nearly equivalent size to the vertebræ already described. Here the backward slope of the spinous process is strongly marked, the bone resembling the modern sloth, *Cholæpus*, more than *Mylodon robustus* in this regard and in the slenderness of the element. The centrum is rather small and distinctly triangular in outline, because of the prominent ventral keel flanked as before by nutritive foramina. Another large foramen is seen in the center of the neural aspect. The anterior and posterior faces of the centrum, although the epiphyses are absent, give evidence of having been slightly convex with a depression in the center of each. The lateral aspects are each concave along the antero-posterior axis and there is a long straight depression having a width of about  $5^{mm}$ , which runs from below upward and slightly backward across either side of the centrum. This mark is also discernible on five other centra among those preserved, although sometimes upon one side only; it is again somewhat variable in position.



FIG. 6. Seventh? dorsal vertebra of Mylodon harlani. One-fourth nat. size. a, anterior, p, posterior, and l, left lateral aspects; cf, capitular rib facet; tf, tubercular facet; other lettering as in fig. 4.

The neural canal is large and elliptical in outline, with the long axis, which is greater than the width of the centrum, horizontal in position. The neural arch arises from the anterior half of the centrum and juts forward to bear the rib facet and to support the prezygapophyses. The latter are borne entirely upon the broad roof of the neural arch, while the postzygapophyses lie upon the under side of the roof where it narrows into the spine. The latter commences as a low ridge at the extreme anterior margin of the neural arch as preserved, rising gradually at an angle of only 25° above the horizontal plane. The transverse processes are heavy, rugose at their extremity, and bear a small tubercular rib facet on their outer aspect. The capitular rib facets are two on a side, a relatively large anterior one borne partly on the centrum but mainly on the neural pedicel, while the posterior facet is small though the loss of the epiphysis probably reduces its area. As preserved its lower limit is horizontal with that of the anterior facet. The intervertebral foramen is very large, in keeping with the dilated neural canal and implying the innervation of large muscles and other organs in the neighborhood of the vertebra under discussion.

## Dimensions.

Centrum, length (estimated)	$54^{ m nm}$
breadth over rib facets	78
depth	51
Neural canal, height	46.5
breadth	57
Neural arch, antpost. diameter	70
width over zygapophyses (estimated).	90
Width over transverse processes	154
Total length preserved of spinous process	130
Total height of vertebra	145

*Caudals.*—Of the anterior caudals, seven are preserved out of an estimated twenty-one, one-third the number but constituting nearly half the total length of the tail.

Proximal caudal.—What is apparently the proximal caudal is present and well-preserved, lacking only the transverse processes. It is a massive bone, with low neural arch and welldeveloped articulations. The centrum is somewhat pentagonal, this time with a well-developed keel-like ridge with a nutritive foramen on either side on the neural aspect, and a concavity below. The anterior articular face is convex, with a slight median depression, while the posterior face presents a peculiar curve in that the central depression seems to be prolonged horizontally across the entire face, owing to the development of a low prominence toward each upper lateral angle. Ventrally articular facets for the hæmapophyses or chevron bones are present, though small compared with those of more posterior vertebræ. They also contrast with the latter in being connected with each other and with the base of the transverse process by a flat bridge of bone which forms a canal passing obliquely downward, backward and inward, suggestive of the vertebrarterial canals of the cervical vertebræ. In the other caudals the chevron facets are borne on separate pedicels, the canal being at most but a deep and well-marked groove. The neural arch is very heavy and the pedicels especially are so broad and massive that both the neural and intervertebral

canals are much smaller than in the dorsal last described, though bearing about the same ratio to each other. The zygapophyses are well-developed, the anterior ones being large and bounded externally by prominent wing-like projections which rise nearly to the height of the spinous process. The postzygapophyses, while strong and well-buttressed, are proportionately small, as they are entirely enclosed below and laterally by the prezygapophyses of the following vertebra. The transverse processes unfortunately are not preserved, but must have been of considerable lateral expanse, to judge by those of the succeeding bones.

## Dimensions.

Centrum, length	$51^{\rm mm}$
depth	60.2
width of articular face	67
Neural canal, height	25
width	38
Neural arch, antpost. diameter over zygapophyses	80
width over prezygapophyses	87
Total height of vertebra	132
0	

Third caudal.—This bone may belong to another animal, but its general proportions are what one would be led to

# FIG. 7. FIG. 7. nc. f nc. f a p $f_{ac}$

FIG. 7. Third caudal vertebra of Mylodon harlani. One-fourth nat. size. fac, chevron facet; other lettering as in fig. 4.

expect were there a single intervening bone between it and the one just described. It may possibly, however, represent the second caudal of a somewhat larger animal.

In contrast to the first caudal, the median ridge of the neural aspect of the centrum is very slight, though flanked by the usual nutritive foramina which, however, become confluent below the surface. Another smaller foramen lies anterior to the pair but only on the right-hand side. Ventrally the bone is deeply excavated and exhibits numerous symmetrically placed foramina. The articular faces are nearly flat, with rounded margins and a very slight central depression. The curves of each face are comparable to those of the anterior caudal, but much less pronounced. As already stated, the chevron facets arise on separate pedicels, those of the anterior face being the more prominent. There is a tendency toward the bridging over of the lateral grooves to form canals as in the previous bone, and where this tendency is most pronounced there is a small foramen leading into the centrum on either side.

The transverse processes are complete, arising from the upper half of the centrum in contrast to those of the first caudal, wherein they spring from the mid-height. In the vertebra under consideration, these processes are deflected slightly downward and backward, and taper somewhat, to dilate again into a rugose end. The origin of the neural arch covers nearly the entire length of the centrum on either side, indicating a slightly developed intervertebral foramen, the formation of which is shared by the two adjacent vertebræ in the proportion of about two to one, whereas in the first caudal it lies entirely within the limits of the posterior portion of the one vertebra. The neural canal is elliptical behind, but has its roof drawn upward between the postzygapophyses in such a manner as to be almost triangular when viewed from the front. The ill-preserved spinous process was evidently low, while the lateral limiting walls of the prezygapophyses arise to approximately the same level. The zygapophyses are nearly horizontal when viewed from the side, though facing upward and inward and downward and outward, respectively, the chord of their arcs being about 45° from the perpendicular.

#### Dimensions.

Centrum, length	$59^{mm}$
breadth, articular face	72.5
depth	63
Neural canal, ant. end, height	38
breadth	39
post. end, height	23
breadth	38
Neural arch, length over zygapophyses	86
width over prezygapophyses	94
Breadth of transverse processes	230
Total height of vertebra (estimated)	140

Eighth ? caudal.—The smallest caudal preserved is the eighth or ninth. Here the centrum is somewhat hexagonal, deeply excavated below, with a narrow bridge of bone connecting the anterior and posterior (chevron) hæmapophysial



FIG. 8. Eighth ? caudal vertebra of *Mylodon harlani*. One-fourth nat. size. Lettering as in fig. 7. facets. This closure is variable. Owen speaks of it in *Mylodon robustus* as being present in the third to the ninth inclusive, or, as he expresses it, in these vertebræ the spinal artery pierces the angle on either side of the ventral depression. In the material before me a canal is formed in the second, eighth and ninth, and not in the fourth, fifth, sixth and seventh. This may, however, be an individual variation, as the caudals probably did not pertain to one animal.

The neural canal is somewhat smaller relatively to the bulk of the centrum and is nearly circular in section, although the posterior face thereof rises in such a way as to occlude the lower half of the canal when the vertebra is viewed directly from the rear. The anterior zygapophyses are large and heavy and their slightly curved facets look more directly inward than before owing to the reduction of the horizontally expanded lower portion. The postzygapophyses have been lost and the vertebra is abraded in such a way that there is little indication of their presence. The same is true of the spinous process, which could not, however, have been prominent.

The transverse processes are broken off, but their base shows them to have been well developed and to have extended along the entire length of the centrum, excluding the epiphyses. The hæmapophysial facets are well developed, betraying the presence of chevron bones of considerable size. The anterior pair of facets is the longer in antero-posterior extent.

#### Dimensions.

Centrum, length	$50^{\mathrm{mm}}$
depth	55
breadth	63
Neural canal, height	12
width	14
Neural arch, width over pedicels	35.5
" " prezygapophyses	49.5
Total height of vertebra as preserved	84

# Pelvis.

At least four individuals are represented by their pelvic elements. Of these one, Cat. No. 10264, is essentially complete except that it lacks the pubes and ischia. Two other sacra, Nos. 10265 and 10266, are represented by three and five coössified centra respectively, the latter being much the more complete. There is also preserved a large portion of a left ilium with its acetabulum, a right acetabulum, and a detached pelvic symphysis, all arbitrarily referred to No. 10265. Two more acetabula have been referred to 10266 and another left ilium fragment with its acetabulum has been referred to No. 10267.

The description will be based upon the complete pelvis No. 10264 and sacrum No. 10266 which gives additional data due to its fractured condition.

Sacrum.-This element in the Texas Mylodon consists of ten coössified vertebræ of which the centrum of the most anterior one is lost though the neural arch is still present. Of these, according to Owen, the seven posterior vertebræ are true sacrals, the anterior three being lumbars, the whole complex forming a synsacrum. The coössification of the sacrum embraces not only the centra themselves but the neural arches, the spinous processes of which are blended into a continuous crest. In the fractured sacrum, No. 10266, the anterior first lumbar centrum exhibits an almost circular articular face, the convex outline being broken along the dorsal side where it is depressed to form the floor of the neural canal. The sides of the centrum, however, are compressed, the two faces meeting on the mid-ventral line in a rather acute angle. In the second lumbar vertebra the ventral aspect begins to broaden and flatten in its posterior half, this flattening becoming a pronounced concavity downward, bounded by slightly diverging ridges, when the first sacral is reached. The second sacral presents the rather curious anomaly of the almost total reduction in depth of the centrum, which is merely a widely expanded plate of bone, owing in part to the progressive increase in size of the neural canal and the gradual rise of the ventral limitation of the centra. A little material may have been lost in the sacrum No. 10266 by abrasion, but at its anterior end the second sacral centrum has a depth of 31.5<sup>mm</sup>, while at the point of fracture, a little beyond mid-length, its thickness is but 10<sup>mm</sup>.

Nutrient foramina pierce each centrum vertically and, as Owen says,\* "assist in the completely confluent state of the bodies of the vertebræ in determining their true number."

 $^{*}$  Owen, R., Description of the skeleton of an extinct gigantic sloth, p. 64, 1842.



FIG. 9. Sacrum of *Mylodon harlani*, No. 10266, Yale collection, fractured to show extent of neural canal. Cross lines indicate broken portions. One-fourth nat. size. a, dorsal aspect. b, viewed from the rear, showing reduction of centra. nc, neural canal.

The progressive dilatation of the neural canal to the middle of the sacrum has also been remarked by Owen, who speaks of its increase in size from a width of 2.5 inches and a height of 2 inches at the first lumbar in Mylodon robustus. He does not, however, record its maximum width. In the specimens before me I can only record a width of 2.375 inches (5.5<sup>mm</sup>) at the first lumbar to (circa) 4.5 inches (11.4<sup>mm</sup>) at the second sacral. The more perfect specimen, No. 10264, gives a height of 2.625 inches  $(5.8^{\text{mm}})$ . The height at the second sacral I can not now record because of the degree of preparation of the specimen. Posteriorly, the more perfect pelvis records a height of 30.5<sup>min</sup> and a breadth of 55.5<sup>min</sup> for the neural canal, showing a very considerable decrease in its size at the seventh sacral. The centrum of the seventh sacral, especially at its hinder end, begins once more to assume a more typical form. The intervertebral foramina also exhibit a progressive increase and decrease in size in correspondence with that of the neural canal.

This gives abundant indication of the ample innervation of the huge muscles of the pelvis, hind limbs, and tail, and one is reminded irresistibly of the corresponding dilatation of the neural canal in the Upper Jurassic dinosaur, Stegosaurus.\* It is not possible to compare accurately the sacral content of the two forms Stegosaurus and Mylodon, but the sloth sacrum No. 10266 as preserved—approximately half of its original length—would just about contain the sacral cast of *Stegosaurus* (Cat. No. 1857), the paratype sacrum referred to S. ungulatus and originally described by Marsh. The relative bulk of the two animals was approximately two to one in favor of the dinosaur, hence the vaunted sacral dilatation of the reptile is far exceeded relatively by that of the mammal. In Stegosaurus the brain weight was about one-twentieth of that of the sacral mass. In Mylodon the brain case (see fig. 2) would seem to show about one-third the capacity of the sacral canal (the difference being largely one of length), showing a vastly greater relative mentality over brutal reflex action in the Mylodon. In the modern sloths *Cholapus* and *Bradypus* the brain is vastly larger than the sacral cord, due perhaps not so much to an increased cranial capacity as to a decrease in the relative muscular development, especially of the loins and tail. Compare fig. 15.

The transverse processes of the first and second lumbars are missing, but were irregularly rounded plates of bone. Those of the third lumbar are fused with the expanded processes of the sacrals and in turn with the inner margins of the ilia. The separate elements are discernible only by the paired fora-

\* Lull, this Journal, (4), vol. xxx, p. 372, fig. 9, 1910.

mina for the exit of the posterior branches of the sacral nerves which lie on either side of the spinous crest.

These are somewhat variable in their size and not equidistant in their spacing. Between sacrals two and three there arises a second series of apertures on either side, the smaller additional foramina being without and somewhat in advance of the others. From the third sacral onward the apertures of the outer series increase rapidly in size and replace the original row, which entirely disappears. At the sixth sacral these foramina merge with the intervertebral foramina for the exclusive exit of the sacral nerves. This occurs opposite the large sacroischiadic foramen of the innominate bone. The relative regu-

# FIG. 10.



FIG. 10. Pelvis of Mylodon harlani, No. 10264, Yale collection, viewed from above. One-twelfth nat. size. ac, acetabulum; ob, obturator foramen; pb, pubis.

larity and size of these foramina would seem to distinguish the Texan Mylodon from the specimen of M. robustus described by Sir Richard Owen, if one may judge from his published figures of the pelvis.\*

Innominate bones.—Although in reality part of the appendicular skeleton, it is most convenient to describe these elements at this place in connection with the sacrum. The entire pelvis, No. 10264, is slightly larger than that of M. robustus described by Owen, the dimensions of which are: greatest width 3 feet 5 inches, antero-posterior diameter of ilium, 1 foot 6 inches. These measurements in the present specimen are 3 feet 6 inches and 1 foot 7 inches respectively. The ilium is rounded anteriorly, the labium or anterior margin being deflected anteriorly in such a way as to be broadly convex upward and concave on its under anterior face. From the

\* Owen, R., pl. 10, 1842.

anterior superior spinous process the outline is deflected toward the acetabulum at an angle of about 80°, but the margin is nearly straight and not so sinuous as in Owen's figure and description. Medially the anterior margin is continued into a sharp crest, deflected outward and slightly downward to form the superior limitation of the sacro-ischiadic foramen. Irregular radiating ridges on the surface of the ilium mark the origin of the huge gluteal muscles which must have been of great importance when the animal reared into the semi-erect posture. The ilium is very thin in the center of its expanse, so that the bone has been broken away here for a distance of several inches in the center of each ilium.

The acetabula are large, well buttressed, and capable of resisting the thrust of the thigh in both the quadrupedal and semi-erect postures. The Harderian depression for the lodgment of the round ligament lies, as Owen has described it, on the side of the acetabulum which is next to the obturator foramen and increases in depth as it decreases in width. Its linear extent, however, is variable from less than one-third the width of the socket measured upon the curve in the complete pelvis to nearly half, as in Owen's specimen, in the pair of acetabula No. 10266. The termination is very deep and irregular in the latter pair and relatively shallow in the pelvis No. 10264.

Of the pubes only the basal portions remain, forming, though the sutural limitation is no longer in evidence, the lower portion of the acetabulum and extending downward in a relatively slender flattened process of bone which terminates on either side about  $75^{\text{mm}}$  from the margin of the articular surface of the acetabulum. It does not differ in any marked detail from Owen's figures of M. robustus.

The ischia are even less evident in all of the material, as practically only that part which enters into the acetabulum is present. This bears, however, a thin ridge of bone inclining somewhat obliquely inward to form the ischiadic tuberosity which is confluent with the sacrum and bounds posteriorly the sacro-ischiadic foramen. No trace of the ventral limb of the ischium is present. There is a well-preserved pelvic symphysis, to which the number 10265 has been assigned. This is of much less antero-posterior extent than in Owen's figure and also differs from it by showing a prominent reinforcing ridge running transversely on the inner aspect. Ventrally the two sides meet in an angle of about 90°. Anteriorly this angle is prolonged into a rugose process, the inner surface of which is smooth and concave, the sharp limiting margin being continuous with the anterior edges of the pubes. Posteriorly the ischial margins are sinuous in that they approach, swing paral-

AM. JOUR. Sci.—Fourth Series, Vol. XXXIX, No. 232.—April, 1915. 24 lel with each other, and then approach and meet in the middle line. They thus embrace a pit-like depression. This peculiarity of structure is lacking in the modern sloths, and in all the figures of *Mylodon robustus* now available. Whether a constant feature among the Texan types I can not tell, as but one such symphysis is preserved.

## Dimensions.

No. 10264, in which the centrum of lumbar one is not p	preserved.
Sacrum, total length	$515^{\rm mm}$
greatest breadth (circa)	30
2d lumbar, length of centrum	. 74
width " " , ant. face	90
height of centrum, ant. face	67.5
height of neural canal	58
width " " " …	57
total height of vertebra, as preserved	232
7th sacral, length of centrum	. 56
width of centrum, post. face	82
height " " " " "	57
" " neural canal*	30.2
width " " "	55.5
total height of vertebra	118.5
Ilia, breadth over all	1066
Right ilium, antpost. diameter to margin of ace-	
tabulum	480
breadth	520
width of acetabulum	125
height " " "	116
Least distance between iliac crests	140
Pelvic symphysis, antpost. diameter	82.5
thickness at median line	65

#### Ribs.

A number of ribs were secured from the Mylodon quarry, some twenty-seven in all. Of these at least four apparently pertained to the young *Elephas* which was found in association, while three others were clearly equine. This leaves approximately twenty ribs which may be referred to *Mylodon*; some other fragments may be the distal portions of certain of those enumerated or may represent additional ribs. Of the twenty which may pertain to *Mylodon*, about half are from the left and half from the right side.

The ribs are all characterized by small facets, the capitular ones particularly, in contrast to those of the associated mam-

**36**0

<sup>\*</sup> A median ridge along the floor reduces this height. Without the ridge it is  $36^{\rm mm}.$ 

moth. In the anterior ribs the two facets lie in a plane nearly perpendicular to the long axis of the bone and are closely approximated, whereas in the more posterior ribs the tubercular facet lies at a level some distance below the capitular and widely removed from it horizontally.

The anterior rib of the left side has the following dimensions:

Distance over capitular and tubercular facets	$70^{\rm mm}$
Capitular facet, antpost.* diameter	33.5
" " transverse "	23.5
Thickness of mid-shaft	9.5
Breadth " "	35

This rib is quite sharply curved and its outer surface gives evidence of abundant muscular attachment in its irregularly ridged condition.

The *eighth rib* of the right side is perhaps two-thirds complete, lacking the distal end. The proximal end exhibits three distinct facets, two capitular and one tubercular. Of the former, that articulating with the centrum in front lies nearly at right angles to the curved axis of the rib. It is small, subovate, and very slightly convex. The second capitular facet is nearly parallel with the axis of the bone and is distinctly saddle-shaped, the convex axis of the curve lying at right angles to that of the rib itself. The tubercular facet lies  $48^{mm}$ distant and is preceded by a pronounced depression; it is concave along a line perpendicular to the rib axis. The shaft of the rib is heavy, with sharp anterior and posterior edges and with distinct muscle roughenings on its outer face.

## Dimensions.

Distance over capitular and tubercular facets	$112^{mm}$
Proximal capitular facet, antpost. diameter	22
transverse diameter	17
Distal capitular facet, antpost. diameter	26.5
transverse diameter	30
Tubercular facet, antpost. diameter	25
transverse diameter	25
Mid-shaft, thickness	23
(greatest) width	54

# Appendicular Skeleton.

#### Scapulæ.

Four scapulæ are present, two right and two left. Of these one is more than half complete while another is little more

\* With reference to the animal as a whole.

than one third; the other two have only the portion adjacent to the glenoid fossa preserved. The two more perfect specimens, a right and a left, may constitute a pair, but this is doubtful, as the less complete one is greater in its several comparable dimensions. Of the more perfect specimen, Cat. No. 10265, a right scapula, there is preserved the glenoid cavity entire and most of the prescapular area, though none of its outline is present. The coracoid process is indicated and in its present condition resembles in shape and size that of a young *Cholæpus.*\* It is probable, however, that were it preserved in its entirety, it would be found to be connected with the acromion by a bridge of bone arching over the proximal portion of the prescapular fossa, as in *Mylodon robustus*.

There is in the prescapular fossa the characteristic aperture mentioned by Owen as representing the "supraspinal notch" of other animals. In the Texan scapula this is not nearly circular as in *M. robustus*, but has the form of a narrow isosceles triangle, the base of which is uppermost when viewed directly from without. Viewed obliquely from the rear, the aperture becomes subovate as it passes through the scapula obliquely downward and forward. The spine begins about  $30^{\text{mm}}$  above the margin of the glenoid cavity and its inferior margin rises in a decided curve to be lost through abrasion.

The left scapula, however, shows what is evidently a complete summit of the acromion process which rises in this, the slightly larger animal, 40<sup>mm</sup> above the level of the bone. The appearance of the acromion itself, even though the missing bridge were present, would be quite different from M. robustus, but similar to the forms preserved in the Rancho La Brea.+ The prescapular fossa is roughened by irregular ridges of bone, which, as in the case of the ilium, betray the enormous muscular development of the creature, and the same is true of the inner face of the bone. The glenoid cavity is of marked antero-posterior extent, while transversely the diameter is but two-thirds the other extent, in decided contrast with the extent of the humeral head. Two-thirds of the glenoid cavity lies beneath the prescapular fossa which had approximately the same area as the postscapular portion, if one may judge from M. robustus and the Rancho La Brea skeleton.

\* In none of the three skeletons of *Cholœpus* which I have before me is the final union of the coracoid and acromion complete, although one (Cat. No. 282) is that of a large animal with worn dentition and totally obliterated cranial sutures.

<sup>+</sup> As shown by a photograph of the mounted skeleton in the Museum of History, Science and Art at Los Angeles, presented through the courtesy of Mr. Frank S. Daggett, director.

#### Dimensions.

Height from rim of glenoid fossa (estimated)	$330^{mm}$
Antpost. expanse (estimated)	370
Length of spine "	300
" " spinous ridge	190
Glenoid fossa, length	114
width	73
Prespinous foramen, height	22.5
width	11





FIG. 11. Humeri of Mylodon harlani. Anterior aspect. One-fourth nat. size. a, of the adult, No. 10265. b, of the juvenile, No. 10271. dr, deltoid ridge; gt, great trochanter; lt, lesser trochanter; p, pronator plate; rc, radial condyle; uc, ulnar condyle.

# Fore Limb.

Humerus.—We were fortunate in securing an almost perfect right humerus which articulates perfectly with the scapula No. 10265 just described, and may be assigned the same number. There is in addition another right humerus not more than twofifths the linear dimensions of the first. It must pertain to Mylodon, as it differs from the larger bone only in the degree of development of the muscular ridges. It is a less perfect bone, lacking both articular extremities, but there is no reason for considering it other than an extremely youthful member of the same Mylodon species as the rest. The juvenile jaw, No. 10267, is only a third smaller than the largest, so that this small humerus must represent a fifth individual of less than half the adult stature. To it I have assigned the catalogue number 10271.

The humerus is an immensely powerful bone resembling only slightly that of the tree sloth and showing the great expansion, especially of the distal end, which we are led to associate with fossorial habits. The shaft of the bone is massive, somewhat flattened in the antero-posterior diameter, but with a powerful deltoid ridge which overhangs the musculospiral groove on the postero-external aspect. The limits of the deltoid area are distinctly defined, though the surface is relatively less rugose than in Owen's figures of *M. robustus.*\* The pronator plate terminating in the internal supracondyloid has a relatively greater lateral expanse and its upper corner is more hooklike than in the figured bone. The supinator plate has been broken away so that its whole extent can not be determined. The trochlear shows an almost hemispherical radial condyle implying great freedom of rotation of the forearm and the ulnar condyle is saddle-shaped though tending to flatness toward its inner limitation. The head of the humerus exhibits a beautifully rounded segment of a spheroid passing through an arc of nearly 180° in the antero-posterior direction and of about 90° transversely, but the curve of the latter is of greater radius. The greater and lesser tuberosities are prominent but vary in proportions compared with those of M. robustus.

I have before me for comparison casts of two humeri, both of which exceed the present one in size. One of them, a right humerus from the Walhammat (Willamette), a tributary of the Columbia River, was originally described by H. C. Perkins in 1842.<sup>†</sup> This is one of many casts received from Doctor Perkins many years ago. The humerus bears upon its surface the name "Orycterotherium Oregonensis." # But Doctor Har-

<sup>\*</sup> Owen, R., pl. 11, fig. 1, 1842. † This Journal, (1), vol. xlii, pp. 136-140, 1842. ‡ Harlan, this Journal, (1), vol. xliv, p. 80, 1843. "Dr. Perkins proposed to name his specimen, if it proved to be a new animal, *Orycterotherium Ore- gonensis*. We have casts of the os humeri from both Dr. Perkins and Dr. Harlan, and can discriminate no difference; they must have belonged to the same animal. Eds."

lan in 1843\* refers to it as *O. missouriense.* The cast also bears the words *Mylodon harlani*, the name under which the specimen was recorded in the catalogue of the old Yale Cabinet, which was the repository of such things before the establishment of the Peabody Museum. The second cast is again a right humerus slightly larger than the first and bearing the same old catalogue number (700). It comes from the same locality and was also presented by Doctor Perkins. Its further history is unrecorded.

A comparison of the three humeri, the two casts and the larger Texan form, fails to disclose any marked differences either in form or proportions between them, although the last is materially smaller than either of the others. What distinctions they show are of very minor importance—only the extent and degree of rugosity of the muscle areas and the fact that the olecranon depression is a little more marked in the casts. There is certainly nothing which would justify a specific separation of the three animals.

	Texan Mylo- don Cat. No. 10265	Orycterothe- rium oregonensis Cast of type	Ratios
	mm	mm	
Length over all	442	509	115
Girth, proximal end	452	530	117
<ul><li>over deltoid ridge</li><li>below deltoid ridge</li></ul>	296	328†	111-
(least)	246	278	113
" at distal end	560‡	640	114 +
Diameter (greatest) at			
proximal end " (least) at proximal	166	188	113 +
end (articular)	122	148	121+
<ul> <li>(least) of shaft</li> <li>(greatest) at dis-</li> </ul>	60	70	116+
tal end (least) at distal	260‡	290	112-
end Width of trochlear (artic-	67	92	136
ular)	120	156	130
			Av. 118

Dimensions.

\* Harlan, op. cit., p. 80.

+ Slightly broken.

‡ Estimated.

It will be seen that the measurements of the two bones bear a pretty constant ratio to one another. The three measurements wherein the greatest discrepancy is shown were taken over the articular surfaces themselves, which would naturally be relatively larger in an older and more powerful animal.

Radius and ulna.—The radius is practically perfect though somewhat abraded, and from its size and general appearance has been assigned the same catalogue number as the humerus, No. 10265.

This bone is straight, with a well defined proximal dilatation which bears the concave humeral facet. Of this the front margin is not preserved, but the shape must have been oval. with a somewhat flattened portion where it adjoins the ulnar facet. Distally the radius expands rapidly to a diameter half again as great as the proximal end and two and a quarter times as great as the least lateral extent of the shaft. The shaft is trihedral, the front, rear, and inner aspects being separated from one another by rather sharp angles, while the inner front angle bears a well defined tuberosity for the insertion of the biceps muscle. This tuberosity lies about one third of the distance from the proximal end of the bone, giving a comparatively great leverage for wielding the forearm and The distal aspect presents two distinct facets, a conhand. cave one for the articulation with the lunar and a somewhat saddle-shaped one for the scaphoid bone. Of these the lunar facet has the greater area and is sub-oval in shape, the lesser scaphoidal facet is irregularly triangular, with a sharply convex antero-posterior axis, while the transverse one is slightly Great mobility of wrist is indicated in keeping concave. with the freedom of rotation of the forearm, the whole mechanism implying ample prehensile powers. I can only compare the bone with that of Mylodon robustus, from which it differs in the more constricted shaft just below the proximal articulation and the lesser area of the humeral facet as compared with the "convexity [ulnar facet] lodged in the small sigmoid cavity of the ulna" (Owen).

Distally the proportions of the bones seem to vary, that of M. robustus being thicker for its width, especially toward the

## Dimensions.

Length over all	$270^{\mathrm{mm}}$
Proximal diameter, transverse	69
antpost. (est.)	45
Least diameter of shaft, transverse	42
antpost.	34.6
Least girth of shaft	13
Distal diameter, transverse	100
antpost.	64
outer side. The longitudinal ridges are present on the rear aspect of the radius in both instances, but they vary slightly in their position.

Two ulnæ are present, a left and a right, but as they vary in size they can not have pertained to the same animal. I have therefore assigned to the right the catalogue number 10265, and to the left, No. 10266. Of these, unfortunately the former is the least perfect, though neither is present in its entirety. The ulna is a roughly triangular bone, widest at the proximal end instead of at the distal as in the case of the radius, trihedral in section, with an enormously developed, inwardly bent olecranon. The proximal sigmoid facet is very large and consists of two areas, a slightly concave one articulating with the inner condyle of the humerus, and a deeply concave portion which embraces the rear part of the outer condyle. Below this latter area is a deep excavation which receives the proximal end of the radius and within which it rotates. There is a rounded notch confluent with this excavation which extends up into the outer humeral facet and which doubtless lodged a well developed ligament. This is present, though in variable degree, in both ulnæ from Texas and also in one of the Perkins casts from Oregon, but is not visible in Owen's figures of Mylodon robustus. Nor does Sir Richard mention it. This notch would seem therefore to be distinctive of the North American forms. On the inner aspect, the ulna is smooth and concave, the concavity being bounded proximally by the inwardly bent olecranon, posteriorly by the inwardly deflected hinder margin, and proximo-anteriorly by the rim of the humeral facet. The outer aspect of the bone bears a prominent ridge, apparently, as Owen says, parallel with the hinder margin. This ridge arises from the posterior rim of the humeral articulation and passes toward the front margin of the bone as it moves distalward. Posterior to the ridge the bone is deeply concave, especially behind the humeral articulation. Distally, however, this area becomes slightly convex as in M. robustus. None of the distal extremity is preserved in either ulna, but the Oregon cast seems to show the bone in its entire length, although even here the distal end was broken.

I can see no marked distinction between the Texas and Oregon ulnæ other than superior size and a greater rugosity in the northern specimen, which may well have been the result of greater individual age, as in the case of the humeri. There is quite as much difference in the character of the humeral facet of the two Texan specimens Nos. 10266 and 10265 as between 10265 and the Oregon cast, though the variable extent of abrasion and other mutilation to which the Texas material has been subjected renders a precise proportional study difficult.

	Texas Mylo- don Cat. No. 10266	Oregon cast	Ratios
	mmʻ	mm	
Length over all	375*	406	108
part	101	115	114-
Humeral facet, breadth	108	123	114
Shaft, least thickness	32.5	45	138
			Av. 118

### Dimensions.

\* Estimated.

It will be seen that the average of the ratios of ulnæ and humeri is exactly the same, 118, in each case.

Manus.—The hand is represented by two scaphoids, a right and a left, a right magnum, a left metacarpal IV, and two unguals, both presumably of digit III of the left hand.

Scaphoid.—The scaphoid preserved apparently articulates with the radius already described, No. 10265, in such a way as to accentuate the marked flexibility of the wrist, as the articulations are full curved and of ample extent. The bone is roughly triangular when viewed from above, with a rounded anterointernal angle and a deeply concave postero-external side. Threequarters of the superior surface is articular and is convex in both dimensions in its outer part, becoming concave first along the transverse diameter and then in all directions in the broadly expanded inner portion. The anterior aspect of the bone is continuous with the outer face and the latter bears a rather long, narrow lunar facet which is continuous with that of the upper aspect though demarcated by a pronounced angle. The lower margin bears two deeply rounded bays, the limits respectively of the magnum and trapezoid facets. Except for the facets the entire surface of the bone is highly rugose. Posteriorly the bone is prolonged into a compressed angle bearing on its external face a sub-circular facet with which articulated the metacarpal of the first digit. When the bone is held with its superior face horizontal, this facet nearly coincides with the vertical antero-posterior plane. In its proper orientation, however, as indicated by the distal end of the radius, the upper surface of the scaphoid is inclined sharply downward and outward, which inclines the metacarpal facet obliquely downward in such a manner as to make the articulation feasible.

## Mylodon harlani, from Rock Creek, Texas.

Ventrally, two-thirds of the scaphoid is articular, the remaining third being the roughened under surface of the backwardly projecting process just mentioned. Of the two facets, that for the trapezoid is concave along one dimension and approximately flat along the other. It is sub-oval though somewhat asymmetrical, full rounded on its anterior outline and slightly concave on the posterior, while the magnum facet is of slightly smaller area, and of approximately the same outline but concave along all axes.

### Dimensions.

Height of scaphoid No. 10265	$40^{mm}$
Breadth	79
Antero-posterior diameter	75

Magnum.-A right magnum of approximately equivalent size to the scaphoid and radius has been given the same catalogue number, 10265. It is an extremely irregular bone of which much of the surficial area is covered by articular facets. eight in all. Of these three are confluent on the inner, upper, and outer aspects of the bone. The first of these, the scaphoidal facet, is a pronounced, somewhat conical curve, fully convex in the antero-posterior diameter, slightly so in the transverse. This bounds the lunar facet, the largest of all. from which it is separated in part merely by a ridge, elsewhere by a slight groove with elevated margins. The lunar facet is flat along one side with a continuous curve embracing the others, so that it is rather more than a semi-circle in area. It is convex, with a tendency toward concavity along certain of its borders. The unciform facet bounds the lunar articulation along the straight side and is a long, narrow area with a sinuous outline. Adjacent to this is the large facet, sub-triangular in shape and somewhat concave, with which the third metacarpal articulated, while adjoining this is the small articulation of the second metacarpal.

Both of these carpal bones have approximately the same form as in *Mylodon robustus* but may differ in details and proportions. My only means of comparison, however, is with the figures of the assembled manus given by Owen, which show but two aspects of each bone, making adequate comparison difficult.

#### Dimensions of magnum.

Height.	$47^{\rm mm}$
Transverse diameter	55
Antero-posterior diameter	57.5

## R. S. Lull-Pleistocene Ground Sloth,

Right metacarpal IV.—This is a splendidly preserved bone of remarkable form, showing a strongly depressed shaft and widely expanded articular ends. It is extremely rugose for tendon attachment. Proximally there are three distinct though continuous facets which bore respectively upon the unciform and the two adjacent metacarpals. Of these the unciform and the fifth metatarsal facets met in a high, straight ridge about 43<sup>mm</sup> long, which coincides with the anconal-palmar diameter of the foot. Of these facets, that which bears against the fifth metatarsal is very slightly concave and is toward the anconal side of the foot, covering about half the expanded area of the proximal end of the bone. The facet which articulates with the unciform is much the larger and is first convex and then concave in one dimension and straight in the other. The plane of this facet forms an angle of about 55° with the long axis of the bone and while the greater part lies on the inner aspect it seems to include the straight ridge and about  $6^{mm}$  of the outer surface of the metacarpal. The third proximal facet, that for metacarpal III, is slightly convex in all diameters and forms a truncated ellipse, the lines of demarcation with the unciform facet causing a break in the curve. Along this line the outline is slightly concave instead of convex. The angle formed with the axis of the bone is now about 40°. Distally the articular face is most peculiar, the keel being oblique instead of normal to the plane of the foot, giving a torsional appearance to the bone and implying that the digits instead of lying prone upon the ground lay more or less on their outer side with the claws turned inward. On the anconal side the metacarpal is stiffened by a longitudinal buttress arising on the distal expansion and running up the shaft, parallel with the inner aspect, for about two-thirds the length of the bone. This buttress divides the surface into two unequal concave areas. The inner aspect is keeled, the keel running from the distal dilatation to the facet of the third metatarsal, to which it lends support. The palmar side of the bone bears a prominent tubercle at the proximal end, some distance below which lies a distinct smooth-walled channel running across the bone in a slightly oblique direction.

### Dimensions.

Lengt	h	$108^{mm}$
Proxir	nal width	46.5
66	antero-posterior diameter	55.5
Shaft,	width	23
Í	antero-posterior diameter	35.5
Distal	width	40
66	antero-posterior diameter	50

The proximal two-thirds of the fifth metacarpal of the right manus is present, but too imperfect to characterize in detail. It is remarkable, however, for the obliquity of its proximal facets.

Unguals.—The two ungues present are not distinctively characteristic, though with the exception of the basal sheath in one, they are admirably preserved. I have compared them with Cope's description of *Mylodon sodalis*, which is based upon a single ungual from Oregon, with the following results.



FIG. 12. Ungual phalanx of Mylodon harlani, No. 10266, Yale collection. One-fourth nat. size. a, lateral aspect. b, palmar aspect.

The sodalis has the basal sheath developed on one side only. Texan specimen No. 10265 has none, it having been entirely broken away. Texan specimen No. 10266 has it well developed all around, though slightly fractured on the right side. The rest of Cope's description could apply to either Texas claw. The proportions of the Texas claws vary in that the somewhat smaller one, No. 10265, is more highly arched on its dorsal outline and hence actually and relatively a little deeper. It is also more compressed. Herein it agrees with Cope's description of M. sodalis, which he says is more compressed than M. harlani. As M. harlani type includes only a jaw, this statement, based doubtless upon subsequently referred material, should be taken for what it is worth.

We have therefore in the M. sodalis type a larger claw of much the same proportions as the Texas specimens, standing between the two in the degree of preservation of the basal sheath. I do not believe, therefore, that Cope's description brings out characters other than those of individual variation or degree of preservation and hence it is entirely inadequate as the characterization of a valid species.

# Hind Limb.

*Femora.*—Two femora, a right and left, are represented by their diaphyses only, but the articular ends seem to have been lost by breakage rather than by the removal of the epiphyses through imperfect coössification. One other right femur is indicated by a little more than its distal half, with the articulation fairly intact, and there is an additional internal condyle from the left thigh.

I am able to make a direct comparison of the femora only with Owen's M. robustus. Allen describes rather briefly a femur in his memoir on *M. garmani* but does not figure it. Two of the Texan femora, Nos. 10264 and 10265, are smaller than in *M. robustus* and lack the decided rugose character of the latter, due in part doubtless to abrasion. The diaphyses are rather featureless but show well the massive character of the bone. They differ from M. robustus in that the lesser trochanter is relatively small and in the sharper curve of the inner outline of the bone, especially in its lower portion, implying apparently a relatively wider distal extremity. The longitudinal ridge shown by Owen to be parallel with the outer margin on the anterior aspect is indicated in the right femur for about half its length, but hardly at all on the left, while the subsidiary ridges which limited the areas of attachment of the great thigh muscles are lacking in each. The general contour of surface aside from these minor irregularities is similar in all. The distal end of the third femur is of greater size, but in its present condition shows no points of contrast with that described by Owen, nor am I able to compare with the data brought out by Allen in his description.

## Dimensions of Cat. No. 10264.

Length over all, estimated	$450^{mn}$
" of diaphysis, as preserved	380
Breadth across proximal end, estimated	240
Least diameter of shaft, trans.	120
antpost.	57
Breadth across distal extremity, estimated	210

Tibiæ.—Two right tibiæ are present, both in excellent preservation. They show the characteristic generic features in marked degree—the shortness of the element compared with its extreme width, and the proximal breadth, exceeding threequarters the entire length of the bone in M. robustus and in one Texan specimen, while it is slightly less in the other.

The proximal articular area forms a broad platform supported from beneath anteriorly by the shaft, but overhanging it though strongly buttressed on the inner side. Posteriorly and externally the overhang is very pronounced, especially beneath the articulation of the external femoral condyle. Here, however, a facet, sub-triangular in outline, marks the point of articulation of the fibula which thus lent its support to withstand the crushing weight transmitted through the thigh. This facet looks outward and downward at an angle of about 45°. The cnemial crest arises somewhat broadly on the outer forward angle of the proximal end of the tibia and, narrowing to an acute angle, fades into the surface of the shaft a little below its mid-length. Distally the tibia dilates, though not so widely as above, the greatest distal width being a little more than half the length of the bone in both specimens. The shaft is an elongated oval in transverse section at the point of its least circumference.

Proximally the articular surface bears two unequal facets, a greater concave one to receive the inner femoral condyle, and a lesser flat area for the external one; both are sub-oval in outline. Distally the articular surface is very peculiar, as it is the complement of the oddly shaped astragalus. There are three very distinct areas, although the synovial surface is confluent. The outermost one is small, flat, and almost semi-circular. facing outward and downward at an angle of about 45° instead of being almost horizontal as in Owen's description of M. robustus. As he says (p. 116), " it forms the lower surface of the outer distal protuberance of the bone, and rests upon a corresponding surface at the lower part of that excavation of the fibula, which receives the said protuberance." This surface lies almost directly beneath the fibular facet at the proximal end of the tibia and the two surfaces are approximately but not quite par-The remainder of the distal end of the tibia articulates allel. exclusively with the astragalus and consists of two surfaces, that on the inner side being an ovoid depression which cuts deeply into the remaining area, the line of union describing an arc of about 180°, although the curve is not the segment of a true circle, being somewhat flattened on the outer The larger articular surface thus formed is irregularly side. crescentic, concave in its outer moiety, and flattened toward the inner side of the bone. The tibial shaft bears heavy roughenings for muscular attachment and the entire bone gives evidence of the enormous muscular power of the foot and leg.

I have before me two casts of this element from the Perkins specimen of M. harlani (vide supra p. 364). Neither is perfect, especially at the proximal end, which gives the bone a totally different aspect. They seem to have been more slender



FIG. 13. Tibia and astragalus of Mylodon harlani, No. 10266, Yale collection. One-fourth nat. size. t, tibia; f, fibula, restored. a, anterior, b, posterior aspect of astragalus; nf, navicular facet.

in proportion to their length and do not give, at any rate in their present condition, so great an impression of power.

	Cast	10264	10266
Length over all	mm	mm	mm
	264	2 <b>3</b> 3	222
Girth of shaft at mid-length	226	216	$202 \\ 166 \\ 111.5$
Proximal end, transverse diameter		170	
antpost. diameter	99*	111 $\cdot$ 5*	
Distal end, transverse diameter	101*	$     141 \\     96.5 $	$\begin{array}{c}133\\103\end{array}$
Shaft, least ant. post. diameter	49	49	46
least transverse diameter	90	87	79

# Dimensions.

\* Somewhat reduced through abrasion.

Foot.—Astragalus. (see fig. 13 a, b.)—There were three astragali collected from the Texas quarry and unfortunately all were from the right limb. One, the most perfect, articulates very well with tibia No. 10266, a second not so well with No. 10264, while the third, the least complete, has been assigned the number 10265. These astragali differ materially in certain proportions, notably 10266, which has much the stoutest ascending process, though in certain other dimensions it is the smallest of the three. This bone shows a remarkable difference in the character of the navicular articulation, which is deeply concave, the concavity covering the entire facet. In No. 10264 this area is almost a plane, with a very small depression in the center which seems to be largely the result of fracture, while in the third astragalus this surface has unfortunately been destroyed. Of two naviculars which are preserved, one has a rounded protuberance corresponding to the depression in No. 10266, while the other shows a flat surface, although otherwise the two bones compare curve for curve. A cast from the Perkins series is that of a left astragalus, and while this portion of the bone was somewhat injured, there is no appreciable depression indicated, though a slight one may have been present.

Owen says (p. 117): "The astragalus is of an irregular pyramidal form, the posterior end forming the apex, and the base, which is turned forwards, being rudely divided into three large tuberosities. If the foot be placed with the sole flat on the ground . . . the astragalus, naturally coadapted to the other tarsal bones, has its fibular or outer side uppermost, and

AM. JOUR. Sci.—Fourth Series, Vol. XXXIX, No. 232. – April, 1915. 25 a great part of the articular surface for the tibia looks inwards; when articulated, therefore, to the leg, placed vertically above it, the foot rests upon the ground by its outer edge, not by its sole, and the peculiarities of the metatarsal structure relate to this inversion of the foot." The Mylodon astragalus is certainly one of the most oddly shaped elements in this most uncouth animal. The upper surface bears a tibial articulation divided into two confluent synovial areas, as in the distal end of the tibia, the ascending portion is ovoid with one face distinctly flattened in the peculiar No. 10266, much less so in the others. The surface from which it arises is convex in part, this convexity being most pronounced in No. 10266, least so in No. 10265. The surface loses its curved aspect toward the inner side of the articular area, and in No. 10264 actually becomes slightly concave. The ascending process in No. 10266 is much the stoutest, less so in 10265, and least in 10264, though its height in all three remains approximately the same. The horizontal surface is continued down over the anterolateral aspect of the bone in a slightly convex area, irregularly quadrilateral, with slightly curved sides, three convex and one concave. From this a narrow area passes backward, forming the lateral margin of the tibial facet. This area articulates with the malleolar process of the fibula.

Below and anteriorly there is a long continuous area of articulation with the calcaneum, cuboid, and navicular. That which meets the calcaneum is the most posterior and is roughly triangular, narrowest and most convex at the hindermost extremity, growing gradually flatter and wider anteriorly. The antero-posterior axis, on the other hand, is first gently convex, then concave in a long, sweeping curve, giving to the entire surface a saddle-like aspect. Anteriorly the margin is cleft by an entrant angle which is the posterior limitation of the depression bounded by the calcaneal, navicular, cuboidal, tibial and malleolar facets-a depression, like certain others on the bone, irregular and deeply pitted, the pits being the orifices of the vascular canals. The remaining part of the anterior limit of the calcaneal facet adjoins the cuboidal, the line of juncture forming a full curve, almost the segment of a circle, and passing through an arc of about 130°. The extension of this curve toward the inner side of the astragalus gives an area to the calcaneal facet which is apparently much wider than the complementary facet on the calcaneum itself, though of this I have to judge from a very imperfect bone. If this be true, it implies a considerable range of movement between astragalus and calcaneum.

The cuboidal facet of the astragalus is a cylindrical though somewhat warped curve and is continuous with that of the navicular, no apparent line of demarcation between the two being visible. The navicular facet is remarkable, especially in the peculiar pit-like depression in its flattened upper portion. Owen does not remark this depression in his description nor does he figure it, but the area is flattened. Barnum Brown (p. 581) in his description of *Paramylodon*, however, describes an astragalus precisely like the Texan 10266 which is the subject of this sketch, hence this seemingly variable feature within the Texas group is considered by Brown to be a character of generic importance.

	10264	10265	10266	Ratio between latter two
	mm	mm	mm	
Extreme height	111*	110	119.5	108.6
Antero-posterior diameter	129	127.5	131	103-
Transverse diameter	101*	100	103	103
Antpost. diameter of ascend-				
ing process	41.74	39.5	54	111.7

Dimensions.

### \* Estimated.

The ratios between the bones bring out the relatively greater depth of 10266, but especially the strength of the ascending process. May not the tendency toward a ball and socket articulation between astragalus and navicular in this specimen be simply a further mechanical reinforcement of a more powerful joint and therefore merely a matter of individual variation?

Naviculars.—Two naviculars, both from the left side, are preserved, fortunately representing the two types, one with a distinct rounded boss on the astragalar surface which fits into the above mentioned depression, in other words *Paramylodon*like, and the other with the surface plane or slightly concave like that of *Mylodon*.

The general form of the navicular is irregularly quadrilateral, with somewhat rounded angles, and is a comparatively thin expanse of bone concave proximally, and convex distally. The entire proximal surface is occupied by the astragalar facet, concave throughout in No. 10265 and convex over half its area in No. 10266. Distally a large ovoid surface, evenly convex, characterizes both bones. This area, which includes about half the entire surface, is the external cuneiform facet and adjacent to it is the small synovial surface which came in contact with the internal cuneiform. The distal face of the navi-

<sup>+</sup> Imperfect.

cular is pierced in its approximate center by a large foramen for the entrance of nutrient blood-vessels, and this occupies the same relative position in both specimens. Externally the navicular is bounded by a flattened synovial area, somewhat

### FIG. 14.



FIG. 14. Naviculars of Mylodon harlani. One-fourth nat. size. a, b, No. 10265, Mylodon type with concave astragalar facet, af. c, d, No. 10266, Paramylodon type with conical boss in astragalar facet articulating with depression seen in fig. 13 a, nf. ext. cun, facet for external cuneiform; cub, cuboidal facet.

lunate in outline, which bore against the cuboid. This also has approximately the same form and extent in both specimens.

	10265	10266	Ratio
	$\mathbf{m}\mathbf{m}$	$\mathbf{m}\mathbf{m}$	
Thickness, greatest	28	31	111-
Antero-posterior diameter	75	75.5	101-
Transverse diameter	60.2	56*	92

## Dimensions.

\* Somewhat abraded.

Calcaneum.—One very imperfect left calcaneum is present, showing few characters other than the astragalar and cuboidal articular surfaces. Of these the former, which may not be quite perfect, is sub-triangular and presents a somewhat twisted surface, convex in its long (antero-posterior) dimension and concave in the short transverse one. Anteriorly this surface is confluent with the cuboidal facet, but separated therefrom by a pronounced angle, straight when viewed directly from above, concave when viewed from the side. Adjacent to this ridge on the postero-external side is a deep incision into the area of the astragalar facet in the angle of which lie nutritive foramina. The cuboidal articulation is also triangular and concave in all dimensions. The huge, rugged, posterior portion which, as Owen says, makes the os calcis of the *Mylodon* equal in size that of the elephant, is here missing. In the remaining portion of the bone I see no characters in my limited opportunity for comparison which would be of taxonomic value.

### Dimensions.

Antero-posterior diameter of calcaneal facet	$98^{mm}$
Preserved width of calcaneal facet	60
Antero-posterior diameter of cuboidal facet	<b>27</b>
Width of cuboidal facet	55

## TAXONOMIC SUMMARY.

Chester Stock, a pupil of that inspiring teacher, Professor J. C. Merriam, of the University of California, who is responsible for the paleontological awakening of the Pacific Coast, has had a splendid opportunity for the study of mylodont variation as shown in the great series of sloths from the Rancho La Brea. Mr. Stock's studies are not yet complete, but a summary of his conclusions regarding the skull and dentition has just appeared.<sup>\*</sup> He finds the Rancho La Brea Mylodons to be extremely variable and to include within the limits of their variation the generic characters assigned by Brown to *Paramylodon* and the specific features shown in *Mylodon harlani*, *M. renidens* Cope, *M. sulcidens* Cope, and the skull described by Cockerell from near Walsenburg, Colorado. All of these forms, together with those from Rancho La Brea, he refers without question to the original species, *M. harlani* Owen.

*M. garmani* of Allen, Stock considers apparently distinct from the Rancho La Brea series, although certain of its characters are closely approached in specimens from the asphalt, *garmani* differing principally in the extremely narrowed cranial portion of the skull and in the antero-posterior elongation of the last inferior tooth. In certain other characters *M. garmani* finds its parallel in one or another of the Rancho La Brea skulls. Stock deems it unsafe to base primary specific differences on the size or form of the teeth, as the dentition is so very variable in the mylodont sloths.

The Texan material which has been the basis of this memoir emphasizes the variability in the rest of the skeleton as well. It must be remembered that but a single Rancho La Brea

\* Stock, C., Skull and dentition of the mylodont sloths of Rancho La Brea. Univ. of Calif. Pub., Bull. Dept. Geology, vol. viii, No. 18, pp. 319-334, 6 text figs., Dec. 5, 1914.

skull was available for comparison and the differences which were emphasized in the present description might well have disappeared had other asphalt skulls been accessible. There seem to be no distinctions of specific rank and I know of no reason for referring the Texan material to any other species than that which includes the Rancho La Brea forms, namely, *Mylodon harlani*.

Comparison with the cast of the type of *M. harlani* shows that the three Texan jaws exhibit collectively the same features, some in one specimen and some in another, so that all the important specific characters of the type jaw are to be seen within the limits of variation shown by the Texas specimens.

Moreover, the Perkins casts of other skeletal material from Oregon which has been referred to the type species, *M. harlani*, are indistinguishable except for size and certain minor proportions which may be expected in somewhat older individuals. I therefore unhesitatingly refer the Rock Creek material to the variable and widespread species, *Mylodon harlani* Owen.

*M. sodalis* Cope is founded upon such meager material that its validity may well be questioned. The type ungues are not separable from those of the Texan form other than by slight individual variations and the degree of preservation.

The mylodont sloths of the Lower Pleistocene of North America may therefore be referred first to:

Mylodon harlani Owen, including material from the Big Bone Lick, Kentucky; Oregon; Hay Springs, Nebraska; Rock Creek, Texas; and Rancho La Brea, California.

As synonyms of the species M. harlani the following should be included:

Mylodon sodalis Cope M. renidens Cope M. sulcidens Cope Paramylodon nebrascensis Brown.

Mylodon garmani Allen alone probably represents a distinct though closely related form.

### BIONOMY.

Much has been written concerning the probable appearance and habits of the ground sloths. Sir Richard Owen, with his marvellous insight and ability to appreciate anatomical characteristics, has given an interpretation of habits which I see no reason to question in the light of later discovery.

Mylodon was of elephantine bulk although it by no means attained the stature of the later Megatherium. The fore feet

 $\mathbf{380}$ 

with their armament of claws must have been used to loosen the soil from around the roots of trees. Then, rearing on its hind limbs, the enormous grasping power of the arms could be used to bring the undermined tree to the ground. The hind



FIG. 15. Restoration of Mylodon harlani and modern sloth  $Chol\alpha pus$  hoffmanni (after Flower and Lydekker), drawn to scale. Compare with fig. 3, wherein the relative cranial capacity is shown. One twenty-fourth nat. size.

limbs, loins, and tail were immensely muscular and abundantly innervated and formed an entirely adequate support for the creature's fore quarters when engaged in this herculean task.

The character of the mouth with its imperfect, though continuously growing, dentition points to a community of feeding habit with the modern tree sloths, and the general consensus of opinion seems to be that the foliage of trees formed their dietary staple.

Brown\* in discussing *Paramylodon* has this to say of its habits:

"Paramylodon seems to have been less specialized than Mylodon, retaining features of the older, more primitive sloths. From the long nasals it seems improbable that it had a proboscis, while the greatly inflated muzzle and the large movable premaxillæ indicate a large prehensile lip. The reduction of the twelfth nervet shows a less specialized tongue than in Mylodon. The rounded condyles, with the greater part of the articular area on the ventral surface, and the aspect of the skull instead of backward, show that the head was carried more at right angles to the vertebral column than in Mylodon. The long calcaneum with posterior end resting flat on the ground, and the astragalar facet looking forward, indicate a primitive foot more flexible at the ankle than in the contemporaneous Mylodon.

"The sum of these characters points to a difference in feeding habits and indicates that *Paramylodon* was a grazer."

Allen<sup>‡</sup> in speaking of a mylodont jaw from Walhaumet (Willamette) River, Oregon, says:

"It [the ramus] more nearly resembles *M. robustus* in having a broad truncate lower lip, and was thus adapted more for a grazing habit, while *Paramylodon* and *M. garmani* with their elongate and compressed rami, were probably *browsing* animals [italics mine]. The reduction of the humerus in the latter may also be correlated with this habit, implying that it raised itself up to reach for branches rather than to grub for roots [but has "grubbing for roots" anything to do with grazing?]...

"Of the genus *Mylodon*, there were at least two types in the North American Pleistocene, one represented by *M. harlani*, a grazing type; the other by *M. garmani*, here described, apparently a browsing type. The one had a broad lip, heavy humerus, tibial and astragalar facets of the fibula separate; the other has a narrower, more compressed skull and rostrum, a lighter humerus, tibial and astragalar facets not separated (agreeing thus with *Paramylodon*). Also, as a further adaptation to the browsing habit, certain of the dorsal vertebræ have

<sup>\*</sup> Brown, B., op. cit., p. 569.

<sup>+&</sup>quot; As indicated by the small condylar foramen in the skull."

<sup>‡</sup> Allen, G. M., op. cit., p. 344.

three articulating facets for greater mobility in reaching upward, a condition found in *Megatherium* but not in *Mylodon robustus*, a grazing species of South America."

I think Doctor Allen is correct in the assumption that M. harlani and M. garmani show certain contrasting features, and that the latter was the lighter and slenderer animal, but I do not believe these points of contrast sufficiently great to imply so marked a difference of feeding habits in creatures of similar tooth structure. The "doctors disagree" also, for Brown's arguments which prove Paramylodon a grazer have not impressed Allen, who thinks that Paramylodon and M. garmani are both browsers. The latter further believes that *M. harlani* was a grazing type, which agrees with Brown's statement, since Paramylodon and M. harlani are one, and not with Allen's previously expressed view. I can not but feel that the statement I have made above should apply equally to all Mylodons and to *Megatherium* as well, though in the somewhat more generalized Mylodon an occasional variation from a strictly phytophagous diet might well have been possible when opportunity or necessity arose.

### RELATIONSHIPS AND DISTRIBUTION.

Mylodon represents the family Mylodontidæ, which, as Scott\* says, was numerously and variously represented in the Pleistocene of South America, but much less so in that of North The Mylodontidæ also include the South American America. genera Lestodon, larger than Mylodon; Scelidotherium, the smallest Pleistocene member of the family, with a narrow, elongate skull; *Glossotherium*, with an arched bony bridge connecting the anterior end of the nasal bones with the premaxillaries; and *Grypotherium*, the hide of which has been preserved in a cavern in Last Hope Inlet, Patagonia, and has a thick covering of coarse hair and, within, a continuous armor of small ossicles. Similar ossicles have been found at Rancho La Brea, in fact, a number were contained in the matrix clinging to the skull at Yale, and the inference is therefore that the external covering of Mylodon was similar to that of Grypotherium.

Geologically the Mylodontidæ range back into the Santa Cruz formation of South America, and Scott says further :†

"There is evidence that at least two of the ground sloth families, the Megalonychidæ and the Mylodontidæ, were distinguishable in the Deseado stage [Upper Oligocene], but

\*Scott, W. B., A history of land mammals in the western hemisphere, p. 601, 1913.

† Op. cit., p. 610.

FIG. 16.



FIG. 16. Map showing distribution of the giant sloth *Mylodon* in North America. Maximum glaciation shown by oblique lines. Probable migratory route indicated by arrow.

tory route indicated by arrow.

 Washtuena Lake, Washington. 2. Willamette River, Oregon. 3. Silver
 Lake, Oregon. 4. Paisley, Oregon. 5. Rancho La Brea, California.
 Hay Springs, Nebraska. 7. Walsenburg, Colorado. 8. Llano Estacado,
 Texas. 9. Big Bone River, tributary of Osage River, Missouri. 10. Mammoth Ravine, Mississippi. 11. Big Bone Lick, Kentucky. 12. Port Kennedy bone cave, Pennsylvania. 13. Petite Anse, Louisiana. 14. Ashley
 Ferry, South Carolina. 15. Rock Creek, Texas. 16. Seneca, Kansas.
 Additional localities learned from Hay's Lowa report, received while this paper was in press are: Harrison Co., Lowa: Tecumseb. Nebraska: Look

Additional localities learned from Hay's Iowa report, received while this paper was in press, are : Harrison Co., Iowa; Tecumseh, Nebraska; Lookout Mt., Tennessee ; Blue Lick Springs, Kentucky; Savannah, Georgia; and a doubtful Mylodon from Austin Co., Texas. materials are still lacking to give us any real knowledge of the suborder in that or the more ancient stages."

The map which has been compiled (fig. 16) indicates no fewer than sixteen distinct localities wherein remains of the genus *Mylodon* have been found in North America, while the arrow points to the probable migratory route during early Pleistocene or late Pliocene time. Mexico should give evidence of this migration, but except for the questionable Austin Co. occurrence I am at present unaware of the discovery of *Mylodon* south of the Texas panhandle.

The northernmost limit of distribution coincides with the southern extent of maximum glaciation, two localities, the Port Kennedy bone cave and Big Bone Lick, being right on the line of demarcation; while Seneca, Kansas, Tecumseh, Nebraska, and Harrison Co., Iowa, are within the limits of the ice. In Oregon the localities follow the outline of the projecting glacial spur most curiously. This northern limit of distribution is open to two interpretations, one, that of a climatic limit for warmth-loving beasts, being the first to be suggested by the map. On the other hand, the genus may well have had a more northerly limit during a warm interglacial period, their remains being destroyed by the subsequent advance of the ice. This is the only explanation in my mind for the distribution in Oregon, while in the Kansas locality, actually within the limits of glaciation, the specimen came from a well, implying a depth sufficient to guard the remains from destruction.

The Texas *Mylodon* is associated with warm climate animals —horse, elephant, camel, peccary and *Glyptodon*—representing what Osborn calls the first Pleistocene fauna. The Seneca, Tecumseh, and Iowa Mylodons lay within the limits of the Kansan drift\* and as they were buried deep within it the assumption is that the genus lived not later than the Aftonian interglacial period which preceded the Kansan glacial period at the very beginning of Pleistocene time. The Texan fauna embraces several Aftonian forms as given by Calvin,† which include *Mylodon*. On the other hand, Calvin's list contains some forms which apparently had not yet put in their appearance in Texas, as, for instance, *Mammut americanum*, but this may be due to geographical and environmental rather than to time distinction. This evidence serves to check the inference derived from the specimens found within the limits of the ice.

\*See Hay, O. P., Smithson. Misc. Coll., vol. lix, No. 20, fig. 7 on p. 9. 1912.

†Calvin, S. E., Iowa Geol. Surv., vol. xx, p. 316, 1910.

# ART. XXIII.—A Simple and Inexpensive Apparatus for Tidal Analysis; by ERNEST W. BROWN, F.R.S.

THE object of this paper is the description of an apparatus for the analysis of tidal observations which anyone may quickly construct for himself at an expenditure of a dollar or so. Darwin's well-known apparatus<sup>\*</sup> has disadvantages which he himself recognized. It consisted of strips of xylonite on which the observations were written, and of guide sheets carefully printed to show the positions in which the strips were to be placed for the evaluation of any particular tide. He had these made for a year's observations and about a dozen different periods; each sheet was to serve for 74 days and there were thus some 60 large sheets to be used.

The device described here is intended to obtain precisely the same result as that of Darwin. The strips are replaced by endless paper bands and the guide sheets by simple instructions for arranging the bands and for testing the correctness of the arrangements. The simplification is partly due to the introduction of adding machines, now in practically universal use where large masses of additions are to be performed. With them it is no longer necessary that the digits should be very accurately in column for easy addition; so long as the complete numbers are sufficiently nearly in a column as not to be confused with numbers in a neighboring column, the operator has no difficulty in following his work: with accurately ruled paper, however, the numbers can be put into accurately placed columns as easily as in Darwin's method. Nothing else in the device requires any great care. As its successful use depends mainly on small details, I have described the latter somewhat fully. There is also another reason for this. Experience has shown that a considerable proportion of the time of the operator is often taken up with the arrangement of his work, frequently more than the actual calculation. There is thus more opportunity for the saving of time and trouble and consequently expense (which is now the chief factor in reducing tidal observations) by the simplification of the arrangement of the work, than in any other part of it. An apparently triffing detail in operation may make the difference between success and failure in this respect.

The materials required are ruled paper, sheets of cardboard, paper cutter, a few brads and double-pointed tacks, and a board.

The ruled paper should be of good quality with smooth finish and not so heavy as to prevent it from folding easily. The horizontally and vertically ruled lines are to be uniformly

\*Roy. Soc. Proc., A, vol. lii, p. 345, 1892, Sc. Papers, vol. i, 216.

a quarter of an inch apart. This size permits two figures to be written in each square with no parts of the figures projecting over the ruled lines.\* Its width is to be 19'' (72 squares + an inch overlap) and height at least 8'' (32 squares).

The cardboard should be fairly flexible so that if bent into an arch whose height is about one-sixth of the base, it will not tend to break and will return to its original form when released. The height of the card should be about 12", its width rather less than 9". The latter measurement is to be such that when two sheets of the ruled paper are folded closely over it one edge of the outer sheet shall come accurately over the ruled line on the sheet 18" from that edge.

A cover to the cardboard is made by folding a sheet of the same kind of paper (ruling is unnecessary) closely over it and pasting the edges together, care being taken that the cover does not stick to the cardboard. If the latter be bent a little the cover can easily be slipped off and on.

A convenient paper cutter is that used to trim photographs; it must be large enough to make a 9" cut.

Four brads are driven into a board so as to form a rectangle about  $8'' \ge 6''$ . They should be a little inclined inwards along the direction of the 8'' sides of the rectangle. The doublepointed tacks are partly driven in close to the brads with their lengths in the same direction, so that when the sheet of cardboard is bent and the edges placed between the pairs of brads it will remain bent and will be slightly raised above the board. Each brad and tack may be replaced by a small wood step nailed to the board.

In Darwin's scheme for the analysis of a year's observations, hourly heights are used. He also suggested that such units should be adopted (e. g. tenths of a foot or inches) that all heights could be expressed by two digits. It is convenient to describe the use of the apparatus on this basis, although there is room for four digits if necessary. The 24 observations for the first day (day 0) are written in every third square of the top line of the ruled paper beginning with the third square from the left and ending with the 72d. The second and succeeding days are similarly written in the following lines up to the end of the first block, which, for the solar tides, contains 30 days. At the end of several of the blocks one day of observations is not used for these tides : it must, however, be inserted. Thus 12 sheets contain all the observations; these may be written in, as they are measured from the tide curve. They are then summed according to Darwin's published instructions,

\* I have found two figures between ruled lines a better guide to the eye than one figure between closer rulings, especially when dealing with numbers of several digits.

both horizontally and vertically, and the results used for the analysis of the solar and long-period tides.

For this and future arrangements, the number of the day is written in red ink twice on each line in any one of the unoccupied squares, once between the left edge and the observation for  $11^{h}$  and once between the observation for  $11^{h}$  and  $23^{h}$ . A pair of single red lines is ruled so as to enclose all the observations at  $0^{h}$  and a pair of double red lines to enclose all those at  $12^{h}$ .

The observations have now to be regrouped so as to give an analysis for mean lunar time. For this purpose the first sheet is placed face down on the table and the two edges folded over so that the left edge comes on to the ruled line following the observations at 23<sup>h</sup>. It is pasted in this position by using the inch overlap; care being taken that the inside portions of the paper do not stick together; the position of the folds is immaterial. The folded sheet is then placed on the paper cutter and each day of observations is cut off; it will form a closed band. The first 37 of these bands are placed in order on the paper cover, previously made, by bending the cover in one hand and slipping the bands on with the other. The cover carrying the bands is then flattened out and the sheet of cardboard bent and slipped in. The remaining 9 cards each carrying 37 days of observations are treated in the same manner. Thus the whole year's observations are contained on bands stretched over ten cards.

The bands have now to be arranged in accordance with a scheme made out in advance. Suppose that the arrangement required is such that the observations at the following times are to be brought into the same column: 0<sup>d</sup>, 0<sup>h</sup>; 1<sup>d</sup>, 1<sup>h</sup>; 2<sup>d</sup>, 2<sup>h</sup>; 3<sup>d</sup>, 3<sup>h</sup>; 4<sup>d</sup>, 4<sup>h</sup>; 5<sup>d</sup>, 4<sup>h</sup>; and so on. The first card with cover and bands is bent and the edges placed between the brads on the board, care being taken that a band does not rest on the tacks. Any band is then easily movable round the card; it can be rapidly and certainly brought into any position by gently pressing on it with a piece of soft red rubber and sliding it to the right as required.\* If the band be pinched over the edge of the card when it is brought into position it will remain there while the other bands are being placed. The card and cover being about 12" long and the sum of the widths of the 37 bands being only 9". 25, there is ample room for the movement of the bands, it being not necessary that they should lie very close to one another. The remaining 9 cards being treated in the same way, the observations are ready for the summing which gives the M series of tides.

\* If slid to the left there may be trouble owing to the inside pasted edges of the band catching on the edge of the cover.

+ If the covers be made of fairly stiff paper, the cards and the board may be dispensed with and the bands moved by one hand while the other holds the cover. But this method is not quite so convenient for use. The other rearrangements follow a similar process; a separate set of instructions for the ordering of the bands is given to the operator for each arrangement. After the process is completed the cards are slipped out of the covers carrying the bands, and the latter can be stored away in an envelope on which it is only necessary to write the year and the port. The observations have thus only been written once and are always available for future reference.

If the observations be typed on to the sheets, the dimensions of the apparatus may be conveniently reduced in the ratio 3:2.

It remains to explain the instructions to be given to the operator. The single and double pairs of red lines and the number of the day are the guides; one pair and one day number will be found on each face of the card when the bands are placed over it. Define 'no step' for any day as a case when the observation at  $0^{h}$  on its band is immediately under that for  $0^{h}$  on the band next above, and 'one step left' when that at  $1^{h}$  is immediately under that at  $0^{h}$  on the band next above. Similarly for 'one step right'. The words 'left' and 'right' need not be repeated since there are never both left and right steps with any one tide. The instructions to the operator consist only in giving to him the step for each day, and some other fact which will enable him to test his work. The method of obtaining the instructions and the test will be explained by giving in detail those for what Darwin calls 'mean lunar time'.

The speed of this time in degrees per mean solar hour is  $14^{\circ} \cdot 4920521$ . It therefore moves  $347^{\circ} \cdot 80925$  in 24 hours. This, on division by 15, shows that  $23 \cdot 187283$  mean lunar hours are equivalent to 24 mean solar hours. As we can only use observations at exact solar hours, the position of the band on day n is obtained by finding the nearest integer to

## $(n+\frac{1}{2})23.187283,$

the approximate coincidence being made in the middle  $(12^{h})$  of each day of observation. Thus, for days 1, 2, 3, 4 the red lines must be one step left of those on the previous days, respectively, for day 5 no step, for days 6, 7, 8, 9, 10 one step left, for day 11 no step, and so on. The whole series is obtained by converting '187283 into a continued fraction. The successive convergents are

1	, 2	, 3	, 53	, 162	,
5	11	16	283	863	
0	11	10	200	000	·

The third convergent shows that the successive 6th, 5th, 5th days are to be no-step days, while the fourth convergent shows that for 283 days there must be 18 cases in which the no-step day is the 6th and 35 cases in which it is the 5th (18 + 35 = 53, 35)

 $18 \times 6 + 35 \times 5 = 283$ ). We have thus the series 6, 5, 5, repeated 17 times, then 6, 5, and finally 6, 5, 5, to the end. The above examination of the first eleven days shows that the first no-step day is day 5, the next day 11, which facts give the start of the 6, 5, 5 series. It is easy to run through and find the days on which 0<sup>h</sup> comes into the first column. Thus the instructions to the operator are as follows:

'Place each band one step to the left of the previous band except on the following days when no step is to be made: 5, 11, 16, 21, and thereafter the 6th, 5th, 5th in succession until the no-step day 277 is reached. The days 283, 288, 294, 299, 304 are no-step days and thereafter the 6th, 5th, 5th in succession until the end. For testing the arrangement, note that the observations at 0<sup>h</sup> for the following days are in the same column :--0, 29, 58, 59, 88, 118, 147, 177, 206, 236, 263, 295, 324, 354.'

Similar instructions may be made out for the other periods.

This apparatus is more convenient for tidal analysis than that which I described\* some years ago and which has been continuously in use for the synthesis of the small terms in the moon's motion which are to be inserted in the lunar tables. It is not, however, applicable, like the earlier device, to general harmonic analysis.

Yale University, New Haven, Conn., Feb. 8, 1915.

\* Monthly Notices R. A. S., vol. lxxii, pp. 454-463.

# ART. XXIV.—The Radio-active Content of Certain Minnesota Soils; by JAMES C. SANDERSON.

# Introduction.

In a previous article,\* the writer described methods by which the freely emanating radium and thorium contents of a characteristic New Haven soil were measured, and showed how the thorium content of a soil could be estimated from a sample of about fifty pounds. The results obtained for the disintegrated red sandstone, near the Sloane Physical Laboratory, were 8.9 x 10<sup>-14</sup> gram of radium and 1.35 x 10<sup>-6</sup> gram of thorium per cubic centimeter of the soil. In an article entitled "A Study of the Radium Emanation of the Air Contained in Various Soils,"<sup>+</sup> Satterly discusses three methods of measuring the radium content of soils; the first two are comparison methods, but the third, which he calls "the bottle experiment," gives quantitative results, and he finds for a sandy soil in Cambridge, England, 22 x 10<sup>-14</sup> gram of radium per cubic centimeter of moist soil and 18 x 10<sup>-14</sup> for the same soil when dry. His figures show that about twenty per cent of the volume of the moist soil was water, so that, in a given volume, the radio-active material actually present was very much less than in the case of the dry soil. Since the apparent radioactivity, or amount of free emanation, was higher in the moist soil, we must conclude that the amount of moisture in a soil is a large factor in its emanating power. On the other hand, soil chemists consider the hygroscopic properties of a soil to be a valuable index of its fertility.

Although it has been known for some time that the radiations from radium and its products have a stunting and deforming effect upon vegetable organisms, just as they have a destructive effect on animal tissue, only recently has it been demonstrated conclusively that radio-active enrichment of the soil, with extremely minute quantities of radium, acts very beneficially upon vegetation and results in a marked increase of fertility. J. Stoklasa and V. Zdobricky‡ describe experiments in which various plants are treated with waters containing radium emanation. Lentils, peas and wheat, treated with radio-active water, showed respective gains of 62, 116 and 164 per cent over the control plants. When buckwheat was supplied with 30 Mache units every five days, it showed an increase of 43 per cent over the control culture, but with 60

> \* This Journal, vol. xxxii, p. 169, 1911. † Proc. Cambr. Phil. Soc., vol. xvi, part 4. ‡ Comptes Rendus, vol. clvii, pp. 1082-4.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, NO. 232—April, 1915. 26 Mache units the increase was 107 per cent. Some poppies gained 117 per cent in the fruit and 32 per cent in the stems. Various vegetables and grains were grown in ordinary soil, but with the air surrounding them charged with radium emanation; these showed earlier maturity and increased yield of from 30 to 90 per cent. In all cases they found that large quantities of emanation, in either the soil or the air, injured and retarded the plants. Dr. H. H. Rusby, of Columbia University, has done some very interesting work along these lines. Unfortunately only a popular account of it is at hand. He used radium ore tailings, containing small residual quantities of radium, to enrich several acres of land. Great care was



taken to standardize the work, and all plots, enriched and control, were treated exactly alike. Only three of twenty-seven kinds of vegetables failed to show a gain due to the radio-active enrichment, and the average increase was fully thirty per cent. Dr. Rusby also found that too much radio-active material had a detrimental effect.

In view of these results, it seemed desirable to determine the radio-active content of several soils from different localities, to see whether there is any apparent interdependence between the radio-activity of a soil and its fertility. First it was necessary to modify the radium method so that it became applicable to comparatively same samples of soils.

### Apparatus.

The electroscope and ionization vessel were of the same type as those described in the article cited above. The cylindrical ionization vessel, 35 centimeters in height and 14 centimeters in diameter, was provided with brass connecting tubes, one near the top and one near the bottom. The central electrode,

after passing through amber insulation and guardring in the top of the ionization vessel, served as a support for the gold leaf in the electroscope. The latter had double walls, to prevent thermal air currents, and a magnetic charging device, which was very reliable and convenient, and, perhaps, merits a short description. AA', in the figure, is a flat permanent magnet, pivoted at O, and with a counterpoise W which makes its equilibrium unstable in a horizontal position. Under the end A' is an electromagnet. A small loop of fine wire is attached to the end A by a bead of sealing wax. In one position of the magnet, this loop dips into two cavities in the piece of amber B; in the other position it is withdrawn. The cavities contain mercury, and one is permanently connected to the central electrode and gold leaf; the other to the high potential battery and the guardring. One lead of the electromagnet is grounded; the other passes out of the case through a glass tube. A similar tube serves for the high potential lead. A single battery cell and the momentary throw of a reversing switch send the magnet AA' from one position to the other, alternately charging and insulating the leaf and electrode. The handling of dry, fine soils is very dusty work, and the arrangement just described is particularly desirable, in that it involves no openings in the electroscope through which dust might enter. A galvanized iron cylindrical vessel, 60 centimeters in height and 14.5 centimeters in diameter, was provided, at the top, with a narrow channel of rectangular crosssection, and a depth of about one centimeter, which was filled with paraffine and into which the cover fitted. Brass connecting tubes were soldered at the center of the base and the center of the cover.

### Method of Procedure.

A piece of cotton was placed over the small opening in the bottom of the cylinder, which was then filled completely with the soil to be tested, well packed and shaken down. The cover was sealed in place and the lower end of the cylinder was connected with the filter pump. The soil was rinsed thoroughly, with frequent exhaustions, to get rid of all possible free radium emanation. During a known period of three or more days the radium emanation was allowed to build up in the soil, the lower end of the cylinder being sealed, and the tube in the cover left open, so that any rinsing action, due to changes in atmospheric pressure, might affect only the upper layers of soil. The air from these layers did not reach the ionization vessel.

After this period of recuperation, the lower end of the cylinder was connected to the ionization vessel through a short

piece of pressure tubing, and the ionization vessel was connected, in turn, to a manometer and filter pump. Pinchcocks were provided between the manometer and the pump, between the ionization vessel and the cylinder and at the top of the cylinder. First the ionization vessel alone was exhausted, the first pinchcock closed and the pressure  $p_1$  noted. Then the second pinchcock was opened and the ionization vessel and cylinder allowed to come to an equilibrium pressure p which was noted. Finally the pinchcock on the upper end of the cylinder was opened and the whole system came to the atmospheric pressure  $p_2$  (the gross barometric height), the air passing through the soil. After three hours, the active deposit was in virtual equilibrium with the emanation, and readings of the electroscope were taken (in divisions per minute over a definite part of the scale).

### Determination of the Radium Content.

Call the volume of the ionization vessel  $V_1$  and the volume of the cylinder  $V_2$ . Then the porosity P, or the ratio of the volume of the interstices of the soil to the total volume, is given by

$$P = \frac{V_{1}}{V_{2}} \frac{p - p_{1}}{p_{2} - p}$$

The volume of air in the soil is, of course, P V<sub>2</sub>, and the volume of air, at atmospheric pressure, which enters the ionization vessel as it passes from  $p_1$  to  $p_2$  is  $V_1 \frac{p_2 - p_1}{p_2}$ . Hence the number of cubic centimeters of soil from which emanation is taken equals  $\frac{\text{air entering ionization vessel}}{\text{total air in soil}} \times V_2 = \frac{V_1 \frac{p_2 - p_1}{p_2}}{P V_2}$ 

$$\times \mathbf{V}_2 = \frac{\mathbf{V}_1}{\mathbf{P}} \quad \frac{p_2 - p_1}{p_2} = \mathbf{V}_2'$$

Let *n* be the fraction of a gram of radium per cubic centimeter of the soil, which would account for its free emanation; then  $n V_{2'}$  is the mass of radium which supplied the emanation in the ionization vessel. If this emanation caused a leak of N divisions per minute in the electroscope,  $\frac{n V_{2'}}{N}$  is the mass of radium which would cause a leak of one division per minute. But it is known, from the standardization of the electroscope, that the emanation in equilibrium with M gram of radium (from a standard solution of radium bromide) gave a leak of A divisions per minute; whence  $\frac{M}{A}$  is the mass of radium whose equilibrium quantity of emanation would give one division per minute. Equating, substituting for  $V_2'$  and P, and

solving for n, we get: 
$$n = \frac{MN}{AV_2} \frac{p_2(p-p_1)}{(p_2-p)(p_2-p_1)}$$

Then  $n_o$ , the mass of radium per cubic centimeter of soil which would account for its equilibrium amount of free emanation, is given by:  $n_o = \frac{n}{1-e^{-\lambda t}}$  where  $\lambda$  is the constant for radium emanation and t the time during which the soil was left standing.

## The Thorium Content and Thorium Standard.

The method by which the thorium content of a soil can be determined was fully described in the writer's previous article. On account of the short life of thorium emanation, a continuous current of air was drawn through the soil and through the ionization vessel. It was necessary to consider the building up of the emanation as a layer of air passed through the soil, its partial disintegration in transit to the ionization vessel, and its average concentration while passing through that vessel; the equation took the form:

$$\mathbf{N} = \frac{\mathbf{K} \ n \ q}{\lambda \ \mathbf{P} \ k_2} \left( 1 - e^{-\frac{\lambda k_2}{q}} \right) e^{-\frac{\lambda k_1}{q}} \left( 1 - e^{-\frac{\lambda k_3}{q}} \right)$$

Where N is the leak of the electroscope in scale divisions per minute, n is the fraction of a gram of thorium per cubic centimeter of the soil which would account for its free emanation, q is the air current in cubic centimeters per second,  $\lambda$  is the constant for thorium emanation, P is the porosity (from radium measurements),  $k_1$  is the volume of the connecting tubes and filters between the cylinder and ionization vessel,  $k_{s}$ is the volume of the ionization vessel,  $k_s$  is the volume of air in the soil and K is the constant of the apparatus. The constant K was determined, as before, by making a run on neutral quartz sand impregnated with a known quantity of ThCl, in solution. On treating thorite with hydrochloric acid, free silicic acid is produced, which, on drying, forms a thin film on each particle of sand. This film contains the thorium and has very great emanating power. It seemed probable that there would be a critical thickness for this film beyond which some of the emanation would be occluded and the emanating power would diminish. To test this point, about three liters of the neutral sand were mixed with enough of the standard solution to give it a thorium content about equal to that of the more active

# J. C. Sanderson—Radio-active Content of

natural soils; i. e., about  $10^{-5}$  gram of thorium per cubic centimeter. Runs with this strength and with twice this strength yielded the same value of K, but when the strength was raised to  $5 \times 10^{-5}$  gram, the value of K fell off by about thirty per cent., showing that the critical thickness of film had been passed.

Name	<b>Ĥertility</b>	Ra gram × 10 <sup>14</sup>	$\begin{array}{c} {\rm Th}\\ {\rm gram}\\ \times\\ 10^7 \end{array}$	<sup>Th</sup> / <sub>Ra</sub> × 10 <sup>-5</sup>	Depth	Character of Soil
Cyrus	A	80	64	80	Surf.	Red River Valley; bowlder-clay; late Wisconsin drift.
University Farm	A	75	71	95	3 feet	Till coating on outwashed plain from late Wisconsin drift.
Preston	A	64	47	73	3 feet	Loess.
Luverne	А	64	41	6,4	3 feet	Loess.
Manitoba J'nc'n	A	62	60	97	Surf.	Red River Valley; bowlder-clay; late Wisconsin drift.
Coon Creek	в	28	27	96	$\frac{3}{\text{feet}}$	Dune Sand.
Guthrie	в	27	25	93	Surf.	Outwashed plain from late Wis- consin drift.
Bemidji	В	25	34	136	3 feet	Outwashed plain from late Wis- consin drift.
Nickerson	в	24	32	133	Surf.	Sandy deposit on moraine from early Wisconsin drift.
Willow River	В	20	32	160	Surf.	Outwashed plain from early Wis- consin drift.
Philbrook	В	20	29	145	Surf.	Outwashed plain from late Wis- consin drift.
Twin Valley	В.	17	28	165	Surf.	Sandy plain ; Lake Agassiz ; rich in nitrogen.
Cloquet	В	13	32	246	Surf.	Moraine from early Wisconsin drift.

# Discussion of Results.

The results of the radium and thorium measurements, as well as some data with regard to the fertility, origin, etc., of the soils, are given in the table.

Quite a wide range of variation will be noticed in the radium content of the soils; the lowest value is well above that found

for the red sandstone soil in New Haven, while the next in order is about the same as that of Satterly's Cambridge soil, the amounts increasing until the highest is nine times the New Haven value. The thorium variation is not so great, but it is very marked, and apparently quite independent of the radium content.

This variation in radio-activity is probably not due to a very wide dissimilarity in the actual radio-active content of the soils, but rather to varying ratios of "free" emanation to total emanation produced. This, in turn, depends on the superficial area of the particles in the soil. In his book, "The Soil," A. D. Hall states that a coarse, sandy soil (like Nickerson) has a superficial area of about 11,000 square feet per cubic foot, while a very fine soil (like Cyrus) may have as much as 70,000 square feet per cubic foot; these limits correspond sufficiently closely to the observed radium limits, 13 and 80.

It so happened that the soils examined are sharply differentiated into two groups from the standpoint of fertility. Those marked "A" are extremely fertile, while the "B" soils range from distinctly mediocre to low fertility. A sharp break in both the radium and thorium contents will be noticed at the boundary between the two groups. This accords very well with the results of the experiments in artificial enrichment, mentioned in the introduction. The conclusion seems justifiable that the hygroscopic properties of a soil are a valuable index of its fertility, not merely because the presence of moisture has of itself a beneficial effect on vegetable growth, but also because the presence of moisture increases the radioactive emanating power of the soil, and because, furthermore, the ability to retain moisture implies fineness of texture, which also means great emanating power, so that at least part of the effect is due to a greater proportion of "free" radium and thorium emanations.

## Summary.

A method has been devised by which the radium content of a soil may be determined from a sample of about fifty pounds.

This method, together with the thorium method, previously described, was used to determine the radio-active content of some thirteen typical Minnesota soils.

Without exception, the very fertile soils were found to be richer in radium and thorium emanations than soils of inferior fertility, which is in accord with the results of experiments on artificial enrichment of soils.

In conclusion I wish to express my hearty thanks to Dr. F. J. Alway of the Department of Agriculture for his invaluable assistance.

Physical Laboratory, University of Minnesota, January 9th, 1915.

# ART. XXV.—The Use of Hydrochloric Acid in the Estimation of Certain Forms of Organic Nitrogen; by W. A. DRUSHEL and M. M. BRANDEGEE.

(Contributions from the Kent Chemical Laboratory of Yale Univ.-cclxv.)

MARKOWNIKOFF,\* while studying the preparation of pyrotartaric acid, observed that nitrogen is quantitatively removed from cyanbutyric acid in the form of ammonium chloride by the action of hydrochloric acid, suggesting that a method of estimating nitrile nitrogen, based upon the action of hydrochloric acid, might be developed which would be fully as simple as the well-known method of Carius for halogens.

The purpose of this investigation was to determine the best conditions for effecting the quantitative decomposition of certain forms of nitrogen compounds and determining rapidly the nitrogen obtained in the form of ammonium chloride. To this end members of several classes of nitrogen compounds were selected for study, such as the nitriles, amides, imides, cyanogen-substituted esters, and amino-acids. In particular the following substances were examined : acetonitrile, proprionitrile, proprionamide. succinimide, cyan-acetic ester, ethyl a-cyan-propionate, ethyl a-cyan-butyrate, normal dipropyl a-cyan-acetic ester, and amino-acetic acid. It is well known that when compounds of these types are heated with aqueous mineral acids they are hydrolyzed to the corresponding organic acids and the ammonium salts of the mineral acids used. By using concentrated hydrochloric acid in excess at suitable temperatures it was found that in these compounds the nitrogen could be fixed quantitatively and could be estimated by titrating the ammonium chloride with standard silver nitrate using potassium chromate as an indicator, after removing the excess of hydrochloric acid. The decomposition of the substances studied, by means of aqueous hydrochloric acid, is represented by the equations on the following page.

In the cyanogen compounds which on hydrolysis yield malonic or substituted malonic acids the decomposition resulted in considerable pressure in the sealed tubes, indicating the further decomposition of the dibasic acids with the formation of carbon dioxide and monobasic acids.

The decomposition was effected by heating the compounds in sealed tubes of thick-walled glass, about  $25^{\text{cm}}$  in length and in inside diameter not less than  $15^{\text{mm}}$ . From one tenth to three tenths of a gram of the substance was weighed out, using capillary bulbs for weighing out and transferring liquid compounds. The weighed material was placed in a combustion tube and  $3^{\text{cm}^3}$ 

\* Markownikoff, Ann. der Chem. u. Pharm., clxxxii, 331.

 $\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CN}+\mathrm{HCl}+2\mathrm{H}_{3}\mathrm{O}\longrightarrow\mathrm{CH}_{3}-\mathrm{COOH}+\mathrm{NH}_{4}\mathrm{Cl}\\ \mathrm{acetonitrile}\\ \mathrm{C}_{3}\mathrm{H}_{5}-\mathrm{CN}+\mathrm{HCl}+2\mathrm{H}_{3}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{5}-\mathrm{COOH}+\mathrm{NH}_{4}\mathrm{Cl}\\ \mathrm{propionitrile}\\ \mathrm{O}\\ \vdots\\ \mathrm{C}_{4}\mathrm{H}_{5}-\mathrm{C}-\mathrm{NH}_{4}+\mathrm{HCl}+\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{2}\mathrm{H}_{5}-\mathrm{COOH}+\mathrm{NH}_{4}\mathrm{Cl}\\ \mathrm{propionamide}\\ \mathrm{CH}_{2}-\mathrm{CO}\\ \mathrm{CH}_{4}-\mathrm{CO}\\ \mathrm{CH}_{2}-\mathrm{COOH}\\ \mathrm{CH}_{2}-\mathrm{COOH}\\ \mathrm{CH}_{2}-\mathrm{COOH}\\ \mathrm{CH}_{2}-\mathrm{COOH}\\ \mathrm{CH}_{2}-\mathrm{COOH}\\ \mathrm{CH}_{2}-\mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CN}-\mathrm{CH}_{2}-\mathrm{COOC}_{4}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{4}\mathrm{O}\longrightarrow\mathrm{CH}_{3}\\ \begin{array}{c} \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CN}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{4}\mathrm{O}\longrightarrow\mathrm{CH}_{3}-\mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{2}-\mathrm{COOC}_{4}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{4}\mathrm{O}\longrightarrow\mathrm{CH}_{3}-\mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{CH}_{3}-\mathrm{C}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{4}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{5}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{5}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{5}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{5}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{5}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{7}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOC}_{5}\mathrm{H}_{5}+\mathrm{HCl}+3\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{7}\\ \mathrm{COOH}\\ \mathrm{COOH}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{COOH}_{2}+\mathrm{HCl}+\mathrm{HCl}+\mathrm{H}_{1}+\mathrm{H}_{2}\mathrm{O}\longrightarrow\mathrm{C}_{3}\mathrm{H}_{7}\\ \mathrm{COOH}\\ \mathrm{COOH}+\mathrm{C}_{3}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}\\ \mathrm{COOH}+\mathrm{C}_{3}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{3}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{3}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{3}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{3}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{1}\mathrm{H}_{6}\mathrm{O}\\ \mathrm{COOH}+\mathrm{C}_{$ 

of hydrochloric acid of about 1.2 sp. gr. were added through a long-stemmed funnel. The tube was then sealed, cooled, and in the case of liquid substances the capillary bulb was broken by giving the tube a few smart raps on the palm of the hand. The sealed tube was now inserted in an iron casing and the whole placed in a Carius combustion furnace. The temperature was raised to between 180° and 215°, preferably to about 200°, and kept at this point for two to two and a half hours. In the case of glycocoll a longer time was found necessary for complete decomposition. After the combustion was considered to be complete the tube was cooled, the end of the tube was fused to relieve any pressure resulting from the decomposition of the substance, after which the tube was entirely removed from its case, the end cut off and the contents washed into an evaporating dish without loss. In order to remove the excess of hydrochloric acid the solution was evaporated to dryness on a steam or water bath under a draught hood, leaving the evaporating dish

on the bath for fifteen minutes after its contents had been reduced to dryness. The dish containing ammonium chloride and other combustion residues was then placed in a drying oven and heated at 110° for five minutes to remove traces of hydrochloric acid not removed by heating on the steam bath.

Several preliminary experiments were made to ascertain if the last traces of hydrochloric acid could be removed in a drying oven without a weighable loss of ammonium chloride. Carefully dried and weighed ammonium chloride was heated on the steam bath and also in the drying oven at different temperatures for varying lengths of time and the loss in weight determined. It was found experimentally that no ammonium chloride is lost during the evaporation process, and that the loss by heating one gram of ammonium chloride in the drving oven at 110° for ten minutes did not exceed two tenths of a milligram. Since the amount of material used for a determination of nitrogen seldom exceeded three tenths of a gram, the loss of ammonium chloride in the drying oven at 110° during a period of five minutes could in no case affect the accuracy of the result. The results obtained with pure ammonium chloride are recorded in Table I.

#### TABLE I.

NH₄Cl taken grm.	Hours on bath.	Temperature of oven.	Time in oven.	Loss in weight grm.
1.0000	$1 \ 1/2$			
1.0425	1 1/2			none
1.0000	1 1'/2	120°	1/2 hr.	0.0091
1.2386		$110^{\circ}$	1/2 "	0.0009
1.2378		$105 - 108^{\circ}$	1/2 "	0.0002
1.0425		105–108°	1'/2 "	0.0008
1.0422		$110 - 112^{\circ}$	10 min.	0.0002
1.2377		110-112°	10 "	0.0002

The most favorable decomposition time and temperature were studied by making a series of experiments with a sample of cyan-acetic ester known to contain a little less than the theoretical amount of nitrogen. It was found that at moderately low temperatures the decomposition was incomplete at the end of two hours, but that at 200° decomposition was effected quantitatively within this time. In this series the removal of the excess of hydrochloric acid was attempted by making repeated evaporations on the steam bath without final heating in the oven. The results obtained in the latter experiments of the series indicate that the hydrochloric acid can not be completely removed by evaporation on the steam bath alone. This led to the expedient in subsequent experiments of heating the

# Estimation of Organic Nitrogen.

dried residue in the oven at 110° for five minutes before titration. The results of these preliminary experiments with cyanacetic ester are recorded in Table II. The results recorded in the subsequent tables were obtained by using the modified procedure, making use of the drying oven to remove the last traces of free hydrochloric acid.

The ammonium chloride resulting from the substances studied and purified from free hydrochloric acid as previously described, was estimated volumetrically by titrating the dissolved salt with standard decinormal silver nitrate in the presence of a few drops of potassium chromate as an indicator. The presence of small amounts of weak organic acids, such as acetic acid and its homologues, does not influence the action of the chromate indicator. In the presence of stronger acids such as succinic acid, it was found best to add a very little sodium acetate to the solution before titration, and preferably before the addition of the indicator.

### TABLE II.

## Cyan-acetic Ester. Nitrogen, 12:39% (Preliminary experiments.)

Weight taken grm.	Time in hours	Temperature of furnace	Titration N/10 AgNO <sub>3</sub> cm <sup>3</sup>	Per cent of Nitrogen found
0.2320	1	100	11.86	7.2
0.2652	1	100	15.79	8.3
0.2006	1	100	10.6	7.3
0.1762	2	115 - 125	11.3	9.0
0.2582	2	125 - 130	19.1	10.4
0.2462	2	145	19.6	11.2
0.3042	2	150 - 165	26.22	12.24
0.2116	2	165-185	18.49	12.24
0.1991	2	180 - 200	18.03	12.4
0.3178	2	180 - 200	28.42	12.5
0.3001	2	180-200	26.80	12.5

In all of the experiments except those recorded in Table VI a very considerable excess of hydrochloric acid was used as previously described. Occasionally this led to the explosion of a tube in the combustion furnace. In the first series of experiments of Table VI the amount of hydrochloric acid was greatly reduced but still in excess of the theoretical amount necessary. In this series no tubes were lost by explosion and in every case the substance was completely decomposed within the time allowed, resulting in the quantitative fixation of the nitrogen. Glycocoll is apparently more slowly decomposed than the other substances studied, a minimum of three and a half hours being

		Cyan-acetic Ester.	Nitrogen,	12.39%.				
Weight taken grm.	In furnace hours	Tempera- ture	Nitrogen found gram.	Nitrogen theory grm.	Error grm.			
0.2920	3	$180^{\circ}-210^{\circ}$	0.0342	0.0371	-0.0029			
0.2565	21/2	دد دد	0.0302	0.0318	-0.0013			
0.2862	<u>، د</u>	66 66	0.0337	0.0354	-0.0018			
0.2765	"	cc cc	0.0353	0.0342	-0.0019			
	a-Cyan-propionic Ester. Nitrogen, 11.03%.							
0.3156	2불	$180^{\circ} - 210^{\circ}$	0.0342	0.0348	-0.0006			
0.3448	56	46 66	0.0377	0.0380	-0.0003			
0.2404	3	$180^{\circ} - 190^{\circ}$	0.0274	0.0275	-0.0001			
0.2561	"	$180^{\circ}-200^{\circ}$	0.0282	0.0282	0.0000			
		a∙Cyan-butyric Este	r. Nitroge	n, 9·93%.				
0.2743	21	180°-220°	0.0270	0.0272	-0.0005			
0.2296		" "	0.0227	0.0225	+0.0002			
0.2394	"	180°-215°	0.0238	0.0237	+0.0001			
0.2784	"	cc cc	0.0280	0.0276	+0.0004			
	n-Di	propyl-cyan-acetic	Ester. Nitr	ogen, 7·26%.				
0.2312	25	$180^{\circ}-215^{\circ}$	0.0163	0.0167	-0.0004			
0.2181		66 66	0.0155	0.0128	-0.0003			
0.2692	66	180°-210°	0.0193	0.0195	-0.0005			
0.2100	66	66 66	0.09.20	0.0921	0.0009			

### TABLE III.

required to decompose one fifth of a gram at a temperature of about 200°. Even with  $5^{cm^3}$  of concentrated hydrochloric acid the decomposition was incomplete at the end of three hours; on the other hand,  $2^{cm^3}$  of acid were sufficient when the heating was continued for three and a half hours. Apparently the

### TABLE IV.

Acetonitrile. Nitrogen, 34.16%.

Weight taken grm.	In furnace hours	Tempera- ture	Nitrogen found gram.	$\begin{array}{c} {\rm Nitrogen} \\ {\rm theory} \\ {\rm grm.} \end{array}$	Error grm.
0.1384	$2\frac{1}{2}$	180°-210°	0.0467	0.0463	-0.0004
0.1860	<i>دد</i> ّ	66 66	0.0635	0.0636	-0.0001
0.1184	66	66 66	0.0401	0.0404	-0.0003
0.1233	2		0.0233	0.0233	0.0000
		Propionitrile.	Nitrogen, 25	•46.	
0.2349	21	$180^{\circ}-210^{\circ}$	0.0602	0.0598	+0.0004
0.1629		$180^{\circ}$ -220°	0.0421	0.0415	+ 0.0006
0.1874	66	62 66	0.0484	0.0477	+0.0007
0.1803	66	66 66	0.0463	0.0459	+ 0.0004
### Estimation of Organic Nitrogen.

		r topionamiue.	Millogen, 10	10,0.	
Weight taken grm.	ght In en furnace Tempera- a, hours ture		Nitrogen found grm.	Nitrogen theory grm.	Error grm.
0.1728	$2\frac{1}{2}$	$180^{\circ}-220^{\circ}$	0.0329	0.0331	-0.0005
0.2084		$180^{\circ} \cdot 210^{\circ}$	0.0392	0.0399	-0.0004
0.1863	66	** **	0.0355	0.0357	-0.0005
0.2028	"	، د د	0.0385	0.0389	-0.0004
		Succinimide.	Nitrogen, 14	15%.	
0.1902	2분	$180^{\circ}-210^{\circ}$	0.0275	0.0269	+0.0004
0.1738	<u>دد</u>	66 66	0.0254	0.0246	+0.0008
0.1890	66	cc cc	0.0261	0.0266	-0.0002
0.1848	.46	۵۵ ۵۵	0.0262	0.0261	+0.0001

### TABLE V.

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TABLE	VI.
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### Propionamide. Nitrogen, 19.18%.

Weight taken grm.	Conc. HCl <sub>3</sub> cm	In furnace hours	Tempera- ture	Nitrogen found grm.	Nitrogen theory grm.	Error grm.
0.1986	1	$2\frac{1}{2}$	180°-210°	0.0379	0.0380	-0.0001
0.2257	1	«č	66 66	0.0423	0.0431	-0.0008
0.1839	2	"	66 66	0.0349	0.0352	-0.0003
0.2040	2	"	۰۰ ۰۰	0.0392	0.0391	+0.0001
		Gl	ycocoll. Nitrog	gen, 16·47%.		
0.2008	2	$2\frac{1}{2}$	$180^{\circ}-210^{\circ}$	0.0287	0.0373	-0.0086
0.2019	2	66	۰۰ ۰۰	0.0301	0.0375	-0.0074
0.2020	5	3	c. cc	0.0361	0.0376	-0.0012
0.2045	2	$4\frac{1}{2}$	$180^{\circ}-215^{\circ}$	0.0379	0.0380	-0.0001
0.2022	2	3	$180^{\circ}-220^{\circ}$	0.0366	0.0376	-0.0010
0.2028	2	$3\frac{1}{2}$	180°-230°	0.0375	0.0377	-0.0005

amount of acid, provided an excess is used, is much less important than the temperature and time used in making the decomposition.

On the whole the results obtained agree well with the theoretical amounts of nitrogen in the compounds studied except in the case of cyan-acetic ester. This ester was used without special purification and was known to contain a little less than the theoretical amount of nitrogen, due to a slight admixture of a non-nitrogenous ester.

From the experimental results obtained the following conclusions have been drawn:

1. The nitrogen of aliphatic nitriles, cyanogen substituted esters, amides and imides, may be quantitatively fixed as amino-

### 404 Drushel and Brandegee—Hydrochloric Acid, etc.

nium chloride by heating with an excess of hydrochloric acid in sealed tubes for two to three hours at about 200°. The nitrogen of glycocoll is fixed quantitatively at this temperature only after three to four hours.

2. The excess of hydrochloric acid used to effect the decomposition of the substances is not completely removed by evaporation on the steam bath, but requires heating in the oven for five minutes at 110°. Under these conditions no measurable amount of ammonium chloride is lost by volatilization.

3. The ammonium chloride resulting from the decomposition of the substances studied may be estimated titrametrically by means of standard silver nitrate with potassium chromate as an indicator, after the removal of the excess of hydrochloric acid used. The other decomposition products do not interfere with the titration of the ammonium chloride.

ART. XXVI.—The Supposed Vanadic Acid from Lake Superior is Copper Oxide; by WALDEMAR T. SCHALLER, U.S. Geological Survey.

IN 1851, Teschemacher described a supposed natural occurrence of vanadic acid as follows\*:

"The surface of the large masses of copper found in the celebrated Cliff mine, on the border of the lake, is sometimes encrusted with thin layers of small crystals of quartz, interspersed with a yellow pulverulent substance resembling peroxyd of iron. On exposing small pieces of these layers to the action of the blowpipe, this yellow powder turns black. Pulverized with the quartz and boiled in dilute nitric acid gives a very light apple-green solution; this powder so treated, washed, filtered and evaporated to about the amount of the water used in washing, was left untouched for about a month, when minute crystalline red globules began to form on the surface, which fell to the bottom when by aggregation they became sufficiently heavy. The form of these crystals could not be determined even by the microscope, the crystalline points were so numerous and in such apparent confusion. From these red crystalline masses, the writer, as well as Dr. A. A. Hayes, produced the vanadiates of silver and lead. No metal having been found in the solution, it is probable that the yellow powder exists here as vanadic acid, VO<sub>a</sub>."

\* Teschemacher, James E. : On the vanadium minerals form Lake Superior, this Journal (2), vol. xi, p. 233, 1851.

Col. W. A. Roebling of Trenton, N. J., has in his collection a specimen of this supposed vanadic other from the Cliff mine, Michigan, and has written on the label that this rare specimen of vanadic ocher came from James Nelson of Cold Spring, Putnam Co., N. Y., who bought the collection of Dr. Lee of Pcekskill in 1860. Lee had made a collection of copper minerals in Lake Superior in 1853, and this original specimen was among them. On request, Col. Roebling very kindly lent the specimen to the writer and it has been possible to identify the material chemically. There seems to be no question but that his specimen is similar to the material tested by Teschemacher. The writer's hearty thanks are expressed to Col. Roebling for his willingness to sacrifice part of the specimen in order to have it determined.

The yellow to orange mineral encrusts quartz and native copper as felted masses of minute long prismatic crystals, so thin that under the highest magnification, the black borders of total reflection cover the entire crystal. A very few of the largest individuals seem to show a slight transparency in orange color. Chemical tests showed no vanadium and in fact only cuprous oxide could be found. Even water was not found although the minute amount of material available made the test of doubtful value, as a small amount of water may have escaped detection. Treatment with HCl turned the mineral white, doubtless due to the formation of cuprous chloride. Comparative chemical tests with the hydrocuprite from Cornwall, Lebanon County, Pennsylvania, gave identical tests and the supposed vanadium other from Lake Superior is probably the same as the hydrocuprite from Pennsylvania. Possibly the Lake Superior material has changed from a colloidal hydrocuprite to crystalline cuprite and would then be a meta-colloid as recently defined by Wherry.\*

In the original description of hydrocuprite,<sup>†</sup> Genth states that: "the cuprite variety chalcotrichite from Cornwall [Penn.] sometimes assumes an orange color, so that on the same piece acicular crystals of a fine crimson color can be seen gradually changing to an orange yellow. It is, therefore, very probable that the orange crystals are pseudomorphs of hydrocuprite after cuprite." According to Genth the direction of the reaction Cu<sub>2</sub>O.nH<sub>2</sub>O  $\implies$  Cu<sub>2</sub>O + nH<sub>2</sub>O is the reverse for the Pennsylvania hydrocuprite to what is suggested for the Lake Superior material. Under the microscope, the Pennsylvania hydrocuprite is seen to be formed of very small prismatic crystals similar to those of the Lake Superior material but not so minute.

\* Wherry, E. T., Journ. Wash. Acad. Sci., vol. iv, p. <sup>1</sup>112, 1914. † Genth, F. A., Preliminary report on the mineralogy of Pennsylvania, Second Geol. Survey Penn., p. 46, 1875.

The color of much of the Lake Superior material is yellow suggesting that the substance is more likely a cuprous hydroxide rather than the simple oxide. The minute size of the crystals, however, also tends to change the red color of cuprite to a yellow. A similar tendency was noted for the red oxide of mercury, montroydite, which, in the larger crystals\* is a deep red, but in feltlike masses composed of minute prismatic crystals is a light yellow brown and as spherical masses composed of minute bristling prismatic crystals is almost light yellow in color.

A microscopic examination of chalcotrichite crystals from Arizona showed moreover that whereas most of the crystals were a deep brownish red, the thinner ones were yellowish brown and the very thinnest ones were yellow. These yellow crystals were much thicker than any of those from the Lake Superior specimen. It may well be, therefore, that both the Lake Superior specimen and the hydrocuprite from Pennsylvania are, in fact, only cuprite and not a distinct cuprous hydroxide.

A second occurrence of "vanadium ocher" was mentioned by Goydert in his description of sulvanite. A specimen of sulvanite in the collection of Colonel Roebling contained a considerable amount of this "vanadium ocher" which was readily identified as cuprodescloizite. In 1909, K. A. Nenadkevich<sup>±</sup> very briefly described a new mineral from the province of Ferghana in Russian Turkestan. This mineral is dark red, silky, soft and moss-like, and was named alaite. Its composition was stated to be V<sub>2</sub>O<sub>5</sub>.H<sub>2</sub>O, but no analysis was given. Alaite may prove however to be a calcium vanadate either related to or identical with hewettite.

The important result obtained is that the so-called vanadic ocher from Lake Superior is free from vanadium and is to be stricken from lists of vanadium minerals.

\*Hillebrand, W. F., and Schaller, W. T.: The mercury minerals from Terlingua, Texas, Bull. 405, U. S. Geol. Survey, 1909. + Goyder, G. A.: Sulvanite, a new mineral, Jour. Chem. Soc., London, vol. lxxvii, p. 1094, 1900.

‡ Bull. Acad. Sci., St. Petersburg, p. 185, 1909.

## ART. XXVII. - The System Anorthite-Forsterite-Silica; by Olaf Andersen.

CONTENTS.

Introduction.

- I. EXPERIMENTAL WORK. Preparation of mixtures. Thermal study. Heating curves. Quenchings. DESCRIPTION OF SOLID PHASES. II.
- Anorthite. Forsterite. Cristobalite and Tridymite. Clinoenstatite Spinel.
- III. THE BINARY SYSTEMS. The system forsterite-silica. The system anorthite-silica. The system forsterite-anorthite.

IV. DISCUSSION OF SOME TYPES OF TERNARY SYSTEMS WITHOUT SOLID SOLUTION.

General remarks.

Type 1.

- Synopsis of terms.
- Crystallization curves.
- Phase relations.

Type 2. Type 3.

General qualities of curves and points. Examples of crystallization.

Type 4.

Qualities of boundary curve jo.

Type 5.

Recurrent crystallization of a solid phase.

- THE ANORTHITE-FORSTERITE-SILICA SYSTEM. V.
  - The spinel field.

Mixtures with excess of MgO.

- The ternary field. The alteration point.
  - The ternary eutectic.
  - The boundary curves.
  - The isotherms.
- Normal crystallization in different sections of the ternary field. The eutectic field.
  - The reaction field.
  - The section anorthite-clinoenstatite.
- Crystallization with removal of forsterite from the liquid.

Some Applications of the Results to Petrologic Problems. General remarks.

- Application of the reaction principle to olivine-bearing rocks. Magmatic resorption of olivine.
  - Summary of application to olivine-bearing rocks.
- Remarks on spinel-bearing rocks.

Summary.

VI.

AM. JOUR. Sci.-Fourth Series, Vol. XXXIX, No. 232.-April, 1915. 27

### Introduction.

THE present study was commenced as an examination of the supposed binary system CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-MgSiO<sub>8</sub>.

The preliminary work proved that  $MgSiO_{3}$  (clinoenstatite) was unstable at its melting point, breaking up into  $Mg_{2}SiO_{4}$ (forsterite) and melt, and the system had to be treated as a ternary system with  $CaAl_{2}Si_{2}O_{8}$ ,  $Mg_{2}SiO_{4}$  (or MgO) and  $SiO_{2}$  as components. The study of this ternary system, however, showed that, though all components were stable at their melting points, there was in certain mixtures a breaking up of  $CaAl_{2}Si_{2}O_{8}$  and  $Mg_{2}SiO_{4}$  in such a way that  $Al_{2}O_{9}$  combined with MgO to form  $MgAl_{2}O_{4}$ , spinel. In fact spinel proved to be the primary phase in a number of mixtures of  $CaAl_{2}Si_{2}O_{8}$ , MgO (or  $Mg_{2}SiO_{4}$ ) and  $SiO_{2}$  where no other phases but the components might be expected. With  $MgAl_{2}O_{4}$  as a solid phase, the composition of the liquid and the course of crystallization can no longer be expressed in terms of the three components here considered nor, in fact, of any three components.

The relations of the system  $CaAl_2Si_2O_8-Mg_2SiO_4-SiO_9$ , therefore, can be properly explained only by considering this system as a part of the quaternary system  $CaO-MgO-Al_2O_3-SiO_2$ . This great system embraces the ternary systems  $MgO-CaO-Al_2O_3$ .  $MgO-CaO-SiO_2$ ,  $MgO-Al_2O_3-SiO_2$ , and  $CaO-Al_2O_3-SiO_2$ , which, in a way form an exterior "skeleton" round the quaternary "body." The "body" itself is then made np of a number of binary, ternary, and perhaps quaternary systems.

One of the "skeleton" systems, the  $CaO-Al_2O_3-SiO_2$  system, has already been worked out in this laboratory" and others are being studied. The general problem of the quaternary system  $CaO-MgO-Al_2O_3-SiO_2$  has not been undertaken hitherto, and because of its complicated character may remain unstudied for a long time to come. In the meantime, any study of the relations between some of the phases occurring in the system will be of interest.

The present paper deals with that part of the quaternary system in which the composition of the mixtures can be expressed in terms of the components anorthite-forsterite-silica. It is explained above that some of the mixtures of these components show relations inexplicable in a ternary system. The particular part of the system to which these mixtures belong will here be only cursorily touched upon, emphasis being laid on the larger part which can be treated as a ternary system.

\* E. S. Shepherd, G. A. Rankin, and F. E. Wright (Preliminary report on the ternary system  $CaO-Al_2O_3-SiO_2$ ; a study of the constitution of Portland cement), J. Ind. Eng. Chem. iii, 1, 1911; G. A. Rankin and F. E. Wright, this Journal (4), xxxix, 1-79, 1915.

### I. EXPERIMENTAL WORK.

The experiments were undertaken on artificial mixtures of pure components. No fluxes were used. All thermal work was done in air under ordinary pressure.

### Preparation of Mixtures.

The preparations were made up from : Ground *quartz* purified with HCl; *alumina* treated with a boiling solution of NH<sub>4</sub>Cl; pure analyzed *calcium carbonate*, *magnesia* obtained by igniting the purest precipitated hydrated carbonate. All the substances were dried to constant weight and kept in desiccators.

Most of the mixtures were prepared in the following way: The compounds were weighed and then carefully mixed by grinding them together in an agate mortar. Charges of 5 gr. were generally used. The finely ground mixture was brought without loss into a 10<sup>cc</sup> platinum crucible and heated in the platinum resistance furnace for about one hour at a temperature high enough to ensure a complete melting. The melt was then suddenly chilled to form glass, which in turn was crushed to a fine powder and sifted. Then the whole operation of melting, chilling, and powdering was repeated and the powdered glass of the second treatment was crystallized by proper heating. With mixtures rich in silica this required several hours or even several days. With less viscous mixtures, on the other hand, it could be done in a few minutes. During the crystallization the powder sintered together to a solid cake, which was crushed and ground. In this way perfectly homogeneous mixtures were always obtained.

In cases where larger quantities of preparations were made up, the melting had to be undertaken in a Fletcher furnace. Otherwise the procedure was the same as that described.

### Thermal Study.

The platinum-resistance furnace was used in all the thermal work. The temperatures were measured with the Pt: Pt-Rh thermoelement in connection with the usual potentiometer installation of the Geophysical Laboratory.\*

Heating curves.—In the preliminary work heating curves were run on mixtures of the series CaAl<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-MgSiO<sub>5</sub>. Charges of about 2 gr. were used, the bare thermoelement being immersed in the charge. The temperature was read every half minute. The results are stated in Table 1. It is

\* W. P. White, Phys. Rev. xxv, 334, 1907.

Compo in weight	sition per cent.	Temperature of heat change.			
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	MgSiO <sub>3</sub>				
20	80	1259°			
30	70	1260°			
35	65	1260°			
40	60	$1260^{\circ}$			
45	55	$1259^{\circ}$			
50	50	1259°			
60	40	1260°			
70 30		1261°			
80 20		1260°			

# TABLE 1.

Heating curves.

seen that in all the mixtures the heating curve shows a break at about 1260° C. If no further examination had been made, this heat change would have been taken as a proof of eutectic melting at 1260° C. The quenching experiments, however, have proved that the break is not due to an ordinary eutectic melting, but, as will be explained further on, to a simultaneous melting of  $CaAl_2Si_2O_8$  and decomposition of  $MgSiO_3$  with the formation of  $Mg_2SiO_4$  and melt.

In some of the mixtures the heating curves showed indications of breaks at higher temperatures, probably corresponding to points on the liquidus. These breaks were very indistinct, however, and in general no other heat change than the one recorded at 1260° C. was observed.

Quenchings.—In order to determine the compositions and temperatures of the invariant points, the extension of the fields of the different solid phases and the shape of the liquidus surface a number of quenchings were made. The quenching method has been described several times in papers from this laboratory.\* The procedure is to hold a charge of a certain composition at a constant temperature long enough to assume a condition ef equilibrium throughout the charge, then to cool suddenly to the temperature of the air and to examine the product under the microscope. By such a sudden cooling, generally accomplished by dropping the charge from the constant temperature of the furnace into cold mercury, most silicate liquids undercool readily, and form a clear glass which at ordinary temperature remains unchanged for an indefinite length of time. The solid phases that may be present in equilibrium

\* E. g., E. S. Shepherd and G. A. Rankin, this Journal (4), xxviii, 308, 1909.

with the liquid at the higher temperature also remain unchanged, unless they pass through inversion points.

In Tables 2, 3, 4, and 5 those of the quenching experiments which have any direct bearing on the determination of invariant points, boundary curves and liquidus surfaces are listed. The data on the forsterite-silica system are given in detail in a previous paper.\*

The following abbreviations are used in the tables and sometimes in the text:

An = Anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>).

Fo = Forsterite  $(Mg_2SiO_4)$ .

En = Enstatite (MgSiO, without reference to modification).  $Cl en = Clinoenstatite (MgSiO_{a}).$ 

 $Tr = Tridymite (SiO_{a}).$ 

 $Cr = Cristobalite (SiO_a).$ 

 $Sp = Spinel (MgAl_2O_4).$ 

Gl = Glass.

### II. DESCRIPTION OF SOLID PHASES.

A very important part of work like the present lies in the identification of the solid phases occurring in the different mixtures at different temperatures. This identification has to be based almost entirely upon microscopic examination of the quenched products. It is therefore essential first to know in detail the optical properties of the phases that are possible in the mixtures considered and then to be able to redetermine such properties with a sufficient degree of accuracy on the finegrained material obtained from the quenchings.

In the present case all the solid phases occurring have been previously described in papers from this laboratory. Their properties have been determined on chemically pure material. As to the recognition and measurement of these optical properties on fine-grained powder under the microscope the recent development of microscopy has made this comparatively easy, although it is still a matter requiring time and patience.

In the following descriptions of the stable, solid phases of the anorthite-forsterite-silica system, the thermal, crystallographic and optical properties are first briefly reviewed with reference to the earlier determinations made in this laboratory and then general descriptions of the phases as they appear in the present system are given.

\*N. L. Bowen and Olaf Andersen, this Journal (4), xxxvii, 487, 1914. + For descriptions of the most advanced methods see: F. E. Wright, The Methods of Petrographic-Microscopic Research, Publ. No. 158, Carnegie Institution of Washington, 1911.

	Co in we	ompositic ight per	on cent.	Tem- pera-	Time		
Comp	ounds		Oxides		ture	in	Results
An	SiO <sub>2</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	degrees		
80.00	20.00	54.60	29.32	16.08	$\begin{array}{c}1486\\1490\end{array}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
70.00	30.00	60.27	25.66	14.07	$\frac{1440}{1445}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
51.00	49.00	71.06	18.69	10.25	$\begin{array}{r}1351\\1355\end{array}$	$\begin{array}{c}2\\2\end{array}$	Tr & An Gl & Tr
01 00	10 00		10 00	10 20	$\begin{array}{c c}1361\\1368\end{array}$	$\begin{vmatrix} 2\\ 2 \end{vmatrix}$	Gl & Tr Gl only

# TABLE 2.The System Anorthite-Silica.\*

\* This system has been described by G. A. Rankin and F. E. Wright in their work on the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. (This Journal (4), xxxix, 1, 1915.)

The results, stated in this table, agree very closely with those of Rankin and Wright, who find the eutectic An: Tr at 1359° of composition An 52.5 SiO<sub>2</sub> 47.5.

	in	Сомро weight	SITION. t per ce	ent.	Tempera-	Time		
Co pou	m- nds		Oxi	ides		ture in degrees	heated in hours	Results
An	Fo	SiO2	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO			
90	10	43•20	32.99	18.09	5.72	$\begin{array}{c}1463\\1468\end{array}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
86	14	43.18	31.52	17.29	8.01	$\begin{array}{c}1442\\1446\end{array}$	$\begin{array}{c} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array}$	Gl, An & Sp Gl only
80	20	43.16	29.32	16.08	11.44	$\begin{array}{c}1457\\1463\end{array}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Sp Gl only
70	30	43.11	25.65	14.07	17.17	1478	$\frac{1}{2}$	Gl & traces of Sp
60	40	43.06	21.99	12.06	22.89	$\frac{1475}{1481}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Sp Gl only
54	46	43.03	19.79	10.85	26.33	$\frac{1462}{1470}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl, Sp & Fo Gl only
50	50	43.02	18.32	10.02	28.61	$\begin{array}{r}1513\\1519\end{array}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Fo Gl only
40	60	42.97	14.66	8.04	34.33	$\begin{array}{c}1618\\1622\end{array}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Fo Gl only

### TABLE 3.

### The System Anorthite-Forsterite.

Composition in weight non cont									
	Compo	SILION .	es	ate					
Com terna	ponent ary sys	s in tem		Ox	ides		mpere degre	ne he hours	Results
An	Fo	SiO2	$\mathrm{SiO}_2$	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	In	in Ti	
90	8.74	1.26	43.92	32.99	18.09	5.00	$\frac{1470}{1474}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
80	8.74	11.26	49.60	29.32	16.08	5.00	$\frac{1457}{1463}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
80	17:48	2.52	44.60	29.32	16.08	10.00	$     \begin{array}{r}       1407 \\       1414 \\       1402 \\       1467     \end{array} $	1212	Gl & An Gl only Gl, Sp & An
70	10	20	54.55	25.66	14.07	5.72	$\frac{1407}{1398}$		$\frac{Gl \& An}{Gl only}$
70	17.48	12.52	50.27	25.66	14.07	10.00	$\frac{1100}{1380}$ 1387	$\frac{\frac{2}{\frac{1}{2}}}{\frac{1}{2}}$	Gl & An Gl only
70	23.08	6.92	47.06	25.66	14.07	13.21	$\frac{1362}{1368}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Sp Gl only
70	26.21	3.79	45.27	25.66	14.07	15.00	$\frac{1416}{1423}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Sp Gl only
60	8.74	31.26	60.95	21.99	12.06	5.00	$\frac{1346}{1354}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
60	20.00	20.00	54.51	21.99	12.06	11.44	$\frac{1306}{1313}$	$\frac{1\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
60	29.71	10.29	48.95	21.99	12.06	17.00	$\frac{1321}{1326}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Fo Gl only
60	31.45	8.55	47.95	21.99	12.06	18.00	$\frac{1344}{1348}$	$\frac{1}{\frac{1}{2}}$	Gl, Fo & Sp Gl only
60	34.95	5.02	45.95	21.99	12.06	20.00	$\begin{array}{c} 1412 \\ 1420 \end{array}$	1 4 1 4	Gl & Sp Gl only
56	22.72	21.28	55.22	20.52	11.26	13.00	$\begin{array}{c} 1278 \\ 1286 \end{array}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
55	26.21	18.79	53·79	20.16	11.05	15.00	$\frac{1275}{1281}$	$\frac{1}{1}$	Gl & Fo Gl only
54·50	25.33	20.17	54.59	19.97	10.95	14.49	$\frac{1260}{1264}$	1 1	Gl & Cl en Gl only
54	30	16	52·17	19.79	10.86	17.17	$\frac{1317}{1319}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Fo Gl only
53	26.21	20.79	54·92	19·43	10.62	15.00	$\frac{1278}{1284}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Cl en Gl only
52.50	20.10	27.40	58·71	19•24	10.55	11.50	$\frac{1240}{1246}$	1	Gl, An & Cl en Gl only
52·00	13.98	34.02	62•49	19 <sup>.</sup> 06	10.45	8.00	$\frac{1268}{1275}$ $\frac{1219}{1219}$	$\frac{2}{2}$	Gl & An Gl only All crystalline loose powder
50.43	 14·92	34.65	62.84	18.48	10.14	8.54	$     \begin{array}{r}       1223 \\       \overline{1240} \\       1249 \\       \overline{1219} \\       \hline       1219     \end{array} $	$\frac{1}{2}$ $\frac{2}{2}$	Gl, An & Tr Gl & Tr Gl only All crystalline loose powder
			1				1223	2	Gl, Tr & An

### TABLE 4. The System Anorthite-Forsterite-Silica.

TABLE 4. (Continued.)

(	Compos	sition i	s	ated					
Comj terna	oonents ry sys	s in tem	Oxides				mperal	me hea hours	$\operatorname{Results}$
An	Fo	$SiO_2$	$SiO_2$	$Al_2O_3$	CaO	MgO	in	Tin in	
50.00	17.48	32.52	61.63	18.32	10.05	10.00	$     \begin{array}{r}       1229 \\       1232 \\       \overline{1221}     \end{array}   $	$\frac{1\frac{1}{2}}{1}$	Gl & Cl en Gl only All crystalline loose powder
							1225	1	Gl & Cl en
<b>49.0</b> 0	15.00	36.00	63.61	17.96	9.85	8.58	$1255 \\ 1260 \\ \hline 1210 \\ \hline 1255 \\ \hline 125$	1	Gl & Tr Gl only All correctabling
							1219	2	loose powder Gl, Tr & Cl en
				•			1306	1	Gl & Fo
50.00	29.00	21.00	55.04	18.32	10.05	16.59	1311	1	Glonly
							$\frac{1302}{1306}$	1	Gl, Fo & Clen Gl & Fo
50.00	41.02	8.98	48.16	18.32	10.02	23.47	$1408 \\ 1416$	12 12	Gl & Fo Gl only
45.00	31.51	23.49	 55·44	16.49	9.05	18.02	$\frac{\overline{1331}}{1340}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Cl en Gl only
41.00	13.00	46.00	69.29	15.03	8.24	7.44	$\overline{1420}\\1426$	1	Gl & Cr Gl only
40.00	24.47	35.53	63·30	14.66	8.04	14.00	$\frac{1318}{1322}$	$\frac{1}{\frac{1}{2}}$	Gl & Cl en Gl only
40.00	28.01	31.99	61.27	14.66	8.04	16.03	$\frac{1345}{1355}$	$\begin{array}{c} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array}$	Gl & Cl en Gl only
40.00	36.00	24.00	56.70	14.66	8.04	20.60	$\begin{array}{c} 1368\\ 1376\end{array}$	1 1	Gl, Fo & Cl en Gl only
30.00	43.69	26.31	57.98	10.99	6.03	35.00	$\frac{1420}{1426}$	$\frac{1}{1}$	Gl, Fo & Cl en Gl only
0 - 00	0.0.0		64.01	0.10	5.09	01.00	$\frac{\overline{1430}}{1437}$	1 ]	Gl & Cr Gl only
25.00	36.70	38.30	04.81	9.10	5.03	21.00	$\frac{1418}{1422}$	$\frac{1}{\frac{1}{2}}$	Gl, Cr & Cl en Gl & Cr
21.00	31.00	48.00	69.34	7.70	4.22	17.74	$\frac{1554}{1564}$	1 $\frac{1}{2}$	Gl & Cr Gl only
20.00	52.43	27.57	58.65	7.33	4.02	30.00	1479 1484	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Fo Gl only
							$1465 \\ 1473 \\ 1457$		$\frac{Gl \& Fo}{Gl \& Cl on}$
							1457	$\frac{1}{2}$	Gl, Fo & Cl en
10.00	59.49	97.55	64.99	2.60	2.01	30.00	$\frac{1508}{1514}$	$\frac{1}{\frac{1}{2}}$	Gl & Cl en Gl only
10.00	02 40	01.01	04.99	5 00		00 00	1492 1501	$\begin{array}{c c} 1\frac{1}{2}\\ 2\\ 1\end{array}$	Gl, Clen & Cr Gl & Cl en Gl Eo & Cl on
					ł		1405	$\frac{1}{2}$	Gl & Fo

### TABLE 5.

## The System Anorthite-Enstatite.

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Composition in weight per cent.											
Compo- nents in binary system		Components in ternary system				Oxides				Time heated in hours	Results
An	En	An	Fo	SiO2	$SiO_2$	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO			
90	10	90	7.	3	44.91	32.99	18.09	4.01	$\begin{array}{c}1489\\1494\end{array}$	1 <u>1</u> 22 122	Gl & An Gl only
80	20	80	14	6	46.59	29.32	16.08	8.01	$\frac{1437}{1443}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
70	30	70	21	9	48.25	25.66	14.07	12.02	$\frac{\overline{1373}}{1377}$	1 1	Gl & An Gl only
62	38	62	26.6	11.4	49.59	22.72	12.46	15.23	$\overline{1319}\\1325$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & An Gl only
60	40	60	28	12	49.92	21.99	12.06	16.03	$     \begin{array}{r}       1306 \\       1309 \\       \overline{1302} \\       1306     \end{array} $		Gl & An Gl only Gl, An & Fo Gl & An
58	42	58	29.4	12.6	50.25	21.26	11.66	16.83	$\frac{\overline{1315}}{1320}$	1 2 1 2	Gl & Fo Gl only
55	45	55	31.5	13.5	50.76	20.16	11.05	18.03	$\frac{1338}{1343}$	1 1 2 1 2	Gl & Fo Gl only
50	50	50	35	15	51.59	18.32	10.05	20.04	$\frac{1358}{1364}$	1212	Gl & Fo Gl only
45	55	45	38.5	16.2	52.42	16.49	9.05	22.04	$\frac{\overline{1390}}{1398}$	$\frac{\frac{3}{4}}{1}$	Gl & Fo Gl only
40	60	40	42	18	53.26	14.66	8.04	24.04	$\frac{1415}{1423}$	$\frac{1}{\frac{1}{2}}$	Gl & Fo Gl only
35	65	35	45.5	19.2	54.09	12.83	7.03	26.05	$\frac{\overline{1437}}{1443}$	1	Gl & Fo Gl only
30	70	30	49	21	54.93	10.99	6.03	28.05	$\frac{\overline{1465}}{1472}$	1 1	Gl & Fo Gl only
20	80	20	56	24	56.29	7.33	4.02	32.06	$\frac{\overline{1506}}{1510}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	Gl & Fo Gl only
10	90	10	63	27	58.27	3.96	2.01	36.06	$\frac{\overline{1542}}{1546}$	1 2 1 2 1 2	Gl & Fo Gl only

### Anorthite.

Anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) melts at  $1550^{\circ} \pm 2^{\circ}$  C.\* The crystals are triclinic. The optical properties are : a = 1.576;  $\beta = 1.583$ ;  $\gamma = 1.589$ ;  $2V = 80^{\circ} \pm 3^{\circ}$ . Optical character negative. Extinction angle on  $(001) = 35^\circ$ , crystals always showing polysynthetic twinning.

In the mixtures of the present system, the anorthite crystals were small and never showed distinct faces. The best crystals separated from melts near anorthite in composition. They were generally lath-shaped, or sometimes tabular, always elongated after the *a*-axis, forming the usual polysynthetic twins. Mean refractive index approximately 1.585; extinction angle determined from 27° to 42°, average 34.5 (20 separate determina-Sometimes the crystals formed thin needles after the tions). a-axis, without twinning, but otherwise showed the usual properties. In very viscous melts, for instance in (or near) the anorthite-silica series, the crystals became extremely small, and all attempts to determine their properties with any degree of accuracy failed. Even in such cases, however, the identification of the crystals could be considered certain. It was seen, for instance, in some mixtures that glass of refractive index 1.57 enclosed minute crystals which had a slightly higher refractive index than the glass and a low double refraction. This single observation proved at once that the crystals could not be forsterite, clinoenstatite, spinel or any of the silica modifications, and made the conclusion that they were anorthite at least very probable. The conclusion was fully corroborated by observations on other mixtures, determining points on the liquidus in cases where the properties of the solid phase could be ascertained. By bringing together these points it was plainly seen that no reasonable course of the liquidus could be obtained if the phase had been anything but anorthite.

Similar considerations can, of course, be equally well applied to other solid phases, when they form crystals included in glass, and are too small or otherwise unfit for measurement of optical properties.

### Forsterite.

Forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) melts at about 1890°.<sup>+</sup> It is found to be stable at the melting point.§ Formed in fluxes it appears in well-developed, orthorhombic crystals with (001) (010) (021) (101) and others as common forms. Cleavage after (001) and

<sup>\*</sup> Arthur L. Day and Robert B. Sosman, this Journal (4), xxxi, 341, 1911. † H. E. Merwin cited by N. L. Bowen, this Journal (4), xxxii, 564, 1912. ‡ N. L. Bowen and Olaf Andersen, loc. cit., p. 491. § See, however, Deleano, Zs. anorg. Chem., lxxxiv, 423, 1914. [E. T. Allen, F. E. Wright and J. K. Clement, this Journal (4), xxii, 391, 1906.

(010). Optical properties :\*  $\gamma = 1.670$ ;  $\beta = 1.651$ ; a = 1.635;  $\gamma - a = 0.035$ ;  $2V = 85^{\circ}16'$ . Optical character positive. Optical orientation  $c = \beta$ ;  $a = \gamma$ ; b = a. The crystals formed in the anorthite-forsterite-silica mixtures

are often well developed, always short prismatic after the c-axis or thick tabular after (010). The combinations are simple : the prevailing forms seem to be (120) (010) (021) and (101); but no reliable measurements could be made.

The best developed crystals were those included in glass from which, however, they could not be separated. In some of the more viscous melts the crystals were very small, appearing as rounded grains, easily determinable, and distinguished from clinoenstatite by their high refractive index, strong double refraction and the lack of twinning. The refractive index was approximately determined in several preparations at 1.65. Optical character positive. Axial angle large, nearly 90°. Distinct cleavage lines were generally seen except on small crystals included in glass. Small glass inclusions, often in symmetrical arrangement, were very common in crystals from various mixtures.

### Cristobalite and Tridymite.

Cristobalite and tridymite are the two modifications of silica stable within the range of temperature of the silica liquidus in the anorthite-forsterite-silica system. C. N. Fenner has shown that these two forms are enantiotropic, with an inversion point at 1470°, cristobalite being the high temperature form. The inversion is very sluggish and either of the forms may remain unchanged for a long time in temperature regions where it is unstable.

The melting point of cristobalite has been determined by Fenner at 1625° and by Endell and Rieke<sup>‡</sup> at 1685.° In the MgO-SiO<sub>2</sub> system, § however, there were indications that the melting point might be considerably higher, and in a later work on the diopside-forsterite-silica system Bowen has shown that the melting point of cristobalite must be higher than any of the values mentioned. This result is fully confirmed by the present work on the anorthite-forsterite-silica system. (See figs. 1, 2 and 10.) A possible explanation of the discrepancies between the different results is indicated by Bowen on the basis of the hypothesis suggested by Fenner for the explana-

<sup>\*</sup> N. L. Bowen and Olaf Andersen, loc. cit., p. 498.

<sup>N. L. Bowen and Olaf Andersen, loc. cit., p. 498.
† This Journal (4), xxxvi, 331, 1913.
‡ K. Endell and R. Bieke, Zs. anorg. Chem., lxxix, 239, 1912.
§ N. L. Bowen and Olaf Andersen, loc. cit., p. 496.
|| N. L. Bowen, this Journal (4), xxxvii, 218, 1914.
¶ Loc. cit., p. 372.</sup> 

tion of variations in the lower inversion points between a and  $\beta$  cristobalite. This hypothesis suggests that cristobalite consists of two or more molecular modifications in one crystal and that variable conditions of formation may bring about variable molecular constitutions with resulting variations in inversion point and melting point.

Cristobalite exists\* in two modifications, the a form and the  $\beta$  form, with an inversion point varying between 198° and 275°. The high temperature ( $\beta$ ) modification is regular, forming distorted crystals and aggregates, usually with the octahedron as the most common crystal form, sometimes with twins after the spinel law. The low temperature (a) form is slightly birefringent;  $\gamma = 1.487$ ; a = 1.484.

Tridymite<sup>+</sup> also forms two modifications, with an inversion region between 117° and 163°. The high temperature ( $\beta$ ) form is probably hexagonal, the low temperature (a) form probably orthorhombic. The crystals generally form hexagonal plates, often combined to characteristic wedge-shaped twins. Optical properties (of a form),  $\gamma = 1.473$ ; a (and  $\beta$ ) = 1.469;  $2\dot{V} = 35.8^{\circ}$ .

In the preparations of the anorthite-forsterite-silica system the silica crystals, formed in the accessible temperature regions, were so small that it was, in general, very difficult to discriminate between the two phases. As the crystals were always imbedded in glass, the refractive index could not be determined, but it was always much lower than that of the glass (which varied between 1.50 and 1.53). The crystals were either isotropic or showed a very faint double refraction. In some cases, at temperatures around 1500°, excellent crystals with cube and octahedron in equal development were seen. These crystals were perfectly isotropic and very probably represented the  $\beta$  form of cristobalite. In most cases, however, the crystals formed rounded grains without distinct faces, mostly isotropic, but sometimes showing indication of double refraction. At the lowest temperatures where silica could be obtained as the primary phase, in mixtures near the ternary eutectic, anorthite-clinoenstatite-silica (1222° to 1300°) the crystals appeared like irregular patches, more frequently showing double refraction than those at higher temperatures. These crystals were probably tridymite.

### Clinoenstatite.

Clinoenstatite<sup>‡</sup> (MgSiO<sub>3</sub>) breaks up at 1557°, forming forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and liquid. The last of the forsterite melts at 1577°.

- \* C. N. Fenner, loc. cit., p. 360. † C. N. Fenner, loc. cit., p. 372. ‡ N. L. Bowen and Olaf Andersen, loc. cit., p. 495.

The crystals are monoclinic, tabular after (100) or prismatic after (110), always elongated after the *c*-axis. Polysynthetic twinning after (100) is very characteristic. Good prismatic cleavage after (110).

Optical properties:  $\gamma = 1.660$ ; a = 1.651;  $\gamma - a = 0.009$ ;  $2\nabla = 53.5^{\circ}$ : Extinction angle  $c: \gamma = 22^{\circ}$ . Plane of optic axes normal to (010).

Near the MgSiO<sub>2</sub> point of the anorthite-forsterite-silica system, the crystals of clinoenstatite were comparatively large, often with distinct faces. The general type was tabular after (100), elongated after the *c*-axis, with (100) and (110) and some "pyramid"\* as prevailing forms. Prismatic crystals with about equal development of (100), (010) and (110) were also seen. Some rough measurements of the prism angle 110: 110 could be made under the microscope on crystals of approximately vertical orientation. Average of 8 measurements (varying from  $86.5^{\circ}$  to  $89^{\circ}$ ) gave  $87.5^{\circ}$  with the orientation of the prism as usual in monoclinic pyroxenes (i. e., acute angle bisected by the plane of symmetry). Cleavage cracks after (110) were often seen. Sometimes some rough cracks after (010) and (100) were also noticed. Very characteristic of the clinoenstatite in most of the mixtures were some curved cracks roughly perpendicular to the *c*-axis. These cracks were probably due to contraction during the cooling of the crystals.

Some of the optical properties were determined on crystals from different mixtures containing from 10 to 55 per cent anorthite. Fairly good determinations of refractive indices could be made only occasionally when crystals free from the including glass were obtained. On mixtures containing 30, 40 and 55 per cent anorthite, the following determinations were made, respectively:

 $\begin{array}{l} \gamma = 1.663 \pm 0.003, \, a = 1.655 \pm 0.003 \, ; \\ \gamma = 1.660 \pm 0.003, \, a = 1.655 \pm 0.003 \, ; \\ \gamma = 1.662 \pm 0.003, \, a = 1.652 \pm 0.003. \end{array}$ 

Numerous rough determinations gave the approximate values of the average refractive index from 1.65 to 1.66. The extinction angle  $c: \gamma$  was measured on carefully selected crystals. Values from 21° to 23.5° were obtained on crystals from various mixtures. Average of 8 good determinations gave  $c: \gamma = 22.1^{\circ}$ .

The crystals showed the usual polysynthetic twinning after (100).

In the viscous mixtures near the ternary eutectic, anorthiteclinoenstatite-silica the crystals became very small, and their

<sup>\*</sup> Actually some combination of monoclinic hemipyramids, which, owing to the polysynthetic twinning, acquires the appearance of an orthohombic pyramid.

properties could not be determined exactly. Twinning could only be detected occasionally. Nevertheless the identification was certain on the basis of the high refractive index and the low double refraction.

In general it appears that the clinoenstatite crystals of the present system are identical with those formed from the pure  $MgSiO_s$  glass. There is evidently no change in the properties following changes in the composition of the mixtures. The principal optical properties, refractive indices and extinction angle, for instance, seem to be the same through all the system, within the limits of error of the measurements.

### Spinel.

Artificial spinel\* (MgAl<sub>2</sub>O<sub>4</sub>) forms regular octahedral crystals without distinct cleavage. The melting point is about 2135°,  $n = 1.723 \pm 0.002$ .

In the mixtures of the anorthite-forsterite-silica system, the spinel crystals were generally very small though they often formed sharp octahedrons. Sometimes they also occurred in more irregular, elongated grains with crystal faces only indicated. Cleavage cracks were never seen. The refractive index was determined in one preparation.  $n = 1.715 \pm 0.003$ .

It was essential for the general consideration of the whole system to decide conclusively whether the present phase was spinel. Although the properties mentioned above in general characterize spinel, some doubt might arise as to their adequacy for microscopic discrimination between spinel and periclase (MgO), so much the more as periclase, *a priori*, should be considered a more probable phase than spinel. The habit of the crystals is exactly the same. Both phases are isotropic, and the difference in refractive index (spinel 1.723; periclase 1.734) is not much larger than the limits of error of rough determinations under unfavorable conditions.

I therefore found it desirable to get some information on the microscopic appearance of periclase in silicate melts as like those of the anorthite-forsterite-silica system as possible in physical qualities (e.g., melting interval and viscosity), but of such composition that the formation of spinel was excluded.

Three mixtures were made up :

\* E. S. Shepherd, G. A. Rankin, and F. E. Wright, this Journal (4), xxviii 293, 1909.

†G. A. Rankin. Personal communication.

A small charge of each was heated for one-half hour at 1500-1600° and quenched. In the first two mixtures the result was glass and periclase, the last one showed forsterite, periclase and glass. The periclase crystals were alike in all mixtures, forming rounded grains without faces. Distinct cleavage lines were frequently observed. Refractive index approximately 1.73. These properties are distinctly different from those of the regular crystals of the anorthite-forsterite-silica system, which crystals, therefore, cannot be periclase.

A conclusive proof was finally obtained by testing the solubility in the following manner: A mixture An 80 + Fo 20 was quenched after one and one-half hours heating at 1316°. It then contained glass with included crystals of forsterite and well-developed regular octahedrons. The octahedrons showed numerous glass inclusions. This quenching product was heated for one-half hour in a mixture of H,SO, and HF. After carefully decanting the acid there was left a little residuum which was examined under the microscope. It consisted of nothing but isocropic crystals with glass inclusions. The refractive index of the crystals was :  $n = 1.715 \pm 0.003$ .

Remembering that periclase is comparatively easily soluble\* in acids and spinel practically insoluble, this test finally proved that the phase considered was spinel, even if the validity of the optical distinctions might be doubted.

#### III. THE BINARY SYSTEMS.

### The System Forsterite-Silica.

The true binary system forsterite-silica has been described in a previoust paper as a part of the MgO-SiO, system. This system contains a binary compound, MgSiO<sub>3</sub>, which is unstable at its melting point. In consequence there is no eutectic Mg.SiO,: MgSiO, (forsterite: clinoenstatite), but an alteration point (point F, fig. 1) where forsterite, clinoenstatite and liquid can exist together in equilibrium. This point has a composition SiO, 2.5, En 97.5 and the temperature is 1557°. The eutectic clinoenstatite : cristobalite is located at a composition SiO, 12.5, En 87.5. The eutectic temperature is 1543°.

The crystallization in the different parts of the system will be briefly described : ‡ In mixtures of composition between D and E (fig. 1), i. e., mixtures between pure forsterite and pure  $MgSiO_{3}$ , forsterite is the primary phase. In cooling the melt forsterite crystallizes out until the temperature of the point F, the alteration point, is reached. Here forsterite begins to

\* The mixture containing glass, forsterite, and periclase treated in exactly the same way as the spinel-bearing mixture left no residuum whatever. † N. L. Bowen and Olaf Andersen, loc. cit., p. 495. ‡ For details see N. L. Bowen and Olaf Andersen, loc. cit.

421

redissolve and clinoenstatite to crystallize out. This reaction goes on as long as there is any liquid left, the temperature and the composition of the liquid remaining constant throughout. When the reaction is completed, and all liquid used up, there is still some forsterite left, and a solid mixture of forsterite and clinoenstatite results. Pure MgSiO<sub>3</sub> melts behave exactly as described, but the last of the liquid and the last of the forsterite are here used up at the same time. The final crys-



$\mathbf{F}$	IG.	1.

tallization product, therefore, is pure clinoenstatite. Between E and F (mixtures between pure En and En 97.5,  $SiO_2$  2.5) forsterite is still the primary phase, and the reaction at point F takes place as before described with simultaneous solution of forsterite and crystallization of clinoenstatite. When, however, the reaction is complete, all forsterite is redissolved while there is still some liquid left. The crystallization continues along the line F G with separation of clinoenstatite. At point G, the eutectic clinoenstatite-cristobalite, the rest of the liquid, solidifies with simultaneous crystallization of clinoenstatite and cristobalite. In mixtures richer in silica than G, cristobalite crystallizes as primary phase, and when G is reached there is again eutectic crystallization of cristobalite and clinoenstatite.

### The System Anorthite-Silica.

The anorthite-silica mixtures form a true binary system of simple type. The results of the quenchings are contained in Table 2. The equilibrium diagram is represented in fig. 2. This system was particularly difficult to work with on account of the great viscosity of the melts. The preparation of the mixtures was a time-consuming operation. The melting and grinding had to be repeated several times to insure homogeneity, and a long time was required to crystallize the glass.\* The products obtained from quenchings were extremely fine-grained, even in mixtures containing no more than 20 per cent free silica.

No actual determination of the silica liquidus could be made,



FIG. 2.

but its general course near the eutectic was inferred from the isotherms in the ternary diagram (fig. 10).

The eutectic was located in the following way: The direction of the anorthite liquidus was first determined by quenchings on the mixtures 20 and 30 per cent silica in connection with the known melting point of anorthite. Then quenchings were made to determine the temperature of the eutectic on the 30 per cent mixture. This temperature was found to be  $1350^{\circ}\pm 5^{\circ}$ . From these observations the location of the eutectic could be estimated at 49 per cent silica. A mixture of this composition was then prepared and quenchings carried out for a more accurate determination. The quenchings proved that the mixture was on the silica side of the eutectic (see Table 3), the eutectic temperature being determined at  $1353^{\circ}\pm 2^{\circ}$ , and the point on the liquidus at  $1364^{\circ}\pm 4^{\circ}$ . These points in connection with the approximate direction of the silica liquidus determined the composition of the anorthitesilica eutectic to be An 52, SiO, 48.

\* The mixture An 51, SiO<sub>2</sub> 49, for instance, required eight days for complete crystallization at a temperature around  $1200^{\circ}$ .

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 232.—April, 1915. 28

Under conditions of perfect equilibrium, the crystallization on cooling may be inferred as follows: In mixtures richer in silica than the point P (fig. 2)\* cristobalite is the primary phase. On reaching P cristobalite inverts to tridymite and the crystallization proceeds with separation of tridymite along P I. At I there is eutectic crystallization of tridymite and anorthite. Mixtures between P and I have tridymite and





those between I and A anorthite as primary phase, and the eutectic crystallization takes place at I.

### The System Forsterite-Anorthite.

Owing to the reaction between forsterite and anorthite with formation of spinel, the forsterite-anorthite system is not really binary. The greater part of the system, however, may within certain temperature intervals be treated as if it were binary. The relations in the part where spinel occurs can not be properly explained more simply than in terms of the quaternary system MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. The two breaking-up points (B and C, fig. 3) and the liquidus were determined by the quenchings contained in Table 4. The point B was approximately located by determining the temperature at which the mixture Fo 10, An 90 first showed crystals of spinel. The intersection between the isotherm through this point and the anorthite liquidus determined roughly the point. To get an accurate check of the result a mixture Fo 14, An 86 was made

\* The point is not determined, but only plotted on the silica liquidus at 1470° according to C. N. Fenner, this Journal (4), xxxvi, 331, 1913.

up. The quenchings showed that this mixture corresponds exactly with the composition of the point as appears from Table 3. The temperature of the point of intersection was  $1444^{\circ} \pm 2^{\circ}$ .

The point C was determined in a similar way to be An 54, Fo 46 at the temperature  $1466^{\circ} \pm 4^{\circ}$ .

The highest point determined on the forsterite liquidus was at 1620° in the mixture An 40, Fo 60. Between this mixture and pure forsterite, whose melting point was previously found (in the iridium furnace) to be 1890°, no determination could be made. Nevertheless the liquidus of forsterite may be considered rather sharply fixed by the determinations stated in Table 3, so much the more as it appears that all points are consistent with each other.

The liquidus of spinel was determined by the points B and C, and three intervening points as appears from Table 4 and fig. 3. It need not be further explained that the maximum shown on this liquidus has no relation whatever to the maximum of ordinary two-component systems with a binary compound. The spinel, MgAl<sub>2</sub>O<sub>4</sub>, can, of course, not be considered a binary compound in a system where MgSiO<sub>4</sub> and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> are components.

The anorthite liquidus was determined by the points A (melting point of An) and B, and the liquidus point of the intervening mixture An 90, Fo 10.

The mixtures between A and B crystallize with anorthite as primary phase. At the point B spinel begins to separate and at the same moment the system ceases to be binary, that is to say, the composition of the liquid can no longer be expressed in terms of the two-component system anorthite-forsterite. The further course of the crystallization, therefore, belongs in the quaternary system MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and can not be discussed on the basis of the present data. Mixtures between C and D behave in a similar way. Forsterite is the primary phase and at the point C spinel begins to crystallize. In the mixtures between B and C spinel is the primary phase, and in consequence, the relations of these mixtures can not be expressed in terms of the binary system. At temperatures immediately below the liquidus B C spinel is the only solid phase. At lower temperatures other phases occur together with spinel in equilibrium with the liquid.\*

\* It is obvious that the temperatures of the points B and C have no significance whatever for any of the mixtures between B and C. These temperatures fix points in the binary system and the mixtures mentioned belong in the quaternary system for all temperatures below the liquidus.

### IV. DISCUSSION OF SOME TYPES OF TERNARY SYSTEMS WITH-OUT SOLID SOLUTION.

### General Remarks.

Before entering into the discussion of the ternary part of the anorthite-forsterite-silica system a synopsis of the general features of some ternary systems without solid solution will be given. The purpose is only to elucidate problems dealt with in this paper, in order to make them intelligible without any elaborate physico-chemical representation. No attempt is, therefore, made to render the strict thermo-dynamic proofs of the principles involved, all statements being simply referred to the graphical representations.\*

The ordinary ternary diagrams are, as is well known, simply topographic maps of the temperature-concentration space model where the shape of the surface is indicated by temperature contours, *isotherms*. In the following figures, which only represent hypothetical diagrams, the isotherms are left out, but the direction of falling temperature is indicated by arrows on all the principal curves and this gives a general idea of the configuration of the surface.

Only systems without solid solution are considered and among them a few simple types are selected as illustrations.

### Type 1. The System without Compounds.

The simplest ternary system is the one with the three components as the only solid phases. The relations of this ordinary eutectic type of three component systems are well known and should need no detailed explanation. However, to form a base for the description of more complex types the general features of this simple system will be briefly repeated.

Synopsis of terms.—The system has three quadruple points, h, i, and k (fig. 4), which all are binary eutectics of the three two-component systems A-B, B-C and C-A. From the quadruple points, three boundary curves (saturation curves), hm, im and km, slope down towards the quintuple point m, the ternary eutectic. The relations of this system (and, in fact, of all ternary systems without solid solution) are, in general, known when the liquidus of the system is determined or in other words, when the temperature at which the first solid appears on cooling has been fixed for all compositions. The

\* More elaborate discussions of ternary systems without solid solutions are to be found, e. g. in the following works : W. D. Bancroft, The Phase Rule, 146, 1897; W. C. Geer, J. Phys. Chem., viii, 257, 1904; F. A. H. Schreinemakers, Roozeboom : Heterogene Gleichgewichte III, 1911; H. Brand, Neues Jahrb. Min., Beil. Bd., xxxii, 640, 1911 : H. E. Boeke, Centralbl. Min. 1912, 257; G. A. Rankin and F. E. Wright, this Journal (4), xxxix, 17 and 51, 1915. boundary curves divide the liquidus into three *fields* each one corresponding to the solid phase, *the primary phase*, which is the first to separate on cooling of any melt within the field.

Crystallization curves.—In ternary systems a curve joining all the points which express the successive compositions, and corresponding temperatures, of a melt during its crystallization



is called *the crystallization curve* for this melt. A crystallization curve may begin at any point on the liquidus and it always ends at a quintuple point. In fig. 4,  $a \ b \ m$  is the crystallization curve for a mixture of composition a. For the sake of convenience the behavior of a liquid of initial composition a on cooling is generally described by using the standard phrase that "crystallization proceeds along the curve  $a \ b \ m$ ." This actually means that while crystallization takes place, with separation of one or two solid phases, the successive compositions and temperatures of the remaining liquid are expressed by the points on the curve a b m.

Phase relations.—The composition of a crystallizing liquid (see fig. 4) is always expressed by a point on the straight line, which joins the composition point of the solid phase (A) and that of the initial liquid (a) from which the solid has separated. This rule also holds true in the case of separation of two solid phases, for instance A and C crystallizing between b and m. The straight line mentioned then goes through the point which indicates the mean composition of the solid separated, and this mean composition is expressed by a point (b') on the line (AC) joining the composition points of the two solid phases. If, therefore, two solid phases have separated on cooling a liquid between two given temperatures the mean composition of the solid is expressed by the point of intersection between the line joining the composition points of the liquids which correspond to the two given temperatures\* and the line joining the composition points of the two solid phases.\* In fig. 4 the crystallization curve of a melt a between the temperatures a and b is the straight line a b, the prolongation of which goes through A. This means that the solid phase A only has separated between a and b. At b the phase C also begins to separate and A and C now crystallize together along the boundary curve b m. The mean composition of the solid separated between b and mis given by the point b', which indicates a mixture of A and C in the proportion b'C: b'A and the mean composition of the total solid separated between a and m (before eutectic crystallization at m begins) is a'. The composition of the solid crystallizing at any point,  $b, \dagger$  on a boundary curve is indicated by a point on the tangent to the boundary curve at the point b. This tangent intersects the line A C at the point b'', which point, therefore, is the composition point of the solid crystallizing at b. When the point m is reached the eutectic crystallization, with simultaneous separation of A, B and C, begins. During this eutectic crystallization the composition and temperature of the liquid are unchanged while the composition of the total solid changes from a' to a, reaching the latter point at the moment the crystallization is complete and the last of the liquid disappears.

The amount of solid of composition A separated between aand b is equal to 100 x  $\frac{a b}{A b}$  per cent of the initial composition a, and the amount of remaining liquid of composition b is equal to 100 x  $\frac{a A}{A b}$  per cent of a. In the same way it is seen

<sup>\*</sup> Or the prolongation of such a line.

 $<sup>\</sup>dagger$  That means through an infinitely small temperature range including b.

that the amount of solid, of mean composition a', separated between a and m is equal to 100 x  $\frac{a}{a'm}$  per cent of a and the amount of remaining liquid, of composition m, 100 x  $\frac{a}{a'm}$  per cent.



The simple principles now outlined concerning the crystallization in ternary systems hold true for all types of systems without solid solutions.\* By applying these principles the state of equilibrium for any melt of a system whose liquidus is known can be expressed in quantitative terms. In other words, the compositions and relative amounts of the different phases at various temperatures can be calculated for all melts of the system.

\* And with small modifications also for systems with solid solutions.

### Type 2. The system with one binary compound which is stable at its melting point.

The simplest type of systems in which two of the components join to form a compound is represented in fig. 5. In this system the compound is stable at its melting point as well as below the melting point in all the mixtures where it appears. In the diagram (fig. 5) the compound between the components A and B is represented by the point D. The line D C between the compound and the third component is called the *conjuga*tion line. All mixtures along the conjugation line belong to a true binary system C-D with a eutectic at n, which point forms a maximum on the boundary curve, o m, between the fields of C and D. The binary system A-B contains two simple binary systems, A-D and B-D, with the eutectic points h and j. It is easily seen that the conjugation line, D C, divides the whole ternary system into two independent ternary systems, namely, A-C-D and B-C-D. Each of these systems contains three quadruple points (binary eutectics) and one quintuple point (ternary eutectic). The diagram shows that the type of these systems is identical with the one already described as Type 1. A further explanation of the diagram fig. 5 is therefore unnecessary.

With Type 2 as a base a number of other types can be inferred by varying the location of the points m, o and h, jand also the shape of the boundary curves o j or m h. A few of these types will be considered below.

### Type 3. The quintuple points o and m lie on the same side of the conjugation line, whereas the quadruple points h and j lie on opposite sides.

When the pure compound, D, is stable at its melting point, but unstable in certain mixtures in which it breaks up at temperatures below the melting point, we have the Type 3 represented in fig. 6.

General qualities of curves and points.—In the case now to be considered the boundary curve j o has such a shape that none of its tangents go through the point D. The most characteristic feature of this system (and also of the following systems) is the extension of the field of A across the conjugation line, whence it follows that the relations of the mixtures of C and D can not be expressed in terms of the two-component system C-D. Two of the boundary curves now intersect the conjugation line in the two points n and q. The boundary curve, m o, between the fields of C and D, has no longer any maximum but slopes gradually down from o towards the ternary entectic m. The quintuple point o is not a ternary entect

tic but an *alteration point*, the qualities of which will be explained below. With the exception of this point o and the curve o m all points and curves of this type have the same general qualities as the corresponding points and curves of Type 2.

*Examples of crystallization.*—To explain the relations of the point o and the curve o m we follow some crystallization



curves, starting from points within the field of A. From a melt of composition a the solid phase A crystallizes between a and b. From b to o A and D crystallize together, but as the total composition of the solid separated between a and o is given by the point a' there must be liquid left when o is reached. As now the crystallization curve always has to end at a quintuple point, it is easy to see that in the present case the final solidification takes place at o. A continuation of the crystallization to m would mean that the final solid consisted

of B, C and D only and still had a mean composition a, and that is impossible. During the final process of solidification the composition and temperature of the liquid remains constant (expressed by the properties of the point o) and the mean composition of the total solid changes from a' to a. During this final solidification at o, while all the liquid disappears, the solid phases C and D crystallize out, whereas some of the phase A is redissolved.

A liquid the composition of which is expressed by the point c on the conjugation line C D crystallizes as follows: From c to b crystallization of A alone. Between b and o simultaneous crystallization of A and D. At o final solidification with total dissolution of A and simultaneous crystallization of A and C.

For a melt whose initial composition is expressed by a point on the conjugation line we thus see that the total amount of the phase A separated before o is reached disappears during the final solidification at that point, and the resulting solid consists of C and D, as if these two phases had formed a simple binary system with eutectic crystallization.

Let us now consider a melt whose composition is expressed by a point d within the part of the field of A that extends across the conjugation line. In this case the crystallization curve cannot end at o because this would mean that the final solid consisted of A, C and D and contained no B, although it must have the composition of d which is a mixture of B, C and D. The curve must, therefore, proceed to the ternary eutectic m. Between d and e, A alone crystallizes out; between e and o A and C crystallize together. The mean composition of the solid separated between d and o is expressed by the point d'. When crystallization begins to proceed along o mthe mean composition of the solid has changed to d''. While crystallization goes on along o m the mean composition of the solid changes from d''' to d''' and during the final eutectic crystallization at m from d'''' to d.

We see that in all the three melts considered there will be a dissolution of the solid phase A at the quintuple point o. In the melt a only a part of A is dissolved and the final solidification takes place at o. In the melt c all A is dissolved at the same time as the liquid disappears and all becomes solid at o. The crystallization of the melt d, finally, proceeds to the ternary eutectic m because there is liquid left when all A has been dissolved at o.

# Type 4.— The points m, o and h, j all lie on the same side of the conjugation line, which is not intersected by the boundary curve j o.

In the type to be considered below the compound **D** is unstable at its melting point and also breaks up in mixtures at

temperatures below the melting point. The diagram in fig. 7 represents a case where the course of the boundary curve j o is such that no tangent to this curve can be drawn through the point D. The two-component system A-B contains the unstable compound D. The relations of such a system have



been explained before.\* In all mixtures between j and A, in this binary system, the compound D is decomposed on heating at the temperature of the point j. The product of the decomposition is A and liquid. The other binary systems of the diagram fig. 7 are of the simple eutectic type.

Qualities of boundary curve j o.—The only principal difference between the present ternary system and the preceding

<sup>\*</sup> P. 17. See also N. L. Bowen and Olaf Andersen, this Journal (4), xxxvii, 487, 1914.

one (fig. 6) lies in the qualities of the boundary curve j o. The relations of this curve are best understood by discussing some of the crystallization curves which intersect it. For a melt of composition e (fig. 7) the crystallization curve has the course e b o. Between e and b the solid phase A crystallizes out. At b the compound D begins to crystallize out and A to redissolve and this process continues all along the curve b o. That this must be so is inferred from the fact that all tangents to the boundary curve j o intersect the prolongation of the line A D and not this line itself. If a tangent intersected the line between A and D it would mean that the solid crystallizing at the point of tangency of any such tangent consisted of a mixture of A and D (see p. 428) and by a further crystallization the amount of A would increase. If the tangent went through the point D itself. D only would separate and the amount of A that might be present in the solid when the point of tangency was reached would neither increase nor decrease. If, therefore, the tangent intersects the prolongation of A D this can only mean that in the solid separated at the point of tangency the amount of A present in the solid when this point is reached decreases, and this holds true for all points on the boundary curve j o. We would arrive at the same conclusion if we calculated the amount of different phases present at b and the amount present when crystallization reaches o. We would see that between b and o the amount of A would decrease and that of D increase. At o there is (exactly as in the case of Type 3) a further dissolution of A and a simultaneous crystallization of D and C until all becomes solid consisting of a mixture of A, C and D.

For a melt of composition a the crystallization curve will have the following course : From a to b A separates. Between b and c D crystallizes out and A dissolves, and in the moment the point c is reached, all A has disappeared. This is inferred from the fact that the mean composition of the total solid separated between a and c is indicated by the point D. From c, therefore, the crystallization breaks away from the boundary curve j o and continues along the line c d through the field of D with D alone separating. From d to m B and D crystallize together and at m the final solidification takes place with eutectic crystallization of B, C and D. For all melts within the section o j D the crystallization curves will break away from the boundary curve j o and pass through the field of D. Some of these crystallization curves intersect the boundary curve h mlike that of the melt a, others intersect o m.

Boundary curves like *j* o (fig. 7) are often called *alteration* curves. Whenever the crystallization curve passes an alteration curve one solid phase will dissolve and the other crystallize

out. For some melts it may happen (as is shown above) that the crystallization curve breaks away from the alteration curve before the quintuple point o is reached. In the diagrams alteration curves are indicated by double arrows,\* whereas single arrows indicate ordinary boundary curves, *melting* curves.



Apart from what is mentioned concerning the boundary curve j o the relations of the present type of ternary systems are not different from those of Type 3. The course of crystallization in different sections of the system is easily inferred from the diagram by means of the rules now repeatedly applied.

### Type 5.

The present type is a modification of Type 4. The only essential difference between the two types lies in the shape of

\* H. E. Boeke, Centralbl. Min., 1912, 275.

the boundary curve j o which in Type 5 has such a course that one of its tangents goes through the point D as shown in fig. 8. The point of tangency, p, divides the boundary curve j o into two different parts, p o, the melting curve, and j p, the alteration curve.

Recurrent crystallization of a solid phase.—Some characteristic crystallization curves will be described. The melt acrystallizes as follows: From  $\alpha$  to b crystallization of A alone. From b to c crystallization of D and dissolution of A, the last of A disappearing at c. Between c and d crystallization of D alone. At d, A begins to crystallize out for the second time and from d to o there is simultaneously crystallization of A and D. At o all A is completely dissolved once more with simultaneous crystallization of C and D. Between o and msimultaneous crystallization of C and D and at m eutectic crystallization of B, C and D. It is seen that during the process of solidification of this melt a there is a twice repeated crystallization and subsequent total dissolution of the phase A. A consideration of the diagram shows that the section in which this kind of crystallization curves appear is bounded by the straight lines o D (not drawn in fig. 8) and p D and the part of the boundary curve j p that falls between these two lines. For other melts, namely those within the remaining part of the section j p D, the crystallization curves also leave the boundary curve j p, but the point d will be located either on the curve o m or on h m, and there will be no second crystallization and dissolution of the phase A.

A melt e within the section A p D crystallizes as follows: From e to b separation of A alone. Between b and p crystallization of D and dissolution of A. There is, however, still some A left at p, where A begins to crystallize out for the second time. Between p and o simultaneous crystallization of A and D. At o A is again partly redissolved while C and D crystallize out and the final solid consists of A, C and D. In this case it is seen that while A never disappears from the solid its crystallization is interrupted twice, each time with a partial redissolution of the crystals already separated.

For other sections of the diagram the crystallization curves show no qualities not already pointed out in the description of the previous types.

### V. THE SYSTEM ANORTHITE-FORSTERITE-SILICA.

### The spinel field.

Among the ternary mixtures of anorthite, forsterite and silica there are, as already mentioned, some which crystallize with spinel as primary phase and therefore cannot be properly

considered in terms of the ternary system. These mixtures are those represented by points within the field B C K in the ternary diagram, fig. 9. The significance of the points B and C has already been discussed. K is the point where the spinel field meets the boundary curve forsterite : anorthite. The point K has been determined at the composition An 61, Fo



MG SIO

29.5, SiO, 9.5, and the temperature 1320°. The lines B K and C K have a similar significance in the ternary system as the points B and C in the binary system anorthite-forsterite. Mixtures within the field A B K will crystallize with anorthite as primary phase and when a point on the curve B K is reached spinel begins to crystallize. In mixtures within the field D  $\dot{C}$  K forsterite is the primary phase and when the crystallization reaches the line C K spinel is also here separated. In both cases, the further crystallization, of course, proceeds in the quaternary system. It is obvious that the lines B K and C K do not coincide with any crystallization curves in the ternary system (like, for instance, G N or N M) but simply represent boundary curves between the spinel field and the adjoining fields.

Mixtures with excess of MgO.—It may be well in this connection to add a brief record of some experimental work on mixtures containing more MgO than is necessary to bind all free silica in the compound Mg<sub>2</sub>SiO<sub>4</sub> (forsterite), that is, mixtures in the section of the system anorthite-MgO-SiO<sub>2</sub> which lies between the line anorthite-forsterite and the line anorthite-MgO. Thermal work with the platinum resistance furnace was possible only on mixtures near the anorthite corner of the diagram and in fact most of these mixtures belonged to the spinel field.

In the system anorthite-MgO spinel separates as the primary phase in mixtures containing more than 7 per cent MgO. At the liquidus point for the mixture An 93, MgO 7 anorthite and spinel are able to coexist in equilibrium with the melt. The temperature of this point is about 1440°. This gives a very steep liquidus curve for anorthite, the temperature gradient averaging about 16° for one per cent MgO. A few points on the liquidus curve for spinel were also determined. The curve rises quickly with increasing amount of MgO. At a composition An 80, MgO 20 the temperature of the liquidus point was higher than 1630°, a mixture quenched from this temperature containing glass and spinel.

The liquidus surface of the spinel field in the section anorthite-forsterite-MgO of the system rises steeply from the line anorthite-forsterite and soon reaches temperatures inaccessible in the platinum resistance furnace. A mixture An 60, Fo 21, MgO 19 quenched from 1620° gave a product consisting of spinel and glass.

Various pure glasses of mixtures within the spinel field were crystallized at temperatures between 800° and 1000°. Spinel was not found in any of the resulting products. This shows that the spinel field is a reaction field or, in other words, that the spinel found in the mixtures considered is redissolved in the usual course of cooling. Besides this nothing definitely can be said about the crystallization curves of mixtures within any part of the spinel field.

### The ternary field.

All mixtures outside the triangle A K D (fig. 9) behave as part of a true ternary system. These mixtures will here be
discussed a little more in detail, particular emphasis being laid upon crystallization by cooling with maintenance of equilibrium.

The general character of the true ternary part of the diagram is that of a system with no ternary compound, one binary compound, MgSiO<sub>s</sub> (point E, fig. 9), unstable at its melting point, and two quintuple points of which the one (M) is an alteration point (An : Fo : En) and the other one (N) a ternary eutectic (An : En : Tr).

The system is not essentially different from that described as Type 4 in the previous general discussion. The only deviations from the type are the occurrence of the spinel field and the sub-division of the silica field into two, the field of tridymite and that of cristobalite.

In the following the determination of the quintuple points, boundary curves and isotherms of the ternary part of the system will be briefly reviewed. The relations of these points and curves will appear from the discussion of the course of crystallization in different types of mixtures.

The alteration point. (Point M, fig. 9.)—The point M represents the junction of the three fields of anorthite, forsterite and clinoenstatite and corresponds to the point o, fig. 7. At this point the three solid phases mentioned are able to exist in equilibrium together with the liquid. As a result of any energy change in the system there will be a reaction between forsterite, clinoenstatite and liquid. This reaction will be discussed further on.

The temperature of the point M was first determined by the heating curves described on p. 409. As the quenchings proved that no eutectic An : En existed, the only way of explaining the heat changes was to assume that they corresponded with the temperature of the alteration point M. The quenchings corroborated the results of the heating curves, all determinations together fixing the temperature of M at  $1260^{\circ} \pm 2^{\circ}$ .

The composition of M was first roughly extrapolated from different quenchings in the three fields of anorthite, clinoenstatite and forsterite, and then several mixtures near the composition found by extrapolation were successively examined as to their primary phase and the temperature of their liquidus points. In this way the composition of M was determined at :

### An 55, Fo 25.5, SiO<sub>2</sub> 19.5.\*

The ternary eutectic anorthite-clinoenstatite-tridymite. (Point N, fig. 9.)—All mixtures near the ternary eutectic formed very viscous melts. Heating curves run to determine the eutectic temperature on mixtures presumably near the

\*SiO<sub>2</sub> 54.20; Al<sub>2</sub>O<sub>3</sub> 20.16; CaO 11.05; MgO 14.59.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 232.—April, 1915. 29

# 440 Andersen-System Anorthite-Forsterite-Silica.

eutectic composition, therefore, gave only approximate results. Breaks were recorded at about 1230°, in two of the mixtures. The exact determination of the eutectic temperature was based on quenchings of mixtures which also were used for



Ma SIO

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the location of the eutectic composition. These quenchings are listed in Table 4. The results were :

Eutectic temperature :  $1222^{\circ} \pm 2^{\circ}$ . Eutectic composition : An 50.5 ; En 23.6 ; SiO, 25.9.\*

The boundary curves.—The general slope of the boundary curves (saturation curves) could, of course, be roughly inferred from the determined quadruple points and quintuple points. The more accurate determination was based on quenchings of

\* An 50.5 : Fo 16.5 ; SiO<sub>2</sub> 33. SiO<sub>2</sub> 61.90 ; Al<sub>2</sub>O<sub>3</sub> 18.51 ; CaO 10.15 ; MgO 9.44.

mixtures made up according to the course of the approximate curves. The points could be determined by quenchings of neighboring mixtures on each side of the curve, or by quenchings on one mixture near the curve, determining the point on the liquidus corresponding to the composition of that mixture (i. e., the temperature where the primary phase disappeared) and the temperature where the second phase appeared or disappeared. The composition of this point was then extrapolated from the slope of the liquidus. Provided that this slope was known with sufficient accuracy, and the mixture examined was not too far removed from the curve, this method would give results as exact as those inferred from quenchings on several mixtures on each side of the curve. It appeared that, excepting the curve G N, the boundary curves deviated but little from straight lines. Their course could therefore be determined by a comparatively small number of mixtures.

The isotherms.—It would require thousands of quenching experiments, carried out on hundreds of mixtures, actually to determine the course of the isotherms; that is to say, to map the surface of the liquidus with such accuracy that any point on this surface could be located in the diagram or space model within the limits of error of experimental determinations. Such work in the case of a comparatively simple system like The numthe present would appear to be of doubtful utility. ber of quenchings carried out, besides those determining quintuple points and boundary curves, are therefore comparatively few. Nevertheless, the general course of the isotherms (as shown in fig. 10), within the part of the system where thermal work has been possible, may be considered fairly well established. It is obvious that, in general, points on the isotherms may be determined with a sufficient degree of certainty by interpolations based on determined points.

### Normal crystallization in different sections of the ternary field.

In the following paragraphs a discussion of the course of crystallization in different types of mixtures will be given. It is always assumed that the cooling proceeds at such a rate that perfect equilibrium obtains throughout the range of temperature considered. This will be referred to as the normal crystallization.

For the sake of convenience the system (as represented in the diagrams, figs. 9 and 10) is divided into different parts by lines connecting the composition points of the solid phases with the quintuple points. To make the relations clearer the principal types of crystallization curves are illustrated in the diagram of fig. 11, which is an arbitrarily distorted representation of fig. 9 with this difference, that the spinel field B C K

# 442 Andersen—System Anorthite-Forsterite-Silica.

and the boundary curve O P are left out in fig. 11, where consequently the points B, C, O and P are not shown and the point K is removed to the side of the diagram. This distorted diagram, therefore, represents a true ternary system of the same type as the anorthite-forsterite-silica system, but without any breaking up of the components A and D and with only

FIG. 11.

one modification of the component H. In the two diagrams the corresponding points are marked with the same letters.

The eutectic field.—The mixtures within the part of the diagram bounded by F M (field boundary Fo : Cl en) and the straight lines M A, A H and H F (fig. 9) behave as if they belonged to a ternary system anorthite-enstatite-silica. This ternary system is of the simplest type, with no compounds, and one ternary eutectic. The crystallization of mixtures of such a system on cooling with equilibrium need no detailed explanation.

A typical example is represented in Table 6, which shows the amounts of the different phases present at the principal stages in the crystallization of a mixture of composition An 15, En 70, SiO<sub>2</sub> 15. This mixture lies within the clinoenstatite field and its crystallization curve is of the type corresponding to  $e \ F \ N$  (fig. 11):\* between e and f crystallization of clinoenstatite alone, between f and N simultaneous crystallization of clinoenstatite and tridymite. At N eutectic crystallization of clinoenstatite, tridymite and anorthite.

#### TABLE 6.+

	Amount present in weight per cent of the initial mixture.							
Phase	1	2	3	3-2				
	When crys- tallization reaches f.	When crys- tallization reaches N.	When solidification at N is completed	Showing amount of eu- tectic crystalli- zation at N.				
Liquid	68	34	0	34				
Clinoenstatite	-32	61	70	+ 9				
Tridymite	0	5	15	+10				
Anorthite	0	0	15	+15				

Illustrating the crystallization of a mixture An 15, En 70,  $SiO_2$  15 (of type *e* fig. 11).

<sup>+</sup> The calculations of the tables 6, 7, 8 and 9 are based on the diagram fig. 9. The figures are rounded off to whole numbers.

The reaction field.—The mixtures within the field D K A M F, the reaction field (figs. 9 and 11), where forsterite appears during some period of the crystallization, behave in a little more complicated manner, and the course of crystallization of various mixtures of this kind will be discussed below.

In mixtures within the field A K M, anorthite is the primary phase and the second step of the crystallization brings out the simultaneous separation of forsterite and anorthite along the curve K M. At the point M there is a reaction between forsterite and liquid in such a way that both decrease in amount, while clinoenstatite crystallizes out. At the same time, anorthite continues to crystallize. If the original mixture has a composition within A K L the liquid will disappear before the forsterite and the crystallization will stop at M, the result being a mixture of anorthite, forsterite and clinoenstatite.

\*To avoid crowding of lines no crystallization curves are drawn in fig. 9. The location of any points in fig. 11 is, of course, quite arbitrary and does not correspond to the ratios of Table 6 (or the following Tables 7, 8, 9).

## 444 Andersen—System Anorthite–Forsterite–Silica.

In mixtures along the line A L (part of the conjugation line anorthite-enstatite) the crystallization takes place in the same way, but when the reaction at the point M is complete, the forsterite and the liquid have both been used up at the same time and there is left a solid mixture of anorthite and clinoenstatite, as if there had been a eutectic crystallization of these two phases. If, on the other hand, the mixture has a composition within the field A L M the forsterite will be the first phase to disappear when the reaction at M is complete, and the remaining liquid will crystallize along the line M N with simultaneous separation of anorthite and clinoenstatite, until the point N, the ternary eutectic, is reached, where anorthite, clinoenstatite and silica finally crystallize out together.

In all mixtures within the field D K M F forsterite is the primary phase. The second step of crystallization depends on the location of the mixtures within the different subdivisions of the forsterite field. Within the field D K M, the second and third steps of crystallization will be exactly like those of the corresponding mixtures on the anorthite side of the line K M described above: simultaneous crystallization of forsterite and anorthite along K M and reaction at M resulting in decrease of forsterite and liquid and crystallization of clinoenstatite together with anorthite. The final result of the reaction, whether the forsterite or the liquid is first used up, again depends upon the original composition of the mixture. In mixtures within the field  $D \ g \ L \ K$  there will be forsterite left after the reaction and the result is complete solidification at M of a mixture of forsterite, anorthite and silica. The result of the crystallization of mixtures on the line q L (part of the conjugation line anorthite-enstatite) will be the same as described for the mixtures LA: complete solidification at M of a mixture of anorthite and clinoenstatite. The principal stages in the crystallization of a mixture of composition An 46, En 54 (point q figs. 9 and 11) are represented in Table 7.

#### TABLE 7.

Illustrating the crystallization of a mixture An 46, En 54 (g figs. 9 and 11).

	Amount present in weight per cent of the initial mixture.							
Phase	1	2	2-1					
	When crystalliza- tion reaches M.	When solidifica- tion at M is com- pleted.	Showing amount of crystallization and dissolution at M.					
Liquid	84	0						
Forsterite	16	0	-16					
Anorthite	0	46	+46					
Clinoenstatite	0	54	+54					

Andersen—System Anorthite-Forsterite-Silica. 445

For mixtures within  $g \perp M$  the reaction at M results in clinoenstatite, anorthite and liquid and the crystallization proceeds to N, where the eutectic mixture anorthite, clinoenstatite, silica is formed.

The crystallization of mixtures within the field D M E will be illustrated by discussing (fig. 11) the crystallization curves of some particular mixtures.<sup>\*</sup> Three mixtures are selected: kon the forsterite side of the conjugation line anorthite-enstatite; l on this line itself and m on the silica side of the line. The course of crystallization of k will be as follows: Along k ncrystallization of forsterite; from n to M solution of part of the forsterite and simultaneous crystallization of clinoenstatite; at M continued reaction with solution of forsterite and crystallization of clinoenstatite and anorthite until all is solid, consisting of forsterite, clinoenstatite and anorthite.

This type of crystallization curve is represented in Table 8, showing the phase relations at the principal stages of crystallization of a melt of composition An 25, Fo 60, SiO, 15.

#### TABLE 8.

	Amount present in weight per cent of the initial mixture.							
Phase	1	2	3	3-2				
	When crys- tallization reaches n	When crys- tallization reaches M	When solidi- fication at M is completed	Showing amount of crys- tallization and dissolution at M				
Liquid	63	45	0	-45				
Forsterite	37	34	25	- 9				
Clinoenstatite	0	21	50	+29				
Anorthite	0	0	25	+25				

Illustrating the crystallization of a mixture An 25, Fo 25, En 50 (type k fig. 11).

For the mixture l the steps in the course of crystallization are the same: Along l *n* forsterite crystallizing; along *n* M forsterite redissolved, clinoenstatite crystallizing out; at M anorthite and clinoenstatite crystallizing, forsterite dissolving. The final solid product now, however, consists of clinoenstatite and anorthite only.

In the last of the three mixtures, m, the crystallization again follows the line m n with separation of forsterite, the line n M with simultaneous solution of forsterite and crystallization of clinoenstatite, and the reaction at M goes on with solution of forsterite and crystallization of clinoenstatite and

\* See footnote, p. 443.

anorthite. In this case there is liquid left when all forsterite is dissolved at M and the crystallization continues along M N to N as repeatedly described. In all mixtures within the field E M g the crystallization proceeds as discussed for m.

It will appear that in all the mixtures hitherto described, lying within the field D K A M E, where forsterite is formed at some time during the solidification, the crystallization curves always pass through the alteration point M, or else the crystallization is completed at that point.

For the little part of the forsterite field which now remains to be considered, the field E F M, the crystallization curves leave the boundary curve F M before the quintuple point M is reached. This will be plainly seen by considering the crystallization of a mixture a (fig. 11). From a to b forsterite crystallizes out. At b clinoenstatite begins to crystallize, forsterite to redissolve, and this reaction goes on while the composition of the liquid changes along the line F M. When the point c (lying on the continuation of the line  $\mathbf{E} a$ ) is reached, no more forsterite is left, and the further crystallization, therefore, does not follow the line F M, but proceeds through the clinoenstatite field along the line c d, clinoenstatite crystallizing all the time until the point d is reached. At this point anorthite also begins to separate, and the crystallization goes on along d N to N, where there is the usual eutectic crystallization of anorthite, clinoenstatite and silica. A mixture of com-

#### TABLE 9.

Illustrating the crystallization of a mixture An 8, En 89, SiO<sub>2</sub> 3 (of type a fig. 11).

	Amount present in weight per cent of the initial mixtur							
	1	2	2-1	3	4	5	5-4	
Phase	When crystallization reaches $b$	When crystallization reaches $c$	Showing amount of crystallization and dissolution between $b$ and $c$	When crystallization reaches d	When crystallization reaches N	When solidification at N is completed	Showing the amount of eutectic crystallization at N	
Liquid	97	49		16	11	0	-11	
Forsterite	3	0	- 3	0	0	9	0	
Clinoenstatite	0	51	+51	84	86	89	+ 3	
Anorthite	0	0	0	0	3	8	+ 5	
Tridymite	0	0	0	0	0	3	+ 3	

position An 8, En 89, SiO<sub>2</sub> 3 has a crystallization curve of this type. Table 9 shows the phase relations at the principal points of the curve. All mixtures within the field E F M have similar crystallization curves. Those within the minor field i M E crystallize exactly as described. For those within i F E there is the difference that the second step of the crystallization consists in simultaneous separation of silica and clinoen-





FIG. 12. A section through the ternary system anorthite-forsterite-silica at AE fig. 9. This figure is, therefore, a convenient projection upon a plane of ternary relations, not a representation of a binary system.

statite instead of anorthite and clinoenstatite. The final result is always eutectic crystallization at N.

The section anorthite-clinoenstatite.-In the preceding discussion mixtures along the conjugation line A E (fig. 9) have been repeatedly mentioned. It is evident that the final solidification product of all these mixtures must be the same as if they belonged to a true binary system anorthite-clinoenstatite. The relations of the phases during the crystallization can, however, not be expressed in simpler form than in terms of the ternary system, and a two-component diagram must be somewhat modified to express the same relations. Fig. 12 represents such a diagram based on the results of the quenchings contained in Table 5. This diagram is, of course, simply a vertical cross section of the ternary diagram along the conjugation line A E. As such cross sections sometimes may be useful in the study of ternary systems the present diagram is given as an illustration, although it does not actually show relations that do not appear from the ternary diagram.

### 448 Andersen—System Anorthite-Forsterite-Silica.

In fig. 12 only the heavy lines A L and L E represent points in the plane of the section itself. The other points (lines F M and M L) are projected on this plane with the point D (the forsterite point) as eye point. In the cross section, therefore, vertical lines, like g M, correspond to straight lines through D in the ternary diagram, and the different points are plotted on these lines according to the temperatures determined. With this explanation in mind the diagram is easily understood and a further discussion of it is unnecessary.

# Crystallization with removal of forsterite from the liquid.

In the preceding discussion it has been taken for granted that the solids were always in contact with the liquid from which they separated, that is, there was every opportunity for a complete reaction between the solids and the liquid. We may now consider briefly some cases where the solid is wholly or in part kept away from the liquid during the solidification. This may be caused by a simple mechanical removal of the crystals as soon as they separate, or by a protection of the crystals by their becoming embedded in crystals separating around them. The effect upon the crystallization of the remaining liquid will in both cases be the same.

We see that in simple eutectic systems<sup>\*</sup> (or eutectic parts of systems) a removal (or protection) of crystals will not in any way affect the further crystallization from the remaining liquid, because no part of the solid is ever taken back into solution during the solidification, and thus the change of the composition of the liquid is simply caused by the separation of solids. We, therefore, consider only that part of the anorthite-forsterite-silica system which lies within the section A D F M (fig. 9), the reaction field of forsterite.

From a melt within the section D E g (fig. 9) forsterite will separate till a point on the boundary curve F M is reached. If all this forsterite were removed as it separated, the further crystallization would not follow the boundary curve F M but would go through the clinoenstatite field with separation of clinoenstatite alone, and the final solidification would take place at the ternary eutectic N with simultaneous separation of anorthite-clinoenstatite and tridymite. We would obtain practically the same course of crystallization if, as a result of the first reaction at the boundary curve, the forsterite crystals were imbedded in a protecting coating (reaction rim) of clinoenstatite. This would prevent a dissolution of forsterite on further cooling and the crystallization would proceed with separation of clinoenstatite and end with eutectic crystalliza-

\* Where all boundary curves are melting curves and all quintuple points ternary eutectics.

tion at N. As in this case no crystals were removed, the final solid would consist of anorthite, clinoenstatite, forsterite and tridymite. It is obvious that this mixture does not represent a stable system, as the solid formed during a normal cooling, when equilibrium obtained and all reactions were completed, would consist of anorthite, clinoenstatite and forsterite (and no silica). Theoretically, therefore, a reaction should take place in this mixture in such a way that all the silica disappeared and combined with part of the forsterite to form clinoenstatite. The rate of this reaction, however, would in the solid state be infinitely low, and we may, therefore, say that the four compounds mentioned practically represent a stable mixture under the conditions considered.

We may consider next some mixtures whose normal crystallization curves pass the quintuple point M, but not the boundary curve F M, viz. the mixtures within the section A K D M. In a mixture on the forsterite side of the conjugation line the normal course of crystallization would be: First, separation of one of the phases anorthite or forsterite, then simultaneous crystallization of both along the boundary curve K M, and finally, reaction at M with partial dissolution of forsterite and crystallization of clinoenstatite and anorthite. The part of this crystallization which takes place before M is reached would not be influenced by any removal or protection of the solid phases. If, however, all forsterite were removed before M was reached, or the first reaction at M resulted in the formation of protecting coatings round the forsterite crystals, or if the latter crystals had been imbedded in anorthite during the crystallization along K M, then the crystallization would not end at M as in the normal course, but would proceed along M N and end at the ternary eutectic N. In this case we would again have a mixture of anorthite, clinoenstatite, forsterite and tridymite, which could remain unchanged for an indefinite time, although it did not represent equilibrium.

# VI. Some Applications of the Results to Petrologic Problems.

#### General remarks.

Earlier writers have already intimated how these physicochemical principles may afford simple explanations of certain textural features of igneous rocks. The phenomena of magmatic resorption and recurrent crystallization have received particular attention.

J. H. L. Vogt\* has explained magmatic resorption as an effect of undercooling, whereas the recurrent and also the so-

\* Tsch. Min. petr. Mitt., xxiv, 453, 1905.

called arrested ("abgeschlossene") crystallization are explained as a result of cooling with equilibrium between the solids and the liquid.\* In giving the latter explanation Vogt refers to a number of possible cases in certain types of ternary systems with solid solutions, discussed by Schreinemakers. H. Brand+ has pointed out how resorption of crystals as well as recurrence of crystallization are possible in ternary systems without solid solution. Other examples of mixtures of this kind are described by Shepherd, Rankin and Wright,<sup>‡</sup> in the preliminary paper on the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, in which the resorption of CaO is discussed and attention is called to the bearing of this phenomenon on certain petrologic problems. H. E. Boekes has again emphasized the importance of applying these principles to the explanation of the corresponding phenomena in igneous rocks.

The first examples of petrologic systems (that is, systems containing rock-forming mineral compounds) in which magmatic resorption and recurrent crystallization have been shown to be a simple result of the process of solidification, were described from this laboratory. In the final work on the system CaO-Al,O,-SiO, Rankin and Wright describe actual mineral compounds (for instance, Al<sub>2</sub>O<sub>3</sub>) showing magmatic resorption on cooling. In the paper on the MgO-SiO, system it was shown that the forsterite crystals in the forsterite-silica part of the system were always partly and sometimes completely redissolved during the cooling of melts containing this mineral as primary phase, and it was indicated that this might explain the resorption of natural olivine so frequently observed in rocks. N. L. Bowen\*\* described the same phenomenon of magmatic resorption of forsterite in the system diopside-forsteritesilica, and showed how in certain mixtures there must be recurrent crystallization of forsterite.

From the data contained in the present paper it is obvious that in mixtures of anorthite, forsterite and silica, the crystals of forsterite will be more or less resorbed whenever they occur, and it may happen that forsterite appears in the earlier stages of crystallization but is completely dissolved before the final solidification.

It has been pointed out in a previous chapter (p. 435) what relations should obtain in a system without solid solution in order that recurrent crystallization of one of the phases may

\*\* This Journal, xxxviii, 207, 1914.

<sup>\*</sup> J. H. L. Vogt, Tsch. Min. petr. Mitt., xxvii, 141, 1908.
† Neues Jahrb. Min., Beil. Bd., xxxii, 650, 1911.
‡ Journ. Ind. Eng. Chem., vol. iii, No. 4, 1911.
§ Centralbl. Min., 1912, 266.
[] G. A. Rankin and F. E. Wright, this Journal (4), xxxix, 1, 1915.
¶ N. L. Bowen and Olaf Andersen, loc. cit., p. 495.
\*\* This Learned paramiti 2007, 1914.

take place. It is seen that the system need not be complex if only one of the boundary curves has a certain convex shape in relation to a conjugation line. The system anorthite-forsteritesilica does not show any instances of recurrent crystallization.

It is evident, then, that maginatic resorption and recurrent crystallization in igneous rocks may be explained as consequences of simple cooling of the magina. This way of explanation by the *reaction principle* is not a new theory, set up with the sole purpose of explaining a certain phenomenon, but is a simple deduction from a great general principle, the phase rule, amply supported by experiments. In each case, therefore, where the question arises as to the proper explanation of magmatic resorption and related phenomena, the reaction principle should receive due consideration before resorting to any of the theories which imply changes of the physical conditions, due to exterior influence, or of the chemical composition of the magma as a whole during the solidification.

# Application of the reaction principle to olivine-bearing rocks.

It would be premature now to discuss the application of the reaction principle to rocks in general with the object to prove or disprove its validity. A discussion of the special application to some olivine-bearing rocks may, however, be justified because of the experimental data available in this case. Such a discussion will also throw some light upon the problem of the general application.

Magmatic resorption of olivine.—It has been shown\* that in the two-component system forsterite-silica, forsterite is wholly or in part dissolved on cooling in all mixtures where it appears as primary phase. If now nothing were known beyond this fact we might still draw some conclusions concerning the behavior of forsterite in systems containing more components. We see that the relations of forsterite would not undergo any sudden change if a third component were added to the system forsterite-silica. In some part of the ternary system the quality of forsterite to dissolve on cooling must be maintained. This part, the reaction field of forsterite, may embrace only a fraction of the entire ternary forsterite field, but may equally well include all this field and also parts of adjoining fields, as in the system anorthite-forsterite-silica. This obvious conclusion is based on what we may call the *principle of continuity*, which assumes a gradual transition between a ternary system and its binary systems, the latter being considered ternary systems with infinitely small amounts of the third component.

\* See N. L. Bowen and Olaf Andersen, loc. cit., p. 496.

In the same way we conclude that if a fourth component were added to a ternary system containing forsterite and silica,\* there would be a reaction field of forsterite in the resulting fourcomponent system. In general, therefore, the relations of forsterite may be expressed as follows: In any system, of any number (n) of components among which are forsterite and silica, there will be a reaction field of forsterite. This reaction field may extend over a part of the *n*-component forsterite field<sup>+</sup> only, but may also embrace all this field and parts of the adjoining fields.

In the preceding discussion we have only considered pure forsterite, which is a rare modification (if occurring at all) among natural olivines in rocks, most of which contain a considerable amount of iron silicate, although the magnesium silicate is by far the predominating one. We know, however, from the relations of olivine minerals in rocks<sup>‡</sup> and from their physical and chemical properties,§ that there is a continual series of solid solutions between the forsterite (Mg,SiO,) and the iron silicate fayalite (Fe<sub>2</sub>SiO<sub>4</sub>). In other words, there is no boundary between a forsterite field and a fayalite field, as there is only one *olivine* field in all systems where olivine occurs. What is stated about the possible field relations of forsterite, therefore, also holds true for olivine in general, and thus we may draw the following conclusion: In a system containing the components of an olivine- and pyroxene-bearing rock there will always be a field (reaction field), the melts of which solidify in such a way that the olivine is resorbed during the cooling.

It now remains to discuss whether it is probable that the compositions of any actual rocks fall within the reaction field. of olivine. We consider the system anorthite-forsterite-silica. By adding different amounts of iron oxides, alkalies and some minor constituents to certain mixtures of this system we come very near the compositions of some actual rocks like gabbros and anorthosites. If we, for example, added between 5 and 10 per cent iron oxides and alkalies to mixtures containing 70–90 per cent anorthite and lying within the reaction field of forsterite, and made some minor changes in the relations of the other constituents, we would obtain the composition of actual olivine-bearing anorthosites. In the same way small changes

<sup>\*</sup> The reaction consists in formation of MgSiO<sub>3</sub> by dissolution of forsterite and cannot appear in systems which do not contain MgSiO<sub>3</sub>, that is, forsterite and silica, or MgO and SiO<sub>2</sub>.  $\uparrow$  By *field* is here simply meant all compositions of melts from which for-

sterite separates as the primary phase. In other connections the term has a similar meaning.

 <sup>‡</sup> J. H. L. Vogt, Tsch. Min. petr. Mitt., xxiv, 481, 1905.
 § H. Backlund, Trav. Mus. Géol. Pierre le Grand près l'Ac. Imp. Sc., St. Petersbourg, 1909, iii, 77.

of other mixtures (50-60 per cent anorthite) lying within the ternary reaction field of forsterite would give the compositions of olivine gabbros. We know that the reaction field of forsterite in a complex system must embrace all the mixtures corresponding to the ternary reaction field and at least some of the complex mixtures. Small changes of mixtures which lie within the ternary reaction field, like those mentioned above, are therefore not likely to move the composition points of the resulting mixtures outside the reaction field in the more complex system produced by the changes. As the olivine in practically all olivine-bearing gabbros and anorthosites show magmatic resorption, the explanation of this phenomenon by the reaction principle seems probable and of general application to these rocks.

Summary of application to olivine-bearing rocks.—It is clear that similar reasoning to that applied above to the reaction field of forsterite (olivine), may be applied to other fields in any system. Without repeating any arguments the conclusions which may be drawn concerning the crystallization of olivineand pyroxene-bearing rocks, based on the principles and experimental data represented in the present paper and other papers from this laboratory,\* are indicated below.

1. When olivine occurs in pyroxene-bearing rocks it should in general begin to crystallize before the pyroxene and its crystallization should also in general be completed before that of the pyroxene. Exceptions to this rule should be found in certain diopside-bearing rocks.

2. The olivine crystals of pyroxene-bearing rocks should be more or less corroded as a consequence of the magmatic reaction during the cooling.

3. Some olivine- and diopside-bearing rocks should show two generations of olivine due to crystallization, dissolution and recrystallization during the cooling.

These conclusions are based on crystallization with equilibrium between liquid and solid throughout the period of crystallization. We may also consider a case where the final product of crystallization does not represent equilibrium between the phases involved.

4. The corroded crystals of olivine may be imbedded in the reaction products (pyroxene, amphiboles) or in other minerals in such a way that they are protected against further reaction with the magma. In this case we may find for example olivine and silica together in the same rock.

In how far these conclusions, based on generalizations of experimental results, are corroborated by observations on actual rocks will be known by all petrologists and need not be pointed out.

\* N. L. Bowen and Olaf Andersen, loc. cit. N. L. Bowen. loc. cit.

### Remarks on spinel-bearing rocks.

With the object of explaining the early crystallization of spinel in rocks Harker\* has suggested in a tentative way that spinel melts were only partly miscible with silicate melts. Under the experimental conditions considered in the present study this does not hold true. We find no necessity for postulating such special limiting conditions. Spinel separates from homogeneous melts and the same melts also yield anorthite, forsterite, etc., that is, there appears to be no essential difference between the mode of formation of spinel and that of the silicates. We may therefore conclude that the spinel found in rocks is formed by crystallization from a homogeneous magma.

#### Summary.

The experimental methods are first briefly described and the results stated in Tables 1–5.

The following solid phases were observed: Anorthite, forsterite, cristobalite, tridymite, clinoenstatite and spinel. The thermal and optical properties of these phases are described.

Among the binary mixtures those of anorthite and silica form a simple eutectic system, those of forsterite and silica form a system with an unstable compound, clinoenstatite (MgSiO<sub>3</sub>) and those of anorthite and forsterite form no true binary system, as spinel is the primary phase in some of the mixtures.

In a theoretic discussion the general qualities of some ternary systems without solid solution are reviewed with reference to temperature-concentration diagrams. The quantitative relations of the diagrams are pointed out and types of crystallization curves discussed.

As some of the ternary mixtures anorthite-forsterite-silica contain spinel as a primary phase, the relations of the whole system cannot be properly expressed more simply than in terms of the four-component system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. After a brief discussion of the spinel field the ternary part of the system is described. The system has two quintuple points, one of which is a ternary eutectic, the other an alteration point. Of the boundary curves one is an alteration curve, the others ordinary melting curves. The crystallization curves in different sections of the diagram are discussed. The resorption of forsterite as a result of cooling with equilibrium between liquid and solid is pointed out. Some cases of crystallization with lack of equilibrium are also discussed.

It is shown how the results may be applied to actual rocks, more especially the olivine-bearing rocks.

Geophysical Laboratory,

Carnegie Institution of Washington, Washington, D. C., Jan. 25, 1915.

\* Nat. Hist. of Igneous Rocks, p. 200.

# ART. XXVIII.—Studies on the Etched Figures of Japanese Quartz; by Shimmatsu Ichikawa. With Plates II to VII.

#### Introduction.

IN 1910 I published in Japanese a paper with the title "Studies on the etched figures of Japanese Quartz." The present article may be regarded as an abridged translation of that work, with only slight changes. My memoir gives an outline of the studies carried on by me during the four years 1905 to 1908. These studies are being continued and a second report with further details will be published later. I am desirous of receiving any suggestions or criticisms from those who may read this paper in regard to any of the points discussed in it.

# 1. Artificial Etching of Japanese Quartz (with Plate II).

The artificial etching of quartz crystals by hydrofluoric acid has already been described by Dr. G. Molengraaff;\* the transformations of the original form of the crystal, however, have not yet been discussed in detail. In 1910 I made similar experiments on Japanese rock crystal and observed an interesting new form of elevations (*Aetz-hügel*) produced by etching, and a few new varieties of pits or depressions (*Aetz-grübchen*). The results of this study are illustrated in the accompanying plate (Plate II).

## Plate II (Concentration of hydrofluoric acid, 55 per cent).

The grooves on the edges formed by etching can be barely observed by the naked eye, and the pits on the faces can only be investigated minutely under a magnification of 75 to 140 times.

Fig. 1, A, shows etched figures on a left-handed rock crystal from Takemori, Kai Province; the double lines on the edges indicate the grooves produced by etching. B shows the figures on the faces  $s\left(\frac{2P^2}{4}\right)$ ,  $x\left(\frac{mPn}{4}\right)$  and mR, etc.; the pits on mR

much resemble those formed by the combination of the two sets on R and  $\infty R$ . C is a horizontal projection on the vertical axis of fig. A; the dotted lines are the edges as seen from the opposite pole. D shows the form remaining after the crystal of fig. 1, A, had been etched for seven weeks, the dotted hexagon giving the position of the axes; the form much resembles the

#### \* Zs. Kr., xiv, 173, 1888, etc.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 232.—April, 1915. 30



Artificial etching of Japanese Quartz. S. Ichikawa, del.

outline of a trigonal trapezohedron and has pits of 7-like shape on its faces. Fig. 2 is a right-handed crystal from the same locality, A, B, C, and D corresponding to A, B, C, and D of fig. 1.

Fig. 3 shows the etching of a left-handed quartz, forming phenocrysts in a quartz-prophyry from Otomezaka, Kai Province. Fig. 4 is on a Dauphiné twin of right-handed quartz from the same locality. Fig. 5, A, is a Brazilian twin of rock crystal from Takemori; B, a horizontal projection on the vertical axis of A.

Fig. 6 is a horizontal projection on the vertical axis of the parallel-growth of left-handed and right-handed rock crystals from Yusenji, Kaga Province. Fig. 7 shows the same for a rock crystal from Kinbuzan, Kai Province; the crystal appears like a simple crystal, but has a trigonal trapezohedron on its left and right sides.

Fig. 8 is an etched Dauphiné twin of right-handed rock crystal from Takemori, in horizontal projection on its vertical axis. Fig. 9 is a front view of a model-crystal of left-handed Dauphiné twin; fig. 10 one of a right-handed Dauphiné twin, and fig. 11 of a Brazilian twin.

The symmetry of the pits on the above crystal faces, and the position of the grooves on the edges, correspond to the trapezohedral symmetry. The pits on the rhombohedron, trigonal pyramid and trapezohedron, etc., can be formed by dilute acid, but those on the prism can be obtained distinctly only by pure acid. The trigonal pits and 7-like shaped depressions in fig. 1, D, etc., are formed by a more dilute acid than in the other two cases. The grooves on the edges of the prism can not be formed so regularly as those on the rhombohedral edges, etc.

The extremities of the vertical axis are more quickly dissolved away than the lateral axes, and those of the positive lateral axes more quickly than those of the negative lateral axes; therefore, the resulting form in the etching proves to be a form resembling a trigonal trapezohedron.

# 2. Artificial Etched Figures of some Spheres of Japanese Rock Crystal (with Plates III and IV).

The artificial etching of a quartz sphere with hydrofluoric acid has already been described by Dr. Otto Meyer and Samuel L. Penfield.\* In that paper, however, the order in which the modifications of the sphere occur, in the interval between the beginning and end of the corrosion, has not been

\* Transactions of the Connecticut Academy of Arts and Sciences, vol. viii, pp. 158-165, 1889.



PLATE III.

Artificial etched figures of some spheres of Japanese rock crystal. S. Ichikawa, del.

described in detail. In 1909, I made similar experiments with rock crystal from Kinbuzan, and observed the dull figure formed on each pole of the vertical axis of the etched sphere at the beginning of the corrosion, which is modified as the etching is continued. I also observed a few interesting varieties of the elevations (*Aetz-hügel*), which may be called ridges or terraces; these are formed on each pole of the vertical axis in more advanced stages of the etching, and can be modified by the concentration of the acid, etc.<sup>\*</sup> The results of the study of these etched spheres are illustrated in the accompanying plates (III and IV).

# Plate III. (Concentration of hydrofluoric acid, 55 per cent.)

The dull figures, striations, etc., on the surface of the etched spheres can easily be observed by the naked eye, but the minute study of the ridges, pits, etc., on their surface require a magnification of 75 to 140 times.

Fig. 1. A, shows a front view of a sphere of a left-handed rock crystal, the dotted line (z z') showing the direction of the vertical axis; B, is a basal view; C, that of a pole seen from the other pole. Fig. 2 is a sphere of a right-handed crystal; A, B, and C corresponding to A, B, and C of fig. 1. Fig. 3 is a sphere of an irregularly developed left-handed Dauphiné twin. Fig. 4 shows a sphere of a regularly developed right-handed Dauphiné twin; A, a front view; B, a basal view.

Fig. 5 shows the dull figures formed on each pole of a sphere of a right-handed Dauphiné twin at the beginning of corrosion; weak acid was employed. A, is a horizontal projection of a pole of the vertical axis of the sphere; B, that of a pole seen from the other pole; the figures do not reveal the direction of rotation. Fig. 6 is a sphere of a left-handed Dauphiné twin, A and B corresponding to A and B of fig. 5; here, also, the figures do not reveal the direction of rotation. Fig. 7 is a sphere of a left-handed crystal more etched than those of figs. 5 and 6, thus revealing the direction of rotation; A and B correspond to A and B of fig. 5. Fig. 8 is a sphere of a right-handed crystal, corresponding to fig. 7.

Fig. 9 is a horizontal projection of a sphere of an irregularly developed left-handed Dauphiné twin. Fig. 10 is a dull figure on a sphere of a regularly developed Dauphiné twin; both poles of the vertical axis are observed horizontally, but when more etched, the direction of rotation is revealed as in fig. 4. Fig. 11 is a plate cut perpendicularly to the vertical axis of a right-handed Dauphiné twin, the plate shows the ridges observed

\*See Journal of the Geological Society of Tōkyō, vol.xvi, p. 197, 1909; xvii, 320, 371, 1910.



PLATE IV.

Artificial etched figures of some spheres of Japanese rock crystal. S. Ichikawa, del.

on the pole of the etched sphere as in fig. 2 B, indicating a revolution of 60° about the vertical axis. Fig. 12 is the same as fig. 11, and the striations on its section show numerous regularly arranged ridges.

# Plate IV.

Fig. 1, A, shows the outline of the sphere in fig. 1 of Plate III: A, observed horizontally through both poles of the vertical axis, the dotted hexagon showing the position of B, is the same as A, but it is more etched, and its the axes. outline resembles a trigonal trapezohedron as in Plate II, fig. 1, D; the dotted circle shows the original outline of the sphere. B', is a front view on h h' of the negative end of the lateral axis (compare (x) in fig. A). C, is more etched than B, and shows that a part of the negative end of the lateral axes at the external part of the dotted circle (n) is just about separated , from the direction of the intermediate axes; the structure in the internal part of the circle corresponds to the structure of Plate II, fig. 1, D. C' is the same as B'. D, shows a sphere more etched than C; the part within the dotted circle (n)successively repeats the action as in fig. C, and gradually dissolves away. Fig. 2, A, those in Plate III, fig. 2, A, and B, B', C, C' and D correspond to B, B', C, C', and D of fig. 1.

Fig. 3 shows horizontal projections of the trapezohedral elevations formed on the base-like face of  $(a \ b \ c)$  at a pole of the etched sphere, A, left and B, right. Fig. 4 shows horizontal projections of these negative and positive trapezohedral elevations formed on base-like faces  $(a \ b \ c)$  at a pole of the etched sphere, A, left and B, right. Fig. 5 shows, magnified, the individual elevations of figs. 3 and 4, and has pits of 7-like shape on its faces; the dotted hexagon shows the position of the axes, A, left and B, right. Fig. 6 is more etched than fig. 5 and has a rough base-like face; the ridges are a little twisted to the left or right of the vertical axes. Fig. 7 is still more etched, the ridges being very much twisted like a left-handed or right-handed distorted quartz.

Fig. 8 shows the trapezohedral elevations with regularly developed base-like face. Fig. 9 shows the pole edges truncated by a trapezohedral face with different coefficient from itself. Fig. 10 shows forms of peculiar shape very rarely observed.

Fig. 11 shows the etching figures formed on a plate cut perpendicular to the vertical axis of a Brazilian twin, revealing the direction of rotation, and in the section, each area of the left (l) and right-handed (r) crystals is indicated as distinctly as in polarized light. Fig. 12 shows a Dauphiné twin as fig. 11. The symmetry of the dull figures (except in Plate III, figs. 5 and 6) on the surface of these etched spheres exhibits the symmetry of the trapezohedral group to which they belong.

Both poles, in the vertical axis of the etched sphere, are more quickly dissolved away than the equator, and the positive ends of the lateral axes more quickly than the negative ends; the result is, therefore, a trapezohedral form as in those of the simple crystal of the quartz with bipyramid (Plate IV, fig. 1, B, compare Plate II, fig. 1, D.).

A sphere of a regularly developed Dauphiné twin reveals the twelve dodecants on its surface by etching, with the vertical axis and intermediate axes, and each dodecant is occupied by the positive and negative lateral axes; therefore when each dodecant belonging to the area of the positive or negative lateral axes of a simple quartz crystal is revolved 60° about the vertical axis, the quartz is supposed to make up the given regular Dauphiné twin.

The etching of basal sections cut perpendicular to the vertical axis of twin crystals reveals the revolved or interpenetrated areas and also the direction of the rotation : the etching of such sections is, therefore, an important method of the determination of a twin crystal.

When the acid is near concentration the section yields trapezohedral elevations (see Plate III, fig. 11), but if very weak the surface shows the negative crystal of the trapezohedral ridges (see Plate III, fig. 4); also if the section is kept in the very weak acid, depressions of 7-like shape are formed on the surfaces of the elevations (see Plate IV, figs. 11 and 12), and these are gradually twisted to the left or right of the vertical axis (see Plate IV, figs. 6 and 7.) Hence, the phenomena prove that the direction of the molecular dissociation in the etching corresponds to that of the circular polarization.

In etching hexagonal prisms or columnal seals, etc., of rock crystals it is found that they are attacked rapidly in the direction of the vertical axis, but barely at all in the direction of the lateral axes; the specimens are, therefore, gradually modified into thinner' hexagonal or rounded forms, and at last are wholly dissolved away.

When etched basal sections, as Plate IV, figs. 11 and 12, etc., are again placed in the pure acid the sections are modified into a translucent, smooth plane by violent action of the acid, but after a day or two the ridges are again formed on the surface, and after three or four days 7-like depressions are formed, and after a week these are twisted in a direction to the left or right of the vertical axis.

The development of etching figures on the poles of the vertical axis of a sphere or a basal section, etc., of quartz crystal Ichikawa—Etched Figures of Japanese Quartz. 463

is closely connected with atmospheric pressure and temperature concentration of solvent, etc.; hence it is difficult to reproduce exactly results earlier obtained.

## 3. Natural Etched Figures of Jupanese Quartz (with Pl. V).

The natural etching of quartz crystals has already been described by Dr. G. Molengraaff;\* in these papers, however, the transformation of the edges has not yet been described in detail. In 1908 I first observed the natural etching of amethyst from Yusenji, Kaga Prov., with grooves on the edges; since then I have visited many quartz localities in Japan and collected some interesting new specimens of natural etching;† the results of the study of these are illustrated in the following plate:

# Plate V.

The transformation of the edges and the depression of fig. 10, etc., can be observed by the naked eye, but the pits on the crystal faces of other specimens can not be investigated minutely unless under a magnification of 75 to 140 times.

Fig. 1 shows the natural etching of a left-handed amethyst from Yusenji, Kaga Prov. A is a front view, and the double lines on the edges of the rhombohedron and prism of the crystal show the grooves formed by etching. B is a horizontal projection on a rhombohedral face. C a horizontal projection of the section cut perpendicularly to the vertical axis. Fig. 2 shows the natural etching of a right-handed amethyst from the same locality, A, B, and C corresponding to A, B, and C of fig. 1. Fig. 3 is the natural etching of a Dauphiné twin of left-handed amethyst and fig. 4 a similar right-handed twinned amethyst, A, B, and C corresponding to A, B, and C of fig. 1 in each case.

Fig. 5, A, shows varieties of natural pits on the rhombohedron and prism of fig. 1, A, but the pits on the former do not reveal the difference between positive and negative forms. B shows pits on the prism of the same crystal that are very rarely observed, but they do not reveal the direction of rotation.

Fig. 6 is the natural etching of an amethyst from Ozawa, Iwaki Prov. A is a horizontal projection on the rhombohedron of the same crystal, and the double lines on the edges show a new face formed by etching that looks like  $-\frac{1}{2}R$ . B is a horizontal projection on the section cut perpendicular

\* See Zs. Kr., xiv, 173, 1888; xvii, 137, 1889.

<sup>†</sup>See Jour. Geogr. Tökyö, vol. xv, 235 and 441, 1908; xvi, 129, 1909; xvii, 320, 1910.



Natural etched figures of Japanese quartz. S. Ichikawa, del. (except fig. 11).

to the vertical axis of the crystal, and its negative edges are rounded by the etching.

Fig. 7 gives horizontal projections on the rhombohedron of rock crystals with natural etching from Yusenji; the double lines show rounded edges by etching, and a triangle on the center shows a pit that is produced in the direction of the vertical axis by etching. (ab) in fig. B shows a groove that is formed on the rhombohedron by etching. The direction of rotation is not shown.

Fig. 8 is the natural etching of rock crystals from Kamiokamine, Hida Prov.; its rhombohedron has ridges suggesting the trapezohedral form found on the poles of the etched quartz sphere (see Pl. III, figs. 1 and 2, B, C, and Pl. IV, fig. 3, A, etc.), A is a front view, and B a horizontal projection on a rhombohedron. Fig. 9 is the natural etching on the prism of a rock crystal from Kinbuzan; the depressions in A much resemble those of fig. 5, B.

Fig. 10 is the natural etching of a smoky quartz from Kamikane, Kai Prov. A gives a front view, and B a horizontal projection on the vertical axis of A; the double line on each edge shows a new face formed by etching that resembles that of fig. 6, A. Both sides of the pole edges of (ab) and (cd) have striations formed by etching, and the angle is larger than the normal angle of quartz; (xy) shows a fissure with many depressions. C shows varieties of the natural pits on the rhombohedron. D shows the difference between the outlines of a natural depression of Molengraaff (b) and I(a) on a rhombohedron of quartz.

Fig. 11 shows varieties of the natural pits on the rhombohedron and prism of a foreign quartz which Molengraaff first observed (compare fig. 5, A). See also the results of Dr. K. Jimbo on the natural etching of a rhombohedron of Japanese quartz.\*

The natural pits on the rhombohedron of fig. 5, A, do not reveal the distinction between the positive and negative forms as do those in fig. 11 taken from Molengraaff's work. Also while the natural depressions on the prism of fig. 5, A, and fig. 9, B, etc., reveal the direction of rotation, the symmetry of the natural pits on the prisms of fig. 5, B, and on the rhombohedron of fig. 5, A, do not correspond to the trapezohedral symmetry; therefore the method that determines the positive and negative rhombohedrons by Molengraaff's model figure (fig. 11) cannot be applied to natural etching of the above Japanese quartz.

The varieties of edges modified by etching are classified as follows: 1 has grooves (figs. 1, 2, etc.), 2 is rounded (fig.

\* Jour. Geogr., Tōkyō, vol. iv, 172, 187, 1897.

# 466 Ichikawa—Etched Figures of Japanese Quartz.

6, B), 3 has a new face like  $-\frac{1}{2}R$  (figs. 6, A, and 10, A, etc.), 4 has a larger angle than the normal angle (fig. 10, B). The position of grooves on the prismatic edges of natural etching is opposite to that of quartz crystal etched with hydrofluoric acid.

#### 4. Vicinal Faces of Japanese Quartz (with Plate VI).

Artificial and natural etching of quartz crystal have already been described by mineralogists, but not the characteristics of the vicinal faces of the crystal, which are closely connected with these etching figures. In 1909, I first observed a smoky quartz from Tanokamiyama, Omi Province, with a different vicinal face on its positive and negative rhombohedral faces; since then I have collected a number of interesting quartz crystals with vicinal faces accompanied by natural etching on a rhombohedral face.\* The results of the study of these vicinal faces are illustrated in the following plate :

#### Plate VI.

The size of the vicinal forms on the rhombohedral faces is larger than the natural pits on the same face, and they can usually be observed by the naked eye.

Fig. 1 shows vicinal faces on a Dauphiné twin of left-handed rock crystal from Kinbuzan. Fig. 2 is a horizontal projection on a pyramid of a left-handed cairngorm with vicinal faces from Naigi, Mino Province. Fig. 3 is a left-handed smoky quartz from the same locality as fig. 2. Fig. 4 is a left-handed rock crystal from Takemori. Figs. 5 and 6 are left-handed rock crystals from Kinbuzan; fig. 6 is a Dauphiné twin with numerous irregularly developed vicinal faces.

Figs. 7 and 8 are right-handed smoky quartz from Tanokamiyama, Ōmi Province; fig. 7 is a Dauphiné twin. Fig. 9 is a Dauphiné twin of right-handed smoky quartz from Naigi. Fig. 10 is a right-handed rock crystal from Takemori. Fig. 11 is a Dauphiné twin of right-handed smoky quartz from Tamokamiyama. Fig. 12 is a Dauphiné twin of right-handed rock crystal from Kinbuzan; the pyramid has innumerable irregularly developed vicinal faces.

Fig. 13 is a Dauphiné twin of left-handed smoky quartz from Tanokamiyama. Fig. 14 is a Dauphiné twin of left-handed smoky quartz from Kamikane, already shown in Plate V, fig. 10, B; the pyramid has many vicinal faces and natural depressions on its surface. Fig. 15 is a right-handed rock crystal from Kinbuzan, with a few vicinal faces and many natural pits; A and B show the pyramid on both ends of the prism.

\*Jour. Geogr. Tōkyō, vol. xvi, 495, 1909; xvii, 239, 1910, and the correction in vol. xvii, 526, 1910; vol. xviii, 82, 1911.



PLATE VI.

Vicinal faces of Japanese quartz. S. Ichikawa, del.

Fig. 16 is a model figure showing varieties of the vicinal faces on the positive and negative rhombohedrons of left-handed quartz and the relation between their outlines to the edges on the positive and negative rhombohedral faces. Fig. 17 shows those on the rhombohedron of right-handed quartz.

Fig. 18 gives the vicinal faces on a rhombohedron of a Dauphiné twin of left-handed rock crystal from Takemori; the character of the rhombohedron is determined by hydrofluoric acid. Fig. 19 shows the relation between regular vicinal faces and natural depressions on a rhombohedron of left-handed quartz, and also the relation between their outline and the edges on the rhombohedron face.

In each of the above figures the symmetry of the vicinal face on the rhombohedron of the quartz crystals corresponds to the trapezohedral symmetry, and it also reveals the distinction between positive and negative forms and the difference between the left-handed and right-handed crystals; therefore, the vicinal faces are a profitable subject for investigation of quartz.

In figs. 14 and 15, the natural etched figures do not reveal the distinction between the positive and negative rhombohedrons, but the vicinal faces show this distinction. The vicinal faces of Japanese quartz are found in smoky quartz rather than in rock crystal, and the faces with them have a stronger luster than those without.

# 5. Theoretical Figures showing the Molecular Structure of Rock Crystal (with Plate VII).

Theoretical figures, showing the molecular structure of rock crystal, have already been described by Lord Kelvin\* and Dr. S. Nakamura.<sup>+</sup> In 1910, I also made a model of the crystal molecule corresponding to the trapezohedral form developed by hydrofluoric acid, and also investigated the molecular structure; the theory of this is illustrated in the following plate:

# Plate VII.

Fig. 1 shows the various types of crystal faces occurring on rock crystal and the relation between them; the striations in the center of the figure give the position of the four trapezohedrals derived from the dihexagonal pyramid. The faces of these forms are commonly seen to the left or right of the prismatic edges, corresponding to the positive lateral axes, but the prismatic edges of the negative lateral axes do not have these faces (see Plate II, figs. 1 and 2, A). A gives the left-handed faces, and B the right-handed.

\* Baltimore Lectures, pp. 602-642, 1893.

† Rigakukuwaishi, vol. iii, No. 13, p. 12, 1910.



Theoretical figures showing the molecular tactics of a rock crystal. S. Ichikawa, del.

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Fig. 2 is a theoretical figure showing the structure of a crystal-molecule of left-handed quartz, in which it is assumed that six molecules of silica  $(SiO_{2})$  go to form the six faces of the trapezohedral form produced by etching; the atom of silicon (Si) with the positive ion takes its place in the direction of the positive lateral axes, and the atom of oxygen (O) with the negative ion takes its place in the direction of the negative lateral axes. The dotted hexagon shows the position of the axes and its internal part represents the limit of area of the crystal-molecule (6SiO<sub>2</sub>). A is a horizontal projection on a pole of the vertical axis of the crystal-molecule; B that on a pole seen from the other pole. Fig. 3 is a theoretical figure showing the structure of the crystal molecule of right-handed quartz crystal; A and B correspond to A and B of fig. 1. Fig. 4 shows a left-handed trapezohedron (in a position opposed to that of fig. 2), supposed to be formed by natural etching  $(K_{a}CO_{a}).$ 

Fig. 5 is a theoretical figure showing the structure of the crystal-molecules of a simple left-handed crystal; seven crystal-molecules are grouped regularly in the direction of the intermediate axes, and they are combined with each other by the energy of the positive and negative ions. Fig. 6 shows the same on a right-handed quartz crystal.

Fig. 7 is a theoretical figure showing the molecular structure of a left-handed Dauphiné twin, in which it is assumed that the crystal-molecule at the end of each negative lateral axis is revolved 60° about the vertical axis. Fig. 8 is a similar figure of a Brazilian twin of rock crystal in which it is assumed that the crystal-molecule belonging to the area of the negative lateral axes of a right-handed quartz penetrates into the area of the positive lateral axes of a left-handed quartz.

The symmetry of the crystal-molecule (six molecules of silica  $(Si_sO)$  with geometric arrangement) in the above figs. 2 and 3 corresponds to the symmetry of the trapezohedron, and the crystal-molecule thus reveals the trigonal symmetry by the revolution about the vertical axis, and the binary symmetry by the revolution about the lateral axes, and it has neither center nor plane of symmetry.

In the above models the structures of simple crystals and twin crystals of the given quartz are readily understood, and there are also numerous cases where the physical and chemical reactions by which the molecules act upon other adjacent molecules can be well explained by the models; a few examples are mentioned in the following:

When a quartz crystal is kept in strong hydrofluoric acid, a groove will be found on each positive edge of its prism (see Plate II, figs. 1 and 2, etc.); if we assume that the prismatic positive edges with positive ion (Si), which belong to the territory of the positive lateral axes are attacked by the acid with negative ion (F), the phenomenon will be easily understood.

When quartz crystal is naturally etched, a groove will be found on each negative edge of its prism (see Plate V, figs. 1 and 2, etc.); this is understood if we assume that the prismatic negative edges with negative ion (O), which belongs to the area of the negative lateral axes, are attacked by a natural solvent (salt of K, Na, etc.) with positive ion.

Rhombohedral pole edges of the combination of +R and +R or -R and -R in a quartz crystal develop a groove in hydrofluoric acid, and the edges have also the same result through natural etching; this can be understood if we assume that the crystal-molecules of the edge to take its place in the direction of the intermediate axes keep the condition of neutrality with each other (see Plate I, fig. 1; Plate V, fig. 1, etc.).

The basal section of quartz crystal is attacked equally by hydrofluoric acid; this is clear if we assume that the crystalmolecules on the plane keep the condition of neutrality with each other (see Plate VII, figs. 5-8).

A quartz crystal is more easily cleaved in the direction of the intermediate axes than in other directions; which suggests that the crystal-molecules of quartz are regularly arranged in the direction of the intermediate axes as in the above models.

When two rock crystals are struck together with each other by their prismatic edges, the crystals will emit a phosphor-escence (triboluminescence) on each individual; if we may assume that this is an electric light by which the negative and positive electricities of the crystal-molecules, developing as the reaction of striking together, neutralize each other with the electricities of the adjoining crystal-molecules in a moment, the phenomenon will easily be understood. Besides amethyst, milky quartz emits phosphorescence, but (cairngorm, smoky quartz, etc.), do not emit it, except after their color is lost by ignition.\*

The phenomena of pyro-electricity and piezo-electricity, etc., can also be explained by the above models, but whether the quartz crystal has the simultaneous development of positive and negative charges of electricity on different edges of the crystal, as well by etching as by temperature or pressure, can not be determined, unless after an exact measurement.<sup>+</sup>

\*See my note "On the relation between the colors and phosphorescence of quartz," (Tōyōgakugezatsushi No. 334, p. 355, 1909, and Jour. Geogr.,

Tökyö, vol. xvi, p. 234, 1909). †See my note "On the development of electricity on quartz crystal." Töyögakugezatsushi, No. 346, p. 338, 1910.

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, NO. 232. - APRIL, 1915. 31

# APPENDIX.

#### QUARTZ WORK IN JAPAN.

In 1906, I personally visited the quartz works at Kofu, Kai Prov.; since then, in 1909, I visited the quartz and agateworks at Onu, Wakasa Prov., and the amethyst and jasperworks at Matsue, Izumo Prov., and obtained some interesting knowledge of quartz-work. I give below a summary of the results:

The cleavage of quartz crystal is not distinctly observed, but it is proved by etching that the fracture surfaces are sometimes parallel with R,  $\frac{mPn}{4}$ ,  $\frac{2P2}{4}$ ,  $\infty R$ , etc.; besides this cleavage is also imperfect parallel with  $\infty P2$ , or the direction of the intermediate axes. This was proved by the experience of a sculptor at Kofu, many years ago; it is found that a crystal can easily be cleaved in two if a shallow groove be dug perpendicular to the oscillatory combination of the prismatic face and struck lightly with a wedge. In this case it emits a stronger phosphorescence (triboluminescence) than when it is cleaved in other directions.

The fracture of quartz crystal is conchoidal or subconchoidal, but the fracture perpendicular to the vertical axis of the crystal is more regularly conchoidal than in other directions. In quartz-work, the needless parts of the original quartz are broken away with a little hammer and a slender chopstick of steel; in this way, a skillful sculptor dexterously makes up the outlines of a sphere, seal or paper-weight, etc., with many conchoidal fractures perpendicular to the vertical axis of the original crystal, the direction in which cleavage is not found, and then these surfaces are polished by emery. In the production of tigers, lions, personages, etc., the needless parts of the original quartz are cut away with a wire of steel and emery.

The hardness of quartz crystal is 7, but it is not the same on all faces of the crystal, the prismatic faces are harder than others and the artificial basal section is much softer than the natural crystal faces. This is proved by the etching and polishing; therefore letters of quartz-seals in Japan are carved on the artificial basal section of the crystal.

Primary quartz is more brittle than secondary quartz, as shown by the fact that the sculptors of Kofu distinguish between the brittleness of rock crystal from the pegmatite of granite from Kinbuzan, and rock crystal from quartz vein of spotted clay slate formed by contact with granite from Takemori.\*

\* See my note "On the luster and brittleness of rock crystal" in Jour. Geogr. Tökyö, vol. xvi, 541, 1909.

The luster of quartz crystal is vitreous, but primary quartz has a stronger luster than secondary quartz. Natural etching gives a stronger luster than artificial etching; in the latter case the strong acid yields a stronger luster than the weak acid. The diaphaneity of quartz crystal is from transparent to opaque, but secondary quartz is more transparent than primary quartz, and in secondary quartz, that from granite pegmatite is more transparent than quartz in metal-veins.

Smoky-quartz, amethyst, etc., lose color by ignition, but milky-quartz does not change in this way; ignited quartz has a stronger luster and is less brittle than before ignition.

The direction of the vertical axis of rock crystal is softer than that of the lateral axes; therefore in making hollow spheres, vases, etc., the hole must be dug in the direction of the vertical axis. In the direction of the vertical axis rock crystal has no double reflection; hence quartz lenses must be cut perpendicularly to this axis. A basal section of a crystal is dissolved by a strong hydrofluoric acid and its plane does not show etching figures in the direction of the vertical axis, like an isotropic body.

In the above studies it has been shown that the principles governing the methods of the crystal sculptors in Japan correspond to those developed by my etching. There are numerous other cases where etching and the principles revealed by it must be applied to the work in quartz.

Kitashinjo-mura, Imatate-gun, Fukui-ken, Japan, 1913.

# ART. XXIX.—Datolite from North Plainfield, Somerset County, New Jersey; by A. C. HAWKINS.

THE datolite crystals here described were collected by the writer in 1905 at the old quarry then being operated in the First Watchung Mountain basalt, at North Plainfield, New Jersey, by the Wilson Crushed Stone Company, now operating on adjoining property.

The crystals were found upon two specimens, viz:—Specimen No. 1 exhibits a large number of intergrown individuals having an average size of  $4 \times 2.6 \times 2.2^{\text{mm}}$ , the largest measured being  $7 \times 4 \times 5^{\text{mm}}$ , and the smallest  $3 \times 1.5 \times 1.5^{\text{mm}}$ . Their color is white to very light green, and their luster is vitreous. They are implanted upon a somewhat porous and granular crystalline mass of the same material, which in turn rests directly against the wall of a 6-inch cavity in the vesicular basalt. Steep white calcite scalenohedra are scattered over the



datolite crystals. The habit of these datolites is closely similar to that of the crystals from Bergen Hill (Dana, System of Mineralogy, Ed. 6, fig. 4, p. 503), being prismatic, with welldeveloped basal pinacoid. Specimen No. 2 shows a few larger crystals, averaging in size about  $4 \times 5 \times$ 7<sup>mm</sup>. These latter crystals are more strongly pyramidal in development (op. cit., fig. 1). They are slightly

deeper in color than those of specimen No. 1, and are not so lustrous.

The crystals were measured on the two-circle goniometer. Twelve crystal forms in all were observed; of these, ten are common, being observed on practically every one of the seventeen crystals examined; two forms are rare. Unit prism and basal pinacoid predominate, other faces being modifications of this fundamental combination. Some forms, as in the case of the unit pyramid [111], are large but uniformly dull; others are narrow, some excessively so. Especially is this true of the new clinodome [043]. This form, though narrow and often rounded or "disturbed," occurs upon the majority of the crystals examined, being thus typical of the locality.

Though the minute size of faces of [043], which appears for the most part as a narrow, bright line, render its signals often uncertain in position, and though the readings obtained (Ro) vary from 37° 00' to 38° 43', numerous readings were obtained which are close to the calculated angle for this form, as is also their average, 37° 50'. The form may, therefore, be considered as well established, inasmuch as there are no other forms in the immediate vicinity.

The normal relations for the clinodomes of datolite now become:

			Zor	ie [0	10 :	001]			
Letter		$\Delta$	е	$\mathbf{M}$	N*	r	0	1	
	0	$\frac{1}{2}$	$\frac{2}{3}$	1	$\frac{4}{3}$ *	$\frac{3}{2}$	2	3	inf.

\* New form starred.

This compares favorably with the normal series  $N_s$  of Goldschmidt.

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#### SCIENTIFIC INTELLIGENCE.

#### I. CHEMISTRY AND PHYSICS.

1. The Production of Chloropicrin from Organic Compounds. R. L. DATTA and N. R. CHATTERJEE have found that aqua regia acting upon a great many organic compounds produces chloro-picrin, CCl<sub>s</sub>NO<sub>2</sub>, which is sometimes called nitrochloroform, or in modern nomenclature trichlorintromethane, a heavy liquid of very pungent odor. Aqua regia decomposes acetone, (CH.), CO, almost quantitatively into chloropicrin, so that the reaction may be employed as the best method of preparing the substance. A mixture of two parts of nitric and three parts of hydrochloric acid is prepared and to this about one-tenth of acetone is gradually added with slight warming, finally on the water bath. The resulting liquid is next subjected to steam distillation and the compound is separated, dried by means of calcium chloride and finally distilled at a slightly reduced pressure. Treated with aqua regia in a similar manner allyl alcohol gave the same product, ether gave only a little of it, ethyl alcohol was partially converted into it, methyl alcohol gave apparently a slight trace of it, while formic and acetic acids were not decomposed by aqua regia and consequently gave no chloropicrin. Many other organic compounds gave this substance as a final decomposition product, so that the action appears to be very general.-Jour. Amer. Chem. Soc., xxxvii, 567. H. L. W.

2. The Determination of Gasolene Vapor in Air.-G. A. BURRELL and A. W. ROBERTSON have used two methods for this purpose, one of which is particularly interesting on account of the principle involved. The apparatus consists of a tubular glass bulb with a constriction dividing it into two nearly equal parts. The upper part is charged with glass-wool and phosphorous pentoxide in order that the water vapor in the sample of air may be absorbed, for otherwise it would count as gasoline vapor. The bulb has an upright stem to the side of which is attached by fusion a simple U-shaped mercurial manometer. Above this is a 3-way stop-cock with a connection with a vacuum pump and another for admitting the sample. To make a determination the air is pumped out of the apparatus, the sample to be analyzed is let in at atmospheric pressure, the bulb is then placed in liquid air which condenses the gasoline completely, the air is next pumped out, the stop-cock is closed and the bulb is warmed to the original temperature, and its pressure is read off on the manometer. The ratio of this pressure to the pressure of the atmosphere gives the percentage of gasoline vapor originally in the sample of air. It is unnecessary to know the volume of the bulb. The other method employed for the purpose consisted in burning the gasoline vapor with air or oxygen in a gas analysis apparatus and determining the contraction as well as the carbon dioxide

formed. Assuming the average composition of the gasoline to be that of pentane,  $C_{b}H_{1,p}$ , the results calculated from the carbon dioxide agreed well with the liquid air method.—Jour. Indust. and Eng. Chem., vii, 112. H. L. W.

3. The Transmutation of the Chemical Elements.-In recent years the ancient idea that the transformation of the elements is a difficult but not impossible problem is gaining many adherents. Ramsay says that it appears to him that only slight imagination is needed in order to expect that while certain elements transform themselves spontaneously (exothermically), giving off helium, others only need external energy to give the same result. J. J. Thomson considers it possible that the gases helium and hydrogen (H<sub>s</sub>) which are evolved from many substances by bombardment with cathode rays may result from a disintegration of the atoms. Fajans is convinced that the transformations of the elements form the basis of the periodic system. He indicates that thallium could be produced from bismuth by an a-ray transformation, and considers it not unbelievable that gold could be obtained from lead or mercury, as was supposed to be possible in the 17th century. W. P. JORISSEN and J. A. VOLLGRAFF propose to study this matter by subjecting several substances to the action of powerful cathode rays, and also to repeat the transformation experiments of Ramsay by means of radium emanation. As the first part of their work they have subjected uranium oxide to the action of cathode rays and have found that this treatment imparts to the uranium no additional activity, although such an effect has been supposed to occur by several investigators.-Zeitschr. physikal. Chem., lxxxix, 151. H. L. W.

4. The Chemistry of Cyanogen Compounds; by HERBERT E. WILLIAMS. 12mo, pp. 423. Philadelphia, 1915 (P. Blakiston's Son & Co.).—This book, which is of English origin, gives an excellent and up-to-date treatment of the subject. The author was led to undertake the preparation of the work on account of the unsatisfactory and often misleading information given in the existing chemical dictionaries. He himself has prepared and examined many hundreds of cyanogen compounds, particularly the metallic salts, and some of his results appear for the first time in this book. The work is divided into three parts, the first of which gives a description of a multitude of compounds. The second part deals with the manufacture and application of cyanogen compounds. The last part is an excellent treatise on the analytical problems connected with these substances. H. L. W.

5. Die Ühemie der hydraulischen Bindmittel; von H. KÜHL und W. KNOTHE. 8vo, pp. 347. Leipzig, 1915 (Verlag von S. Hirzel).—This book deals with hydraulic cements from a scientific point of view and it gives a very full and able discussion of the subject. It will be valuable to all readers of German who are interested in the theoretical side of this great industry, and it may be observed that the scientific aspects of the subject are of great practical importance.

6. Diffusion of Gases through Mercury Vapor. The "Diffusion Air Pump."-When a vessel, such as an X-ray bulb, is evacuated by means of a mercury pump while the pressure is read on a MacLeod gauge it becomes a matter of no little importance to know whether the total pressure in the vessel is really as low as the gauge indicates or whether the pressure can never fall appreciably below 0.0013<sup>mm</sup>, that is, below the pressure of saturated mercury vapor at ordinary room temperature. Since decided differences of opinion exist with regard to this question, the more general problem of the diffusion at low pressures of various gases through mercury vapor has been attacked both experimentally and theoretically by W. GAEDE. A striking and important consequence of this investigation is the invention of a new and remarkable kind of air pump. Since the original paper is comparatively long and involves a number of fairly complicated mathematical formulæ, it will only be possible to give a fragmentary account of this very interesting research in these columns.

The first experiments were made upon the diffusion of air and of hydrogen through saturated mercury vapor. A bulb, A, was connected by a diffusion tube to a cooling bulb, C, which in turn communicated with another bulb, M. The vessel, A, and the diffusion tube were wrapped with a coil of wire through which a heating current could be sent and the temperature regulated at will. The lower end of A opened into a vertical glass tube, which was connected to a mercury reservoir in such a manner as to enable the experimenter to introduce mercury into A or to lower the top of the column below the region of relatively high temperature, as occasion required. The lower end of A was also immersed in an oil bath to facilitate the heating of the upper portion of the mercury column. Each experiment involved three sets of observations. (i) The pressure of the gas in A and M was observed with the whole apparatus at room temperature. (ii) The pressures of the gas in A and M were ascertained when A was heated by the electric current, but when the top of the mercury column was well below the level of the bottom of A. In cases (i) and (ii), therefore, the pressure of the mercury vapor was negligible. (iii) The pressure in M was measured under the same thermal conditions as in case (ii), the only change consisting in the elevation of the mercury meniscus to the level of the hot oil bath. From the observed pressures together with the volumes of the vessels on both sides of the cooling bulb it was

easy to calculate the fraction  $\frac{p'_1}{cp_2}$ , where c (which is nearly unity)

denotes an empirical constant involved in case (ii), and  $p'_1, p_2$  symbolize the partial pressures of the gas in A and M respectively for case (iii). The formula for this fraction, in terms of known quantities involves two legitimate assumptions, (a) the adequacy of the "Boyle-Gay Lussac" gas law, and (b) the constancy of the total mass of gas in the apparatus for cases (i), (ii), (iii).

ratio  $k \equiv \frac{p'_1}{cp_2}$  is a measure of the disparity of pressure in A and

M due alone to the warm mercury vapor when dynamical equilibrium obtains between the saturated vapor and the gas. Curves were next drawn with temperatures of the vapor as abscissæ and the corresponding values of k as ordinates. On the same diagram curves were plotted which show the dependence of k on t when the condition  $p_1 + P_1 = p_2 + P_2$  was assumed to hold. This equation is the one generally used in theoretical discussions of the process of diffusion, and it states that the sum of the partial pressure p of the gas and P of the mercury vapor is constant. The last set of curves fall closer to the axis of k than the set first mentioned, thus showing that the conditions in a vacuum differ appreciably from those which prevail at higher pressures, such as  $0.004^{\text{mm}}$  to  $0.04^{\text{mm}}$ .

The next step in the argument consisted in the calculation of the coefficient of diffusion D from Stephan's law and from data obtained from experiments in vacuo. The values of D came out so nearly constant as to show complete agreement between theory and experiment. Hence, the lack of coincidence of the two sets of curves is not due to theoretical error but corresponds to reality. Consequently, the relation  $p_1 + P_1 = p_2 + P_2$  needs correction for finite pressures. On hydrodynamical grounds Gaede next works out the correction term  $\epsilon$  in the equation  $p_1 + P_2 = p_2 + P_2 + \epsilon$ . This term is too complicated to be given here. However, it involves the coefficient of diffusion D, the radius of the diffusion tube, the coefficient of slip, the coefficient of viscosity, and the several partial pressures. It follows from the form of the function  $\epsilon$  that this term can only become negligible under certain special conditions. On the other hand, it is quite possible for  $\epsilon$ to have appreciable values. That such is the case is tantamount to answering the question suggested at the beginning of this abstract. In brief, it has now been shown both practically and theoretically that it is possible to attain, by means of a mercury pump, pressures lower than the vapor pressure of the mercury involved. Also, these pressures may be correctly indicated by a MacLeod gauge. The fallacy in the argument that total pressures lower than that of saturated mercury vapor at room temperature (0.0013<sup>mm</sup>) cannot be obtained with a mercury pump arises from the tacit assumption that  $\epsilon = 0$  at finite pressures.

Some idea of the principle of action of the final form of diffusion pump, which the preceding considerations enabled Gaede to design and perfect, may be obtained from the following brief description of an illustrative pump of very simple construction. A cylinder of unglazed porcelain, with the upper "base" of the same material, is surrounded at the top and sides by a larger non-porous cylinder which in turn is joined at its top, by means of a suitable tube, to a steam generator. A metal cylinder, closed at the top, projects up inside the porcelain vessel and closes the lower end of the latter completely. Cold water is caused to circulate in the metallic cylinder. The space between the coaxial cylinders communicates with a bulb and a barometer tube. The

lower end of this tube projects below the surface of the mercury in a reservoir open to the outside air. Water vapor at about atmospheric pressure flows down around the outside of the porcelain cylinder and escapes, for the most part, into the surrounding atmosphere. The rest of the water vapor diffuses inward through the walls of the porcelain cup, is condensed by the cooler, and runs down into the collecting bulb. At the same time the air imprisoned between the outside of the cooler and the inside of the porcelain vessel diffuses outward in the direction opposite to that of the diffusing water vapor. The whole apparatus acted as a pump, and the column of mercury rose in the barometer tube until it attained a height 15mm less than the "barometric height." This difference of 15<sup>mm</sup> was due to the pressure of water vapor corresponding to the temperature of the cooler. The action of the pump may be better understood from the following elementary considerations. The water vapor on the inside of the porcelain cylinder is prevented from exerting a pressure greater than  $15^{mm}$  by being condensed and removed from the field of action before it can accumulate. The air in the same vessel diffuses outwards as long as any of it remains. As soon, however, as the air has passed through the porcelain walls it is swept out by the current of water vapor and escapes into the outside atmosphere before it can exert any appreciable back pressure. Finally all of the air will have diffused out of the porcelain cup and the only source of pressure will be the water vapor at about the temperature of the cooler. As Gaede says: "This experiment shows for the first time that one can produce a continuous sucking action by means of the diffusion of vapors and gases alone, without the motion of solid or liquid pistons." The fatal fault of this particular form of pump is the very long time required to reach the lowest pressure which the system is capable of producing. Gaede shows, however, both theoretically and experimentally that holes in (metallic) diaphragms will give the highest rate of evacuation when the diameter of the opening is of the order of magnitude of the mean free path of the molecules of the gas. He therefore replaces the porcelain membrane by slits between metallic jaws. Also, for obvious reasons, mercury vapor is used in the final form of pump. An especially noteworthy result,-which is also predicted by the theory of diffusion,-follows from the tables of test data given in the original article. It is that the speed of evacuation remains constant even to the highest vacua obtainable. This property has never before been observed in any other type of air pump. A few typical numerical data illustrating the general behavior and efficiency of the new diffusion pump will now be given. Beginning with the pressure of 0.25<sup>mm</sup> a Röntgen ray bulb containing air was evacuated in 25 sec. to the extent that the current preferred a parallel spark gap of 16<sup>mm</sup> length. On further pumping, the spark gap increased to 100<sup>mm</sup>. In this case the temperature of the mercury vapor was 119°C. The corresponding times at temperatures of 126° and 135° were 30 and 45

seconds respectively. When the bulb was filled with hydrogen, all other conditions being kept the same as before, the time was reduced to about 5 sec. for temperatures of 116°, 125°, and 132°. It is thus seen that hydrogen can be pumped out about 4 times as fast as air. Gaede says that the limiting value of the vacuum obtainable with the diffusion pump is lower than can be attained by the aid of any pump with mechanically moved parts or even by the method of cocoanut charcoal cooled to  $-180^{\circ}$  C. The only gas or vapor which is not removed by the diffusion pump itself is mercury vapor, and this can be readily and completely condensed by an auxiliary cooling system having a temperature of  $-80^{\circ}$  C. or lower.—Ann. d. Physik, vol. xlvi, p. 357, Feb. 1915. H. S. U.

7. Elektrische Spektralanalyse chemischer Atome ; by J. STARK. Pp. viii, 138, 19 figures, and 4 plates. Leipzig, 1914 (S. Hirzel). -This monograph is the outgrowth of a lecture which was delivered by the author, in February, 1914, at the invitation of the philosophical faculties of the universities of Leiden and Utrecht. The text presents a detailed account of the expermental and theoretical work which has been done by Stark and others on the separation by electric fields of spectral lines, that is, on the so-called electric analogue of the Zeeman effect. More specifically, the successive chapters deal respectively with (a)preliminary investigations, (b) methods of experimentation, (c) dependence upon electric field strength of the distance apart and of the relative intensities of the components of resolved spectral lines, (d) electrical analysis of lines of the same series and of different elements, (e) allied phenomena, such as broadening of lines, pressure shift, etc., (f) theoretical investigations, and (g)bibliography of the subject. Since the monograph has been brought up to date by the inclusion of experimental work which has been done since the delivery of the original lecture and which had not appeared in the scientific journals at the time of publication of the present text, and since the whole subject is presented in a consecutive, unified form by the chief investigator in this special field, the book deserves to be considered as an important contribution to modern scientific literature. It will undoubtedly pave the way for future valuable research in its particular domain.

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8. Advanced Electricity and Magnetism; by WILLIAM S. FRANKLIN and BARRY MACNUTT. Pp. vii, 300, with 217 figures. New York, 1915 (The Macmillan Co.).—In order to avoid the danger of making the study of theoretical physics a purely formal mathematical exercise the authors have laid as much stress as possible on the physical aspect of the subject. The importance which they attach to this fact is emphasized by the following italicized sentence quoted from the preface, namely :—" The character of the treatment in this book has been determined throughout by the desire to keep the student's mind jammed up tight against physical things!" To a fairly large extent, the present volume constitutes a revision of "The Elements of Electricity and Magnetism" by the same authors and publishers (1908).

The text is broadly divided into three Parts, the chapters in the first of these dealing successively with the elementary theory of ferro-magnetism and of electro-magnetism, with induced electromotive force and inductance, with the magnetic properties of iron, and with ship's magnetism and the compensation of the compass. The topics discussed in Part II are, respectively, electric charge and the condenser, theory of the electric field, theory of potential and electric oscillations and electric waves. Part III is coextensive with chapter X, which is entitled "The Electron Theory." 138 problems (with answers) are appended to the several chapters.

The present volume possesses the same desirable features as characterize the earlier text-books by W. S. Franklin and his colleagues (see vol. xxxix, page 314). On the other hand, one error, which has been carried over from the 1913 edition of "The Elements of Electricity and Magnetism," should no longer pass unnoticed. On pages 277, 290, and 296 the ratio of the mass of an electron to the mass of a hydrogen atom is given as "1/800" instead of 1/1830, approximately. H. s. U.

#### II. GEOLOGY AND MINERALOGY.

1. Canada, Department of Mines, (1) Geological Survey Branch; R. W. BROCK, Director: Among the recent publications of the Canadian Geological Survey may be mentioned the following:

Summary Report for the calendar year 1913. Pp. 417; 9 maps. The Twelfth International Congress met at Toronto in August, 1913, and with its numerous extended excursions, absorbed the time of many of the geologists of the Survey, but considerable important work was also done in the field. Some thirty-three individuals and parties are mentioned as having been engaged in investigations in different parts of the Dominion. In addition much was accomplished in the topographical, anthropological and other divisions.

MEMOIRS.—No. 20-E. Gold Fields of Nova Scotia; by W. MALCOLM. Compiled largely from the results of investigations by E. R. FARIBAULT. Pp. 331; 42 pls., 24 figs., 2 maps.

No. 38, Geology of the North American Cordillera at the Forty-ninth Parallel; by REGINALD A. DALY. In three parts. Pp. 1-546, 547-857; with numerous figures, tables, also maps in pocket (Part III.). This important contribution to North American geology will be noticed in a later number. No. 41, The "Fern Ledges": Carboniferous Flora of St.

No. 41, The "Fern Ledges": Carboniferous Flora of St. John, N. B.; by MARIE C. STOPES. Pp. 142; 25 pls. Noticed on p. 219 of the February number.

The Survey is also publishing a series of Museum Bulletins. No. 8 on the Huronian Formations of Timiskaming Region, by W. H. Collins, bears the date of Dec. 28, 1914.

(2) Mines Branch, EUGENE HAANEL, Director: Of numerous publications, the following may be noticed:

Report on the Building and Ornamental Stones of Canada. Vol. III. Province of Quebec; by WM. A. PARKS. Pp. xiv, 304; 52 pls., 12 figs.—The building stones of Quebec, thus far developed, consist largely of excellent limestones, with decorative and structural marbles; also granites, while slate is quarried to a limited extent. The volume is profusely illustrated and the colored plates are of unusual excellence. The same subject is discussed in Vol. I for the province of Ontario, and for the Maritime Provinces in Volume II.

Gypsum in Canada; its occurrence, exploitation, and technology; by L. H. COLE. Pp. x, 256, xi; 30 pls, 27 figs., 6 maps. Gypsum is one of the more important of the mineral products of Canada, and is particularly developed in Nova Scotia, where the beds have in some cases a thickness of 100 feet. The occurrences in New Brunswick are also of importance. The total production in 1913 was valued at nearly \$1,500,000.

A General Summary of the Mineral Production of Canada during the calendar year 1913; by JOHN MCLEISH. Pp. 50. Special publications on the production of iron and steel; coal and coke; lime, clay, and structural materials are given by the same writer. C. T. Cartwright reports on the useful metals. It is to be noted that in 1913 the total value of mineral products was upwards of \$145,600,000, having increased 8 per cent from the previous year, and about three times since 1899. An increase is shown in almost all the metallic and non-metallic products, except in copper, where there was a falling off of about \$1,000,000.

A Preliminary Report for 1914 has also been prepared by Mr. McLeish. The figures here given show the effect of the widespread industrial depression. The total value of products is only \$128,500,000; in metallic products there was a decrease of 11 per cent as compared with 1913 and in non-metallic products a decrease of 12 per cent.

2. State Geological Survey of Illinois. Bulletin No. 28, Oil and Gas in Bond, Macoupin, and Montgomery Counties, Illinois; by RAYMOND S. BLATCHLEY. Pp. 51, pls. I-IV, one fig.—A detailed study of the stratigraphy and structure of a portion of Western Illinois suggests that prospecting for oil and gas may be profitably undertaken in this region. H. E. G.

3. Further Notes on Meteor Crater, Arizona; by D. M. BARRINGER.—A notice of Mr. Barringer's investigations of the remarkable "Meteor Crater" in Coconino county, Arizona, was given in an earlier number of this Journal (vol. xxx, p. 427, 1910). A supplementary paper has recently appeared in the Proceedings of the Academy of Natural Sciences of Philadelphia (1914, pp. 556-565). This is accompanied by three plates, giving a map of the crater, the details of its structure, and the distribution of the meteoric material about it. All the evidence at hand supports the conclusion that the crater owes its origin to an impact of a meteoric mass, probably a dense cluster of iron meteorites and possibly the head of a comet; 10 million tons is given as the minimum estimate of the probable weight of the mass. To explain the fact that explorations thus far made have failed to reveal the presence of a great meteoric mass, it is stated that the drillings have only been carried on in the central portion of the crater. It is now believed that the mass approached from the north at a considerable angle, perhaps as much as 30° from the vertical, and probably "lies under the southern wall of the crater, some two thousand feet from where the drilling was done." It is much to be desired that further and finally conclusive investigations of this interesting subject should be made at the locality.

4. New Meteorites.—A recent paper by Dr. O. C. FARRINGTON gives an account of several new meteorites which have been added to the collection of the Field Museum in Chicago. These may be briefly mentioned as follows : the Ahumada iron, found 60 miles east of Ahumada in the State of Chihuahua, Mexico, in 1909, weight 116 lbs.; the Bishop Canyon iron, weighing 19 lbs., found in 1912 near Bishop Canyon, in San Miguel Co., Colorado; a large iron, weighing 1520 lbs., found in 1903 at the north end of Davis Mountains, Jeff Davis county, Texas. This last iron is remarkable in containing the largest amount of platinum thus far recorded ('03 per cent).—Field Mus. Nat. Hist., Geol. Series, v, No. 1, 1914.

5. Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie. XXXIX Beilage-Band. Festschrift Max Bauer zum seibzigsten Geburtstage gewidment. Unter Redaktion von R. BRAUNS. Pp. 568; with portrait, 32 pls., 47 figs. Stuttgart, 1914.—It is interesting that notwithstanding the conditions existing in Europe it has been found possible to publish and distribute this notable and massive volume. The great services of Professor Bauer are here well and deservedly honored; the table of contents includes twenty-one papers, many of them exhaustive in character, and admirably illustrated by plates and figures.

6. Amethysts in Egypt.—It has been long known that the ancient Egyptians used the amethyst extensively as an ornamental stone. Recently it has been announced that extensive workings have been discovered by G. B. Crookston, near Gebel Abu Diyeiba, where the mineral occurs lining cavities in a kind of red granite. A piece of amethyst had earlier been found by G. W. Murray and C. M. Firth in Wady Bahan in lower Nubia.—Nature, January 21, 1915.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Carnegie Institution of Washington, Year Book No. 13, 1914. Pp. xvi, 399; 7 pls. Washington, 1915.—Some thirteen years have passed since the establishment of the Carnegie Institution in 1902, and of the ten departments to which its funds are being chiefly devoted at the present time, the larger number have been active for about ten years. This fact makes it possible for the President, Dr. R. S. WOODWARD, to review the whole situation and to discuss the special conditions affecting scientific research in general; his conclusions (pp. 16, 17) will be read with profit by all concerned. It is interesting to note that, as in some other similar cases of specially endowed institutions, as that of the Smithsonian Institution, for example, the work being done has appealed to the wider public, and a beginning has been made of special bequests, which may be expected to increase in the future. By the will of Mr. R. T. Colburn, of New York, the American Association for the Advancement of Science and the Carnegie Institution are made residuary legatees, and the bequests are to be devoted "to original research in the physical or psychic demonstrable sciences." The amount of money involved is not stated, but the importance of the movement thus begun is at once obvious.

The past year has been an unfortunate one in the loss of two gentlemen from the Board of Trustees, Dr. S. Weir Mitchell and Mr. John L. Cadwalader, both of whom have been actively devoted to the work of the Institution since its inception. The President pays a fitting tribute to them as also to the late Dr. George W. Hill, an associate in the domain of celestial mechanics. Of the year's funds, some \$818,000 have been devoted to the large projects, \$107,500 to minor projects and research, associates and assistants, \$45,000 to publication, \$44,000 to administration, with also \$862,000 to investments in bonds. The last named increase of the capital is considerably larger than that in any other preceding year. The publications of the year include 23 volumes, aggregating about 5000 octavo and 2000 quarto pages, while twenty-nine additional volumes are in press. A summary of the work of each department is given by the President, and in addition the directors severally present the same subjects in considerable detail. The departments most fully treated are those of Botanical Research, of Experimental Evolution, of Marine Biology, of Terrestrial Magnetism, and also the Geophysical Laboratory and the Mt. Wilson Solar Observatory. Abstracts of reports of recipients of special grants close the volume. The whole matter presented (pp. 63-383) gives an impressive summary of what the Institution has accomplished in 1914.

2. Library of Congress. Report of the Librarian of Congress, HERBERT W. PUTNAM, and Report of the Superintendent of the Library Building and Grounds for the Fiscal Year ending June 30, 1914. Pp. 216; 6 illustrations.—A summary of the contents of the Library of Congress in 1914 shows a total of 2,253,000 books and pamphlets, 142,000 maps and charts, 663,000 volumes and pieces of music, 377,000 prints, and a large number of manuscripts. The accession of books and pamphlets for the year was 125,000, which is a larger total than for any previous year in the history of the Library, except 1909. The most important part of these additions was a second gift of Semitica, 4,200 volumes, presented by Mr. Jacob H. Schiff, to increase the collection given by him in 1912; the library is thus in a very strong position as to Jewish literature. The librarian also notes in detail many other additions of value and considerable interest. He further shows that in order to make the Library thoroughly useful and of benefit to Congress, a corps of experts is called for to give the members promptly information on legislative subjects and specifically as to laws already enacted not only at Washington but also by other jurisdictions, domestic and foreign. It is satisfactory to note that an appropriation of \$25,000 for 1914-15 provides for the employment of "competent persons to prepare such indexes, digests and compilations of law as may be required by Congress."

3. Text-book of Embryology; edited by WALTER HEAPE. Vol. I, Invertebrata, by E. W. MACBRIDE. Pp. XXXII, 692, with 468 figures. London, 1914 (Macmillan and Co.).—This work is not limited to the descriptions of the developmental stages of various groups of animals customary in books on this subject, for the author's aim is so to correlate structure, function, and ancestry as to elucidate the significance of the successive stages through which the different animals pass during the course of their development.

The present volume illustrates the life history of one or more examples of each of the important groups of invertebrates; two additional volumes will be required for the vertebrates.

In order to be of the greatest possible service to the student in Europe and America, those forms which are widely distributed and which can be most easily secured are chosen for description, and for each organism are given the methods by which the material may be prepared for study. The descriptions aim to show the exact state of our present knowledge, and wherever conspicuous gaps occur the author points out the problems that remain unsolved with suggestions as to how they may be attacked. Special emphasis is placed on the general principles which underlie the science of embryology. Experimental work is also given much attention.

This work forms a most important addition to the very few books of its kind, and brings together a vast amount of well assimilated information which would otherwise be available only by the study of a large number of original publications. The advanced student will gain a clear and broad conception of the science, while the investigator can hardly fail to receive an incentive to further productive work.

4. Neue Grundlagen der Logik, Arithmetik und Mengenlehre; von Julius König. Pp. viii, 259. Leipzig, 1914 (Veit & Co.). -The chief work of the scientific life of Julius König was the study of logic and in particular of that highly developed and specialized logic which is necessary for modern mathematical investigations in the theory of sets (Mengenlehre). When he died he left practically complete a book which presented his views and researches and which his son has now seen through the press. The author may fairly be said to hold a mean position between the clean-cut mathematical theorists like Peano, Frege, and Russell, and the psychological investigators like Wundt. His work therefore was not easy and appealing to either mathematician or psychologist. He was a transcendentalist in that he placed confidence in Zermelo's principle of selection (Auswahlsprinzip), which Poincaré and other intuitionalists rejected. The style of the book is such that properly to digest the text would require almost as much work as to write it. E. B. W.

5. United States Coast and Geodetic Survey.—It is announced that Dr. OTTO H. TITTMANN, Superintendent of the U. S. Coast and Geodetic Survey, has retired from office, after forty-eight years of service; also that he will be succeeded by Dr. E. LESTER JONES, now deputy commissioner of fisheries.

6. The Smithsonian Institution.—Dr. WILLIAM H. DALL celebrated on March 6th the completion of fifty years of active, fruitful service in connection with the Smithsonian Institution.

#### OBITUARY.

DR. JAMES GEIKIE, professor emeritus of geology and mineralogy and dean of the faculty of science at the University of Edinburgh, died on March 2 at the age of seventy-six years. His contributions to geological science were numerous and important, particularly in the field of glaciology. He received in recognition of his work many honors in the form of degrees from universities and medals from scientific societies. Among his larger works may be mentioned : The Great Ice Age (1874, 3d edition 1894); Prehistoric Europe (1882); Earth Sculpture (1898); Structure and Field Geology (1898, 3d edition 1912); Mountains, their Origin, Growth and Decay (1913, see vol. xxxvii, p. 561), and Antiquity of Man in Europe (1913, see vol. xxxvii, p. 571).

PROFESSOR G. F. J. ARTHUR AUWERS, the German astronomer, died on January 24 at the age of seventy-six years.

DR. CHARLES EDWIN BESSEY, professor of botany and head dean in the University of Nebraska, died on February 25 in his seventieth year.

LOUIS LINDSAY DYCHE, professor of systematic zoology at the University of Kansas, died on January 20 in his fifty-eighth year.

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#### CONTENTS.

	Page
ART. XXII.—Pleistocene Ground Sloth, Mylodon harlani, from Rock Creek, Texas; by R. S. LULL	327
XXIII.—Simple and Inexpensive Apparatus for Tidal Analysis; by E. W. BROWN, F.R.S.	38 <b>6</b>
XXIV.—Radio-active Content of Certain Minnesota Soils; by J. C. SANDERSON	391
XXV.—Use of Hydrochloric Acid in the Estimation of Cer- tain Forms of Organic Nitrogen; by W. A. DRUSHEL and M. M. BRANDEGEE	398
XXVI.—Supposed Vanadic Acid from Lake Superior is Cop- per Oxide ; by W. T. SCHALLER	404
XXVII.—The System Anorthite-Forsterite-Silica; by O. ANDERSEN	407
XXVIII.—Studies on the Etched Figures of Japanese Quartz; by S. ICHIKAWA. (Plates II to VII)	455
XXIX.—Datolite from North Plainfield, Somerset County, New Jersey; by A. C. HAWKINS	473

#### SCIENTIFIC INTELLIGENCE.

Chemistry and Physics—Production of Chloropierin from Organic Compounds, R. L. DATTA and N. R. CHATTERJEE: Determination of Gasolene Vapor in Air, G. A. BURRELL and A. W. ROBERTSON, 475.—Transmutation of the Chemical Elements, W. P. JORISSEN and J. A. VOLLGRAFF: Chemistry of Cyanogen Compounds, H. E. WILLIAMS: Chemie der hydraulischen Bindmittel, H. KÜHL and W. KNOTHE, 476.—Diffusion of Gases through Mercury Vapor, W. GAEDE. 477.—Elektrische Spektralanalyse chemischer Atome, J. STARK: Advanced Electricity and Magnetism, W. S. FRANKLIN and B. MACNUTT, 480.

Geology and Mineralogy—Canada, Department of Mines, Geological Survey Branch, R. W. BROCK, 481.—State Geological Survey of Illinois: Further Notes on Meteor Crater, Arizona, D. M. BARRINGER, 482.—New Meteorites, O. C. FARRINGTON: Neues Jahrbuch für Mineralogie, etc.; Festschrift Max Bauer zum seibzigsten Geburtstage gewidmet: Amethysts in Egypt, 483.

Miscellaneous Scientific Intelligence.-Carnegie Institution of Washington, Year Book No. 13, 1914: Report of the Librarian of Congress, H. W. PUTNAM, etc.-Text-book of Embryology, W. HEAPE. 485.-Neue Grundlagen der Logik, Arithmetik und Mengenlehre, J. KÖNIG: United States Coast and Geodetic Survey: The Smithsonian Institution, W. H. DALL, 486.

Obituary-J. GEIKIE: G. F. J. A. AUWERS: C. E. BESSEY: L. L. DYCHE, 486.

Librarian U. S. Nat. Museum.

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ART. XXX.—The Formation and Distribution of Fluviatile and Marine Gravels: by HERBERT E. GREGORY.

Outline.

Introduction FLUVIATILE GRAVELS Comparative rates of subaërial and marine erosion Summary analysis of river work Distribution and preservation of river gravel during a single physiographic cycle Distribution and preservation of gravel during interrupted cycles Tectonic interruptions Climatic fluctuations Gravel at river mouths GRAVELS OF MARINE ORIGIN Definitions Physiographic development of a coastal belt Application to the formation and distribution of gravels Distribution and preservation of marine gravel during a single physiographic cycle Initial over-flat profile Initial over-steep profile Evidence from maps Distribution and preservation of marine gravel during interrupted cycles Effect of coastal downwarp Effect of coastal upwarp

Conclusion

#### Introduction.

THE absence of criteria for the interpretation of consolidated and unconsolidated gravels is a particularly serious obstacle to work in the Colorado Plateau Province, where a confusing variety of structure and the extreme scarcity of fossils render the usual means of differentiation of secondary value. During an excursion across the Colorado Plateau in 1900, the import-

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, NO. 233.-MAY, 1915. 32

#### 488 H. E. Gregory—Formation and Distribution of

ance of the problem thus presented was pointed out by Professor Davis,<sup>\*</sup> and at his suggestion an attempt was made to analyze the physiographic features resulting from ocean and river work, in so far as they are related to the deposition of gravel, with the hope that some constant features characterizing conglomerates of various modes of origin might be recognized. Because of the lack of quantitative data obtained from field investigations, the results of this study are unsatisfactory: they have, however, been found useful in field work, in directing increased attention to thickness, extent, and stratigraphic position of beds of gravel and conglomerate, and for this reason the original manuscript has been revised and the conclusion here presented as a contribution to stratigraphy from the viewpoint of physiography.

#### FLUVIATILE GRAVELS.

Although the importance of rivers as agents of erosion and deposition is widely recognized, the methods and results of stream work as conditioned by changing environment have yet to be formulated. The fluviatile deposits which have been studied in detail are too few in number and too exceptional in character to serve as a basis for generalizations founded on induction. Until many streams and typical streams have been examined with reference to habit induced by volume and gradient and load as affected by temperature, precipitation, crustal movements, regolith, bed rock, valley form, and physiographic age, we must be content with an outline sketch drawn largely by the blunt-pointed pen of deduction.

Comparative rates of subaerial and marine erosion.—Even a superficial examination indicates that in preparing and distributing waste, rivers, assisted by the atmosphere, are distinctly more effective than marine agents. A narrow zone of water takes part in marine erosion; the atmosphere reaches all land permanently or temporarily above water. The atmosphere and the rivers may arrange the order in which their work is to be taken up; the sea has little choice. In developing subsequents on less resistant rocks, thus carving inner lowlands as well as reducing highlands, rivers are unimpeded; the sea on the other hand has no opportunity to reach more easily eroded materials except by cutting its way through intervening strata. For the world as a whole, therefore, the estimates of rates of subaerial erosion are many times greater than those for marine erosion.

On the basis of study of the Mississippi drainage basin, subaerial erosion for the United States is placed at 1/4500 of a

\* Davis: An Excursion to the Grand Canyon of the Colorado, Bull. Mus. Comp. Zool., vol. xxxviii, 1901, pp. 107-201.

foot a year, by Reade,\* and 1/3500 of a foot a year by Salisbury.† By using the latter figure, and assuming that the conditions within the Mississippi basin are representative for the 55,000,000 square miles of the earth's lands, 300 cubic miles of land are removed each century by subaerial denudation. The estimate of R. B. Dole, Chemist of the U. S. Geological Survey, that "the surface of the United States is now being removed at the rate of 0.06 cubic miles a year,"<sup>‡</sup> is probably a fair representation of existing conditions, since the estimate is based on a study of all the rivers of the United States. If this rate be applied to the entire earth's surface, the figure becomes in round numbers, 110 cubic miles a century. The estimate of Murray§ is 370 cubic miles a century. The discrepancy between these estimates is to a certain extent the measure of our ignorance of the régime of running water under various conditions. It is obvious that the average rate of removal must include landslides as well as old-age streams whose action in denuding the land is excessively slow, and must include tropic and arctic lands as well as those of the temperate zone. The lack of data for most of the world's rivers gives to all estimates a very low degree of accuracy.

The rate of cliff recession varies with the strength of waves and the nature of the shore. Recession of shore line probably reaches its maximum on the Yorkshire coast of England. At Kilnsea the rate is 12 feet a year, and for 34 miles of coast from Bridlington to the mouth of the Humber 9.75 feet a year, or 975 feet a century. Rates of 300 to 600 feet a century are not uncommon for portions of the English coast exposed to vigorous waves. On the other hand the west coast of England recedes under wave attack probably less than one foot a century and the recession of the world's shore line is probably to be measured by a few feet per century. It is believed that the estimate of 10 feet per century is safely within the average. It is obvious that the rates attained under exceptionally favorable conditions no more represent coast erosion than does the rapid denudation incident to cloudbursts and forest removal represent subaerial erosion. On the other hand it should be borne in mind also that the decreased supply of waste furnished by streams of old-age lands relieves the waves of work in distributing and grinding debris and renders them free to attack the land. If the rate of recession be taken as 10 feet per century, the length of the coast line at 125,000 miles (including

<sup>\*</sup> Presidential Address, Liverpool Geol. Soc., 1884-85.

<sup>+</sup> Physiography, p. 154, 1907.

Personal communication.

t Personal commune S The Ocean, p. 44. Wheeler, The Sea Coast. Geikie, Textbook of Geology, 1903, vol. i, p. 567.

#### 490 H. E. Gregory—Formation and Distribution of

bays in which wave work is negligible), and the height of cliffs at 50 feet (a generous estimate), there will be removed from the coast each century 2.24 cubic miles of material. The contrast between rates of marine and subaerial denudation is well brought out if the lowest estimate for subaerial erosion is compared with the generous estimate of cliff recession. It is thus seen that rivers are approximately fifty times more effective than waves in paring down continents.

The relative proportions of gravel in total marine and fluviatile sediments is an attractive problem awaiting discussion, but there is no reason to believe that at any given time the relative amount along shore exceeds that in valleys on the land, and the figures given above may be taken to indicate that the conditions for the accumulations of gravel for conversion into conglomerate are much less favorable within the coastal belt than over continental areas.

#### Summary Analysis of River Work.

The net tendency of the work of subaerial agents of erosion is to reduce the land surface to a featureless plain. While many essential and conditional factors are involved in peneplanation, for the purpose at hand subaerial erosion may be considered as consisting of weathering and river transportation, the former supplying the waste, the latter distributing it. Rivers, to be sure, furnish their quota of waste by direct corrasion, but as shown by Westgate,\* weathering is an important factor in valley deepening as well as in valley widening. With a constant climate, weathering in comparison with stream corrasion progressively increases throughout a cycle, reaching its maximum in old age.

Since weathering must be relied upon to furnish the supply of gravel, and since both chemical and mechanical phases of weathering are conditioned by climate and rock composition and structure, it follows that the maximum amount of coarse materials is favored by resistant jointed rock in an arid region. On the other hand, where readily decomposed rocks lie on flat surfaces, and chemical activity is facilitated by climate, no gravel may be formed at the surface. Under suitable conditions residual gravel of siliceous materials may accumulate and the regolith may consist of rounded and subangular pebbles and bowlders to a depth of several feet. The origin of such deposits is revealed by the gradation in amount of chemical decomposition from surface to bed rock.

Throughout the larger part of a cycle gravel removal is believed to follow gravel formation without much delay and the products of weathering are furnished to streams to be

\* Journal of Geology, xv, p. 114-122, 1907.

transported and arranged in a manner determined by the resultant effect of all the factors conditioning the work of running water. The method of transportation by suspension need not be considered in the present discussion, for pebbles make their way down stream by saltation, rolling and sliding. For this method of transport, entraînement\* of the French engineers, the basal portion of a stream obviously must be utilized. hence the action of water at the bottom of a current and the nature of the bed of a stream are matters of prime significance. Unfortunately these are features with which we are relatively unfamiliar and which are least susceptible to direct observation. Since, under the influence of a current pebbles advance in large part by saltation, the ability of a stream to transport gravel is fundamentally affected by slope and discharge, two factors whose relations to capacity are, as shown by Gilbert, essentially parallel, with the exception that capacity is slightly more sensitive to changes of slope than to fluctuations in volume.<sup>+</sup> Another significant result of the Berkeley experiments is the demonstration of the fact that fragments of a single size are moved by river currents less freely than mixed debris, and that if fine material be added to coarse, not only is the total load increased but a much greater quantity of coarse material may be carried.<sup>‡</sup>

For a complete analysis of gravel production and gravel distribution, the factors concerned in stream traction which require evaluation are the amount and classification of the load, the discharge, the stream profile, the character of the bottom, and the valley form. The last-named factor includes form ratio as defined by Gilbert,§ and the alignment of the channel. The relative quantitative effects of these various factors as operative in natural streams remains to be determined, but for preliminary physiographic studies only their qualitative influences, conditioned by climate and topographic age, need be considered.

#### DISTRIBUTION AND PRESERVATION OF RIVER GRAVELS DURING A SINGLE PHYSIOGRAPHIC CYCLE.

During the course of a physiographic cycle the landscape passes through a brief period of rapidly increasing relief, followed by a period characterized by strong relief and great variety of form. This stage is followed by a period of relatively rapid decrease in relief, replaced in turn by a very long

+ Gilbert, U. S. Geol. Survey, Prof. Paper 86, pp. 145, 149, 1914.

<sup>\*</sup>The well chosen term "traction" is suggested by Gilbert as an English equivalent of *entraînement*. All hydraulic transportation may thus be classified as suspension and traction.

Loc. cit., p. 11, 184.

SU. S. Geol. Survey, Prof. Paper No. 86, p. 36, 1914.

period during which the relief is increasingly faint. At the beginning of a cycle the features of youth in a landscape may be superposed upon features indicating adolescence, maturity, or old age. But whatever the initial topographic expression, streams of youth start at the long and arduous task of establishing and maintaining grade. If youth follows maturity, gravel is ready at hand; if youth follows old age, gravel must be prepared and furnished to the stream before distribution can be effected. The production of gravel is an accompaniment of vigorous erosion and accordingly its proportion in total land waste is greatest in youth and early maturity. Moreover gravels prepared during youth normally contain a large amount of undecomposed material since rapid down-cutting of channels favors mechanical agents of erosion.

At the beginning of a cycle, the stream finds itself out of adjustment and at once undertakes to remedy this defect. If the initial stream profile is over-flat, grade is established by building steeper slopes beginning at headwaters and, until a profile suitable for carrying gravel with a given volume of water is developed, gravel accumulates in the upper parts of a stream course. If the profile at the beginning of a cycle is oversteep, coarse waste is distributed along the valley to depths required to bridge the concavities and establish grade. If young and mature stages of the stream's history be of long duration, gravel may thus accumulate to great thickness. With fluctuating stream volume in response to seasonal or cyclical flooding, gravels are carried farther and farther down valley. In maturity streams are competent to carry the load furnished; i. e., grade has been established. But probably no stream is in a graded condition throughout its entire course, and the adjusted profile of short stretches changes frequently and at times abruptly. With the continually changing conditions of volume discharge, grade is maintained by shifting the load laterally and distally but with net movement downstream. It is important to bear in mind that pebbles are carried in one direction by rivers, whereas waves and wind transport sediment back and forth. On the gentle slopes of old age the maximum amount of material is carried in solution and gravels are normally absent.

The arrangement of gravel deposits on the stream bed may be observed at stages of low water. As displayed on the floor of certain ephemeral streams on the Navajo Reservation, the masses of gravel are irregular in distribution and yet conform to a poorly defined pattern. For stretches of a few tens, rarely of a few hundreds feet, the entire bed is paved with pebbles or cobbles. More commonly the deposits have the form of henses 10 to 100 feet long, 3 to 20 feet wide, with gentle slope at the upper end and terminating in an abrupt or in a gentle slope downstream. These lenses are roughly parallel with the axis of the immediate valley and are separated by bands of sand or of silt in places underlying shallow pools of water. In addition to the lenticular masses mentioned there is another set of bars which traverse the channel obliquely joining the inner banks of two successive curves. In several places these oblique bars are the only gravel deposits present and the dwindling stream was observed to cross these bars from one pool to another. The pattern woven by these sets of bars is a net stretched in the direction of stream flow. In the meshes of the net are areas of sands and muds of various textures. Between floods the net appears to migrate down stream without substantially altering its pattern. By wading in the stream at flood stage it was found that the position of pool and bar with references to each other was unchanged. One characteristic feature, which I have not observed in sediments of non-fluviatile origin, is the presence of lines of detached pebbles embedded in the sand and arranged like widely-spaced beads on a string. In places an isolated pebble is found resting on sand a foot or more from its nearest companion. In streams with widely fluctuating discharge the pattern of gravel lenses is believed to be maintained and if carried below base level the gravel may be preserved throughout a cycle, and is likely to become consolidated into conglomerate. If stranded above base level these deposits are subject to mutilation or destruction in response to modification of grade induced by tectonic or climatic changes, as is abundantly illustrated by streams of Plateau Province.

When preserved in the sedimentary record inland stream conglomerate deposited during a single cycle lies conformably or unconformably on older deposits. The conglomerate, prevailingly crossbedded, is arranged in long, roughly parallel bands or courses, in the direction of dip or displayed as strands in an interlacing pattern as shown by Johnson.\* Along the strike lenses and belts of conglomerate irregularly alternate with lenses of sandstone. Lenticular deposits of shale and even of peat or lignite may be present since quiet water bodies of small extent are normal features in regions of uneven stream deposition particularly where winds are active. Lenses of conglomerate in roughly parallel or interlaced order a few tens, or at most a few hundreds, of feet wide, and tens or rarely a few hundreds of feet thick, suggest fluviatile origin. Such deposits as shown in section exhibit no regular gradation in coarseness. If the streams are provided with distributaries in the zone of gravel deposition the width of the combined

\*U. S. Geol. Survey, 21st Ann. Rept., 1899-1900.

strands may be tens of miles; and if a group of parallel streams are working under similar conditions the gravels may extend laterally for greater distances. The length of the overlapping and branching gravel lenses will be determined by the net result of all the agents concerned with the transportation and deposition of coarse material.

Observations of modern rivers indicate that gravel in quantity is carried 30 to 40 miles by streams of high gradient and under favorable conditions portions of a gravel bank may be transported a few hundred miles. Thus 60 per cent of a gravel bar examined on the Urubamba River, Peru, consisted of pebbles up to 3 inches in diameter which had been ferried down stream for a distance of 33 miles. Twenty per cent of the pebbles and cobbles in certain bars along Chinli Creek in Arizona have their source 36 miles distant, and scattering pebbles were found 50 miles from their parent ledge. In front of the Rocky Mountains gravel is distributed for distances of 300 miles, and pebbles in the Nile delta "have been riverborne for at least 400 miles."\* Grabau† states that extensive deposits of river gravels in the Triassic of England are found 300 miles from their source and that pebbles of the Pottsville conglomerate have made a journey of 400 miles.

Distribution and Preservation of Gravel during Interrupted Cycles.

Tectonic Interruptions.—Within a single cycle, as discussed above, climate is assumed to be substantially uniform, and the earth's crust stable. The effect of regional or local downwarp or upwarp with constant volume of water is to modify all factors concerned with the distribution and preservation of gravel. In consequence of crustal movement the stream's gradient and consequently carrying power is changed; the area from which gravel is collected may be increased or decreased in size and the area over which gravel is deposited may be modified as to extent and position. Since with general regional uplift streams begin to deepen their valleys and to localize their channels, gravel is left on terraces and on interstream spaces. The thickness of such deposits is obviously some fraction of the amount laid down during the previous cycle. With the development of drainage the removal of these fringing terraces is favored and the gravel stands little chance of preservation. General regional downwarp results in flattening of stream profile since deposition is facilitated on flood plains in the lower portions of rivers while the headward portions of the valleys are still subjected to erosion. On such over-flat profiles gravels tend to

<sup>\*</sup> Wade, Quart. Jour. Geol. Soc., vol. lxvii, 1911. † Principles of Stratigraphy, p. 594.

accumulate along the entire valley and may be brought below base level and thus preserved.

If the downwarp be geosnyclinal in character, accumulations of gravel are favored. The material from the rim of the newly formed basin is readily removed since the increased stream gradient gives added power of traction. The process of deposition may go on indefinitely, since transference of load favors sinking of the floor of the trough, and the rising of the bordering lands. Under such circumstances gravel may accumulate to thicknesses of thousands of feet and will bear variable relations with sands, clays, or adobe forming along the axis of the geosyncline. All such deposits may be carried well below base level and hence may be preserved throughout several cycles of erosion.

Fault valleys, or graben, in which a narrow zone of land is subsiding, furnish conditions for gravel accumulations comparable with geosynclines. If subsidence is long continued, overlapping gravel fans may reach thicknesses of hundreds or even thousands of feet, and in the absence of regional uplift and peneplanation may be preserved for indefinite periods.

*Climatic Fluctuations.*—Changes in climate by modifying discharge affect stream gradients and hence gravel deposition in much the same manner as tectonic movements. Change from a humid climate to an arid may result in the formation of gravel deposits comparable to terraces incident to upwarp. Decreased supply of water finds the grade of streams formed under humid conditions too flat and gravel accordingly accumulates near headwaters. Change of climate from arid to humid produces opposite effects, for in such a case stream gradients are found steeper than necessary for the effective transportation of load; gravels may be removed from headwaters and the filling of concavities along stream may proceed at rapid rates. So far as cyclical fluctuations in temperature are concerned a change from temperate conditions to extremes of heat or of cold tends to hasten the formation of gravel, and, as shown by Barrell,\* oscillations toward cold favor transportation of coarser materials.

As regards the place of deposition of the coarser materials, particularly along stream courses, the working rule that pebbles increase in size and degree of angularity toward their source is subject to important exceptions. In fact, the only conditions under which this hypothesis is wholly applicable are equable climate, perennial streams, and the early stages of an uninterrupted physiographic cycle. If the present arid climate of the Plateau Province became humid, with evenly distributed rainfall and perennial streams, the gravels abundantly

\*Jour. Geol., xvi, p. 381, 1908.

#### 496 H. E. Gregory—Formation and Distribution of

strewn along the present stream channels would probably be rapidly eroded or swept entirely away into the master stream. The supply of waste, on the other hand, would probably decrease in amount because of the newly developed cover of vegetation and the decrease in concentration of runoff resulting from desert showers. Decrease in amount and increase in fineness of waste furnished at the headwaters would result also in an increasing ability of streams to erode their beds and grind up bowlders. The area of deposition of coarsest material would, therefore, probably not be nearest the source of supply but would be followed, upstream, by deposits of waste distinctly finer in texture. An upwarp which steepens grade might produce the same result.

#### Gravel at River Mouths.

The interstratifications of river gravels with marine sediments is not a normal relation. Gravels are prevailingly associated with young or mature topography and the seaward reaches of streams, especially those of large size, are characterized by fine waste. Deltas of rivers, therefore, may contain no gravels resulting from erosion within a single cycle. The inauguration of a new cycle as the result of climatic or tectonic changes may produce, at river mouths, a stratigraphic series, the origin of whose various members may not be definitely determined on the basis of published field study.

In this connection the deltas of vanished lakes are worthy of consideration. In cases which have come under my observation the deposition of gravels over finer lake muds appears to be a normal feature of river work conditioned by crustal upwarp or its equivalent in climatic change. By analogy it follows that conglomerate overlying marine sandstones and shales may be of fluviatile origin.

In a section of an abandoned lake bed in Kayenta Valley, Arizona, a stratum of gravel is embedded in lacustrine deposits, which suggests that fine-grained marine sediments may both overlie and underlie conglomerate of continental origin. Likewise if the finer-grained beds in a series of shale, sandstone and conglomerate show evidence of fluviatile origin, there is little reason to assume that the conglomerate has a different mode of origin. Fans of steep gradient immediately at the lake shore, whose building is conditioned by fluctuating stream discharge and changing lake level, would be expected to show various combinations of coarse and fine strata, both of lacustrine and fluviatile origin. The same conditions doubtless exist on certain marine deltas.

#### GRAVELS OF MARINE ORIGIN.

Definitions .--- For the sake of uniformity in the discussion of coastal physiography it seems advisable to retain the terms suggested by Gulliver.\* viz: Shore line is the line of intersection of sea and land, the region landward of the shore line is the coast, and the region seaward of this line is the shore.+ *Coastal belt* is the zone formed of coast, shore line and shore. Wave base is the controlling plane of marine levelling-a mathematical plane toward which the mature profile of marine denudation tends but does not reach. The submarine platform (or subaqueous shore terrace, or plain of marine denudation) bears the same relation to wave base that a peneplain does to river base level. *Initial* is a technical term defining the form at the beginning of a physiographic cycle. Forms developed at later stages are sequential. The term shifting is used in the present paper for change in position of a shore line resulting from crustal movements, recession for the change in position due to wave cutting, and *migration* for the total movement of the shore line regardless of causes.

#### Physiographic Development of a Coastal Belt.

The formation, distribution, and preservation of marine gravels are controlled by marine currents conditioned by rock structure and physiographic age. A brief analysis of marine action within a coastal belt may therefore serve as an aid in the interpretation of conglomerates.

The net result of the combined work of waves and currents is to establish maturity of outline within the two zones which comprise the coastal belt, namely the coast and the shore. Maturity of outline of the *coast* is attained when erosion, transportation and deposition are so adjusted with reference to each other that all portions of the shore retreat at equal rates; that the landward migration of the shore line in areas of resistant materials is the same as for the less resistant portions of the coast. Under these conditions the shore line tends to straightness and retains that quality so long as sea level remains constant. Development of the coastal contour of continents cannot proceed further so long as any land remains above sea level. On many small islands, however, landward migration of the shore line has continued until all land has been consumed. In such cases a mature coast is succeeded by no coast; land

<sup>\*</sup> Shore line Topography, Proc. Am. Acad. Arts and Sciences, vol. xxxiv, p. 152, 1899.

<sup>&</sup>lt;sup>1</sup> † This use of the term "shore" is obviously technical. The common practice is to consider the "shore" as part of the land. Satisfactory discriminating terms are needed for the loosely used words "coast," "shore," and "strand,"

becomes a shoal without the intervention of significant old-age forms other than the "flying bars."

The profile of the shore also advances to maturity as the result of normal shore erosion, transportation and deposition within a single cycle. Shore maturity is usually reached after coastal maturity has been attained, and in fact is made possible in large part by the establishment of coastal maturity, for the simplification of the coast line by cutting off headlands and building bay bars is to be considered not as a phase of the contest between sea and land as is frequently stated, but rather as a stage in the process of development of shore equilibrium. Like the coast contour, the shore profile does not advance past maturity on continental borders where land remains unconsumed; but on shoals representing former islands, old age may be attained and the surface of the underwater land may continuously progress toward wave base. The normal shore profile both on cutting and building coasts "is a compound curve which is concave near the shore, passing through a line of little or no curvature to a convex front." \* The attainment of this profile of equilibrium is accomplished only after the expenditure of an enormous amount of energy on a complicated piece of work, but the advantages are correspondingly great, for in consequence of previous establishment of coast maturity the coast is now openly exposed to the attack of the waves for long stretches of straightened shore line and wave energy may now be concentrated within the zone where it is most effective. The position of the profile changes with the migration of the shore line; with constant sea level it moves landward. The form of the profile appears to remain constant, but its relative dimensions change in response to the type of initial coastal belt, wave power, and mass of materials provided for transportation.

Steepness and regularity of slope are factors which affect the distances to which materials may be carried, for waves tend to establish conditions where their greatest abrasive energy is concentrated along a narrow belt, the breaker line, and where the profile is of such steepness as to allow for ready seaward transportation of materials provided. An initially over-steep slope retards wave action in carrying material seaward, for the materials worn from cliffs are deposited near the shore line until the profile is placed in adjustment. An initially over-flat profile likewise retards coast erosion, for under such conditions the locus of wave attack is some distance off shore, and before the waves may reach the coast a notch must be cut on the bottom, and a bar, or a series of bars, as the waves again and again rerecover their form, be thrown up. The net result is that much

\* Fenneman, Jour. Geol., x, p. 27, 1902.

material and particularly the coarser stuff is carried landward, thus defeating the object of wave attack. The highest efficiency is reached when a profile of equilibrium adjusted to the strength of the waves of a given shore is established; for under these conditions materials of all grades of coarseness may be carried the maximum distance.

The shape of the shore profile of maturity is directly related to the force of waves. Fenneman has shown<sup>\*</sup> that "there is a certain minimum slope for the bottom upon which the waves may be propagated as a shallow water wave" and "a certain maximum slope for the bottom upon which the wave may be propagated without breaking." Wind acting on waves tends to diminish both the minimum and maximum slope required for normal swells. At and coastward of the line of breakers the work of a normal wave of oscillation (waves of the second order) may be modified or entirely counteracted by water movements of various sorts, primarily waves of translation, undertow, and long shore currents. Waves of translation, or waves of the first order, move toward the shore line both at bottom and surface and transport materials landward, not backward and forward as in the case of waves of the second order.

The effect of the undertow associated with waves is to carry water and sediments seaward and thus offset the work of waves of translation. In the contest between these two sets of forces the waves under average conditions are more effective since their activity is concentrated within a short time, whereas the work of the undertow is more evenly distributed in time. The result of these opposing agencies is to carry materials back and forth over a narrow zone with a net tendency landward. Fenneman‡ calls attention to an exceptional type of returning bottom current, that developed in bays where water has been heaped by wind-made or wave-made long shore currents. The current developed under such conditions is regular and powerful and may carry sediments or even erode below the point of maximum wave agitation. Thus in Lake Michigan, where waves disturb the bottom to depths of 60-70 feet, "a sandcovered or gravel-covered bottom concave upward extends outward to several times this depth with little or no evidence of change of slope at wave base." A similar case is cited from

\* Jour. Geol., x, p. 17, 1902.

<sup>+</sup> This view of the relation waves of the first order bear to those of the second order as presented by Russell, Trans. British Assoc., 1837, is discussed by Hunt (Se. Proc. Roy. Dublin Soc., vol. iv, pp. 251-254, 1883-85), who reaches an opposite conclusion: that there is "no evidence that a wave of oscillation is transformed into a wave of translation on passing into shallow water."

<sup>‡</sup> Journal of Geology, vol. x, pp. 31-32, 1902.

§Loc. cit., p. 31.

#### 500 H. E. Gregory—Formation and Distribution of

Lake Mendota and examples along sea shores might be mentioned.

Long shore currents, which coöperate with waves and undertow, travel in one direction or another in response to wind. The incoherent materials of the coastal belt are accordingly ferried to and fro or deposited in bays or on the lee sides of headlands. If winds of equal strength blow alternately in opposite directions the shore materials may be continually in transport. If winds are of unequal strength, materials make their way in one direction since the weaker currents are unable to return shore debris, particularly that of coarse texture, brought by the stronger current. Materials deposited by currents are thus distributed irregularly but in all cases near the shore line. When waves are present with currents "shingle must go with the wave, sand must go with the strongest current."\* Coarse and fine material may thus move in opposite directions.

The shape of the profile of shore maturity is significantly modified by the load furnished from the coast; in fact, the development of the normal compound curve of equilibrium involves the deposition, transport and sorting of the coastal load. In the absence of a renewed supply of sediment the shore profile of maturity would be a steep descent from shore line to the outer limit of effective work of the undertow, continued outward as a gentle slope.<sup>+</sup> When sediment is supplied deposition will take place at the base of the steep descent leading down from the shore line until a grade suitable for transportation of material is established and the debris is carried seaward ending on a slope with convex front. A concavity in the profile is now formed at the junction of the plain of deposition with the plain leading landward over which material is transported. The resultant profile is the curve of equilibrium. With deficient initial slope of subaqueous profile, barriers may be built, thus steepening the profile. In both these ways the shape of the normal curve may be modified. The outer limit of the convex portion, of the curve and hence the width of the shore belt of combined erosion and deposition is determined by the distance to which materials are ferried seaward by the forces acting along a given coastal belt. For the Atlantic coast of the United States Fenneman has shown that the depth to which the *whole load* can be carried is 50 or 60 fathoms; that is, 40 to 80 miles from shore; and at 100 fathoms or less nothing can be carried except in suspension. It is obvious that the coarse materials may be transported for but a fraction of this depth and distance.

\* Hunt, loc. cit., p. 282.

+ Fenneman, loc. cit., p. 26.

Application to the Formation and Distribution of Gravels.

On an excursion to Marblehead and Nahant in 1898 my attention was called to the tendency of sediments, particularly those of coarse texture, to remain near shore. Observation of shores of New England, California, North Carolina, and Peru have produced a sympathetic attitude toward the erroneous view of Rear Admiral Davis that the sea "rejects or repels" the debris of continents.\* While this statement is obviously an exaggerated figure of speech, the coastward urging of coarse materials during the process of coast erosion, has, to my mind, been too little emphasized in texts for students' use. Without taking an extreme view, it follows from the above summary analysis of the development of coast contour and shore profile, that clastic marine deposits laid down during a single physiographic cycle have no great extent or thickness, and that their limits may be roughly calculated. If the coarser materials, gravel and cobbles, are alone considered, the belt of marine and lacustrine sedimentation is narrowed to a degree not generally recognized. If we could determine the thickness and extent of marine gravel deposits laid down under average conditions upon various types of shore and at different stages in their physiographic history, a useful criterion for the recognition of ancient conglomerates would be established. This I believe may be done with a fair degree of approximation on the basis of the physiographic studies outlined above.

#### Distribution and Preservation of Gravel during a Single Physiographic Cycle.

Whatever the initial topographic expression of a coastal belt, the coast contour and the shore profile experience a series of changes leading from youth through adolescence to maturity following a defined order. The nature and amount of the work to be performed within a cycle and the time required to reach maturity depends upon the initial form, the strength of the ocean forces and the composition and structure of the coast. Gravel is supplied from stream sediments, from older coast gravels or from wave-beaten cliffs, and in the absence of supplies from these sources the sea may expend its power for long periods upon fine stuff alone. In general, however, youth is the time of maximum erosion and maximum deposition for all classes of material. Two types of shore may be distinguished : over-flat, and over-steep initial profiles.

Initial over-flat profile.—If the initial shore profile is too flat for the most effective wave work, a nip is cut in the sub-

 $\ast$  Quoted by Mitchell, U. S. Coast and Geodetic Survey, 1869, Appendix 5, p. 85.

#### 502 H. E. Gregory—Formation and Distribution of

aqueous platform and a barrier beach thrown up. After recovering their form, waves of translation urge material coastward from the barrier, and the barrier itself aids in preventing the return of coarse sediments. The maximum width of gravel is, therefore, found in youth when barriers of no great thickness are farthest off shore, the gravel being confined to the zone between the breaker line and the shore line. As the cycle advances and the barrier progresses landward the zone of gravel is narrowed, and the pebbles are continuously ground to sand. During adolescence, when the barrier is pressed close to shore and currents and tides and oblique waves express their activity in bay bars, spits, tombolos, cuspate forelands and winged beheadlands, gravel in decreasing amounts is kept progressively nearer the shore. At maturity gravel may be absent except at points of origin, for effective shore work in maturity requires that gravel be limited to such amounts as can be ground up by waves and ferried away by currents.

If the above analysis holds for the normal coastal belt it follows that youthful forms on an over-flat profile, if preserved in the sedimentary record, would be represented by a belt of sediment which may include conglomerate, a few miles at most in width and a few tens of feet thick, rather sharply limited seaward and interbedded landward with bands of various materials brought to the coast by streams. If adolescent features were preserved along the ancient shore, the bulk of the coastal gravels would be represented by a band, a few hundred (or at most a few thousand) feet in width and a few tens of feet thick, of crossbedded conglomerates and sandstone unevenly distributed and showing great variation in texture vertically, transversely, and longitudinally. In exceptional cases where strong off-shore bottom currents are initiated by excess of water piled in bays, gravel may be carried to depths beyond the reach of waves and thus preserved. These exceptional accumulations are doubtless small in extent and thickness. If mature features were preserved in the sedimentary record, a narrow band of conglomerate with water-worn pebbles on one side and unassorted debris on the other may mark the plane of unconformity.

It is believed that all flat subaqueous profiles favor landward transportation of coarse sediments. Observations of a group of pebbles on the Long Island Shore and of another on Lake Whitney, near New Haven, showed that in the course of a year about 40 per cent of the fragments had moved landward and none seaward. These experiments were abandoned because of the impractibility of evaluating the effect of ice work. On a reservoir at Tuba, Arizona, of 26 pebbles 1/4 to 1 inch in diameter, in a position unaffected by ice, 19 were found to have moved coastward 1 to 5 inches, 5 had not moved, 2 had gone farther into the lake, during the lapse of four years. Hunt observed that shingle is traveling toward the head of the shallow Lyme Bay.\*

Initial over-steep profile.—If an over-steep shore profile is presented to waves at the beginning of a physiographic cycle, the conditions are favorable for the accumulation of thick but narrow bands of gravel and also of thin bands of greater extent. In early youth of the cycle the wave-cut nip and the wavebuilt barrier, if present, are near the coast. If the initial steepness is such as to preclude the building of a barrier the breaker line may be immediately at shore line. Longshore drift may be negligible at the beginning of the cycle and the materials worn from the upper portion of the cliff may be deposited directly at cliff base. The thickness of the gravel deposited under such circumstances is limited only by the depth of the water. An examination of coast charts indicates that the bases of few if any sea cliffs are submerged in more than 50 feet of water. If, in order to include doubtful examples, this figure be increased to 100 feet the outside limit of thickness of gravel deposited during a single cycle is believed to be indicated. As the cycle advances, a rock platform is developed at first by building and cutting, later chiefly by cutting. Before the profile of maturity is established a platform must be built to a point where grade adjusted to the waves and debris of a particular coast is established. It is conceivable that in certain cases all gravel may be worn to sand before being carried beyond the edge of the wave-cut bench. Recession of the cliff involves the continuous attrition of the materials on the platform, as well as the abrasion of the rock platform itself; otherwise the attack of the waves on the coast is greatly decreased in vigor. Since the newly-cut platform is likely to be of gentler slope than the outer portion of the profile, the coarse debris tends to remain on the shelf rather than to be transported seaward. During adolescence the shore line migrates landward, the coastward portion of the profile is already too gentle for the most effective seaward transportation of debris, but the conditions are favorable for the attrition of pebbles and their landward transportation. When maturity is attained and the profile becomes adjusted to the waves and currents, a thin sheet of gravel may be deposited over the upper concave portion of the slope, but with a net tendency coastward. The gravels deposited in youth may be buried by later, finer deposits as the shore line advances toward the land.

Evidence from maps.--As a check on the above conclusions that gravel is deposited within a few miles of the shore line

\* Loc. cit., p. 283.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 233.—May, 1915. 33 and in relatively shallow water, the distribution of gravel along existing shores may be examined following the list based on age and initial form, as given by Gulliver.

#### Initial Profile Over-flat.

1. Youth.—On the Argentine shore at Bahia Camarones, gravel is charted in 23 fathoms of water at distances of 4 to 8 miles from shore.

2. Adolescence.—On the south shore of Long Island gravel is indicated on the Hydrographic Charts at depths of 15 and 13 fathoms at a distance from the shore line of about 10 miles and at points nearer the coast. Off the New Jersey coast at Barnegat, gravel is charted  $9\frac{1}{2}$  miles from the shore in 15 fathoms of water, and at Cape Henlopen, 13 miles from shore at a depth of 17 fathoms.

3. Maturity.—The material on the shore adjoining the west coast of France is indicated as prevailingly sand, but gravel is indicated off the mouth of the Loire in 26 fathoms of water. The character of sea bottom is not shown on the maps of eastern Italy examined.

#### Initial Profile Over-steep.

1. Youth.—On the California shore, off San Pedro Point, gravel is found in 15 fathoms of water at a distance of less than 2 miles from the water's edge. Off the coast of Southwest Ireland sand covers the bottom except at the immediate shore line. Gravel in 60 fathoms of water at one point off Loop Head is interpreted as belonging to a previous cycle.

2. Adolescence.—On the Pacific coast of Lower California, the outermost gravel is shown off Lagoon Head Anchorage, 41 miles from shore, at a depth of 20 fathoms; between Playa Maria Bay and Rosalia Point no gravel is indicated beyond depths of 28 fathoms, and 4 miles from shore. On the Baltic shore of Germany gravel is indicated at depths of 30 fathoms and less.

3. Maturity.—On the Italian shore near Leghorn, no gravel is shown beyond a depth of 7 fathoms; between Brindisi and Ortona gravel is found inside the 30-fathom contour and one mile from the shore line.

The facts deduced from these shore profiles are not in themselves conclusive, since "gravel" is not a definitive term, and also because soundings have obviously not been made for the benefit of physiographers. Moreover, probably all these shores have experienced more than one physiographic cycle. The measurements, however, indicate that gravel derived from existing coasts is rarely found in more than 20 to 30 fathoms of water, and they gain added significance from the fact that they are in harmony with results of exhaustive studies on the English coast, where wave and current work attain maximum proportions.

Austen\* concludes that "the moving power of the sea at 60 fathoms is limited to fine sand" and that gravels below this depth date from previous cycles. This author also remarks that "no abrasion has been effected over ledges (in the English Channel] under depths of not more than 17 fathoms." Cornish+ states "I reckon that they [the waves from the English Channel) would move shingle at 10 fathoms, hardly at all at 20 fathoms, and probably not at 30 fathoms." The researches of Douglas, Stevenson, Winder and other harbor engineers; indicate that 30 fathoms is about the depth of effective movement of shingle even by heavy swells. That the bed of the English Channel is not traversed by violent currents of translation of any sort is indicated by the unworn state of flints and other pebbles and by the presence of an extensive fauna. If the figures for the English coast be considered as representing the average, 30 fathoms may be taken as the depth to which gravel under normal conditions may be deposited during a single physiographic cycle. The distance from the shore line at which this depth is attained in selected localities is as follows: San Pedro Point, California, S miles; Rosalia Point, Lower California, 3 miles; Atlantic City, New Jersey, 30 miles; Shinnecock Bay, Long Island, 30 miles; Argentine coast, 40 to 70 miles; southwest Ireland, 1 to 3 miles; northeast Ireland, 10 miles; east Scotland, 12 miles; western Italy, 1 to 10 miles; Finland, 30 miles. On those shores where the 30-fathom contour is more than 20 miles distant from the shore line gravel is rarely indicated at that depth; in most cases the outermost gravel is shown less than 10 miles from the coast.

On the basis of data available it appears therefore that gravel deposited during a single physiographic cycle is limited to a narrow zone, probably not exceeding 15 miles in widtha statement in harmony with the conclusions derived from the analysis of marine erosion. Moreover, the proportion of gravel to finer sediments in this belt of 15 miles is not necessarily large, since the coarse materials are not continuous. As preserved in the sedimentary record, a stratum of marine conglomerate exceeding 15 miles in breadth and 100 feet in thickness would be anomalous. As compared with marine action vigorous streams may carry gravel during a single cycle 3 to 300 times farther and distribute it much more widely.

If the above analyses properly represent the methods of river and ocean work, it follows that inland fluviatile gravels

\* Quar. Jour. Geol. Soc., vi, pp. 69-97, 1850.
† Geog. Jour., xi, p. 541, 1898.
‡ Discussed by Hunt, loc. cit., p. 285.

#### 506 H. E. Gregory—Formation and Distribution of

and their ancient representatives, the conglomerates, are in general much thicker and many times greater in extent than are those of marine origin. To a greater degree than streams, the tendency of marine agents during a cycle with constant sea level is to destroy rather than to accumulate and preserve gravel.

#### DISTRIBUTION AND PRESERVATION OF MARINE GRAVELS DURING INTERRUPTED CYCLES.

Effect of Coastal Downwarp.—Coastal downwarp or its equivalent, the rise of sea level, introduces a new physiographic cycle. The work of the waves and currents is put out of adjustment with the coastal contour and the shore profile. Unless the crustal warping were abnormally localized it includes wide subaerial areas and increasing amounts of land are brought within range of the destructive work of the sea. Conditions are favorable for marine planation at rates depending upon the nature of the initial coastal belt and the efficiency of waves in eroding the cliffs. Because of the amount of material to be removed planation is favored by an initial coast which has attained old age and consequently possesses slight relief; while a rugged coast of mature topography is unfavorable for coastal migration of the shore line.

Since the depression of a coast does not materially modify the force of waves, the conditions affecting deposition are directly related to the degree of adjustment of the former shore profile to the supply and transportation of coastal material at the beginning of the cycle initiated by downwarp. If the profile is over-steep it must be reduced by filling; if over-flat, it is cut by waves and bars are developed. With a coastward migrating shore line the section of the compound curve of shore maturity most directly concerned is that part between the outer edge of the concave portion and the shore line; for this is the part of the underwater slope over which gravel is normally deposited. The depth at which the concave curve merges with the plane of deposition is, as shown by Fenneman, 10 or 12 fathoms on the Atlantic shores and 20 to 30 fathoms on the Pacific shores of the United States.

So far as the thickness of gravel deposits is concerned the conditions associated with downwarp are essentially like those in a cycle marked by an initial over-steep shore profile. As in other cases, the work of the waves at any stage of downwarping is between the breaker line and the shore line; but waves during subsidence are effective at continuously higher levels and the gravel of successive submerged beaches may be preserved as a mantle covering the continu-
ously expanding platform. The thickness and width of the gravel deposit, as well as its final place of deposit, varies with the stage reached in the cycle. Gravel below the depth of wave agitation at the beginning of a cycle may be indefinitely preserved. Gravels formed in youth will constitute a thick but narrow vertical wedge comparable to the accumulation of talus and further distinguished by the unworn character of its materials. The deposits of maturity will be thin and limited in extent to the area of the platform.

If this analysis is correct, the evidence of a rising sea preserved in the sedimentary record will be an unconformity between older rock and marine sediments. Conglomerate may be absent, but in most cases a basal conglomerate passing down dip slopes into sandstone and overlain by finer marine sediments will mark the ancient shore. The conglomerate may form a narrow thick band or a widespread sheet of variable thickness.

As regards maximum thickness the conclusion of Barrell is affirmed : "marine conglomerates, except under local and exceptional circumstances, [are] limited to considerably less than 100 feet."\*

Effect of Coastal Upwarp.—Upwarp of a coastal belt or its equivalent, a sinking sea level, gives to the coast a simple contour with swinging curves whose shape is determined by the original inequalities of the shore. The new shore profile presented to the waves is in general over-flat. Under these conditions the forces of the sea tend to crowd gravel landward, and if no other agents were at work a series of abandoned gravel or sand beaches would mark the retreat of the water. The depth of the stranded marine gravel obviously equals the thickness of deposits on the beach slope. In the youth of the newly inaugurated cycle, particularly if the sea level sinks rapidly and intermittently, beaches may be preserved and notches cut by waves may be present as terrace fronts. The new-born subaerial landscape would therefore be characterized by ridges of gravel and well-marked steps or terraces in approximate parallelism to the shore line and at a high angle to general surface slope. In the absence of subaerial erosion and deposition the land surface would be veneered with a superficial sheet of marine gravels of great durability because highly porous and composed of resistant materials. On most coasts, however, rivers are at work and their extension over the exposed shore results in the redistribution of beach material and the accumulation of land sediments. The abandoned shore becomes a coastal plain,—a youthful landscape on which, if the climate be humid, streams and lakes and later swamps will de-

\* Bull. Geol. Soc. Am., 1908, p. 620, abstract.

## 508 H. E. Gregory—Fluviatile and Marine Gravel.

velop. If the climate be arid, streams of fluctuating discharge score the slopes and construct terraces among which dunes may be found as illustrated by the coast of Peru. The stranded gravels may be destroyed by a readvance of the sea or dissected by streams or preserved by burial under delta or river deposits.

When preserved in the sedimentary record the evidence of a receding sea is a widespread stratum composed of lenses of conglomerate usually much less than 100 feet in thickness underlying, with marked uniformity, fluviatile deposits frequently coarser in texture. Within the conglomerate, lacustrine shales and peat or coal and evidences of æolian action may be preserved.

This analysis of gravel deposition conditioned by coastal upwarp is readily checked by an examination of existing coastal plains, of which Patagonia is a typical example. As interpreted by Hatcher,\* the coastal plain of Patagonia extends from the base of the Andes to the sea and is covered by the "Shingle Formation," with an average thickness of 30 feet. The marine gravels consist throughout of a heterogeneous mass of waterworn stones with but a slight admixture of sand and clay and unconformably overlie the Cape Fairweather beds of marine origin. The ancient beaches and sea cliffs are in places still preserved.

#### Conclusion.

There are doubtless more gravel and bowlders strewn over the surface at present than at any time in the earth's history. Youthful and mature landscapes are common, old age forms are rare. Vigorous waves and rivers are supplying gravel in maximum amounts, and the extensive coarse deposits from Pleistocene and recent glaciers are still in place. Of the gravel now in process of deposition by far the greater amount is furnished by the continental agents, rivers and glaciers. Marine erosion yields relatively little. The proportional efficiency of these agencies was doubtless not essentially different at any previous geological period. Thickness and extent and position of gravels and of conglomerate are therefore factors of much significance not only for the reading of the life history of existing rivers and coast lines but also for the interpretative description of ancient landscapes.

Yale University, New Haven, Conn., December, 1914.

\* Princeton Univ. Exped. to Patagonia, vol. i, p. 221, 1903.

# ART. XXXI.—A Coal Measures Amphibian with an Osseous Tarsus; by Roy L. Moodie.

THERE are known at present eighty-eight species of Amphibia from the Coal Measures of North America, representing seventeen families and five orders. These forms were already highly specialized and diversified into distinct geographic groups, the members of which are not generically related. This wide diversity of structure among the earliest known faunas of air-breathing vertebrates is intensified by the fact that one species of this number has an osseous tarsus; which, in other forms, was apparently hyaline cartilage and left no impress of its structure in the rock or coal. A species, therefore, showing such an anomalous condition is well worthy of special consideration, and it is proposed in this place to give an account of the "oldest known" amphibian tarsus\*, and to add what little is to be known of the anatomy of the vertebrate possessing this highly unusual foot.

The only known specimen of this anomalous amphibian is incomplete, representing the posterior half of the skeleton and an abundance of ventral scutellæ or calcified myocommata. The block of coal containing these interesting remains is from Linton, Ohio, and is preserved in the geological collections of Columbia University, from which institution Professor Grabau has very courteously forwarded it for study.

Ichthycanthus platypus was described by Copet from the Linton, Ohio, Coal Measures; locating it doubtfully in the Permian genus Eryops, on account of the unusual condition of the tarsus and reconsidering a former decision in favor of a Coal Measures genus, Ichthycanthus.<sup>‡</sup> In this disposition of the species into the Permian genus he is followed by Hays; but Baur regarded the form as a member of the Coal Measures genus, Ichthycanthus, after commenting on the later definition by Cope (†). The type of the genus Ichthycanthus, to which Cope (‡) first allied the species under consideration, is I. ohiensis, a supposed amphibian from the Coal Measures of Linton, Ohio, founded on incomplete material. There is no relationship indicated between *Ichthycanthus* and the species

\* Baur, George: Amer. Natl., 1886, p. 173; Zool. Anz., No. 216, 1886. At this time Archegosaurus was the earliest known amphibian form having an osseous tarsus.

a osecus tarsas.
† Cope, E. D., Trans. Amer. Phil. Soc., 1888, p. 289, fig. 1.
‡ Cope, E. D., Proc. Amer. Phil. Soc., 1877, p. 574.
§ Hay, O. P., Cat. Fossil Vert., Bull. U. S. G. S., No. 179.
# Baur, George : Beiträge zur Morphogenie des Carpus und Tarsus der Vertebraten, Th. I, p. 16. Jena (G. Fischer), 1888.

R. L. Moodie—Coal Measures Amphibian.

of Eryops; in fact, it is not possible to find on the specimen all the characters indicated in Cope's figure († p. 509, fig. 1) on the basis of which he proposed to place the species in the Permian genus.

The majority of the American Coal Measures Amphibia were small and the form under consideration is no exception. The

FIG. 1.



FIG. 1. Left leg and pelvis of *Eosauravus copei* Williston, from the Coal Measures of Ohio. x 1.

Original preserved in the United States National Museum.

animal when alive probably did not measure over eight inches in total length, and the structures, which are preserved in the block of coal fortunately rescued from the coal mine dump, indicate a very active habit of life, recalling the lizards of the present day. The femora are strikingly reptilian in appearance, as are also the ungual phalanges. The form combines in an unusual and remarkable degree reptilian and amphibian characteristics. The leg bones, the pelvis, the tarsus are all strikingly reptilian, but the phalanges in their arrangement of elements is so typically amphibian that if we had no other means of diagnosis we would incline to locate this Coal Measures species among the Amphibia. The leg recalls in its structure that of another Coal Measures species, Eosauravus copei Williston,\* which is, however, clearly a reptile (fig. 1). While there is a general degree of similarity between the foot structure of *Eosauravus copei* and Ichthycanthus platypus, yet there are very great differences in the phalan-

geal formula and the arrangement of the tarsal elements. These differences are clear, and indicate a separation of the species into distinct classes. The phalangeal formula in the *Eosauravus* 2-3-4-5-4, is typically reptilian; while in the *Ichthycanthus*, 2-2-3-3-3 it is amphibian. The tarsus of the *Ichthycanthus* is amphibian in the presence of an intermedium, but this is very small and the remaining tarsal structures have nothing which might not be found in an early reptile. There may be a single or even two centralia in the reptilian tarsus among the early forms.

The amphibian nature of the species having thus been established, it remains to give a detailed account of its skeletal

\*Williston, S. W., Journ. Geol., xvi, p. 295, figs. 1-2, 1908.

anatomy, with comparative references to such other ancient forms as are available. Little can be said of the vertebral column since only the molds of a few vertebræ remain, and these are so obscured by a closely adherent pellicle of carbonaceous material that their form cannot be distinctly discerned. They are high with relatively broad neural spines. There are no ribs preserved. The *pelvis* is obscured, but it is possible to

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FIG. 2. Left leg and pelvis of *Ichthycanthus platypus* Cope, from the Coal Measures of Ohio.  $\times 1.5$ . Original the property of the Department of Geology of Columbia University.

c= centrale; F= fibula; fi= fibulare; Fe= femur; i= intermedium; Il= ilium; T= tibia: t. 1–5 = distal tarsalia ; ti= tibiale; V= caudal vertebræ; I-V= digits.

determine the presence on an elongate ilium and an ischium. The leg of the left side is the best preserved of all the elements and it is to this that our attention will be confined. The opposite leg is not so complete, yet all the long bones and a part of the tarsus are preserved with sufficient clearness to corroborate the findings of the left side.

The femur, as has been stated, is reptilian in appearance. This is due to the well-rounded articular surfaces, as though the endochondrium were well developed, and to the large development of the greater and lesser trochanters, which are quite prominent, though these are distorted and depressed in fossilization. The bone is stout and well built (fig. 2) and its form suggests an active habit of life. The *tibia* and *fibula* are separate, and do not otherwise have sufficiently noteworthy characters as to call for a special description in this place except to note an unusual anterior crest on the tibia. To the lower ends of these bones articulate the first row of tarsal elements; the tibiale, intermedium and fibulare. The *tarsus* is composed of nine elements arranged in three rows.

The proximal row is composed of the tibiale, the intermedium and the fibulare. On the edge of the tibiale there lies a portion of one of the caudal vertebræ, so that the form of this tarsal element is slightly obscured. The intermedium is a small rounded element lying between the larger elements. The fibulare is rectangular and projects a considerable distance out from the tibia, but articulates directly with the large lateral distal tarsal. The centrale is triangular in form and is opposed directly by the tibiale and tarsalia 1–3. The phalanges are robust in appearance. The entire foot gives one the impression of a very broad structure. The ungual phalanges were apparently bluntly clawed.

The unusual nature of this foot and its disturbing nature in an attempted analysis of amphibian descent has already been commented on,\* and further discussion in this place is unnecsary.

The tarsus of Archegosaurus described and figured by Baur (page 509) is so incomplete and scattered that a direct comparison with the present form is not possible. Further than this form I know of no species with which we may compare the structures of *Ichthycanthus*.

Department of Anatomy, University of Illinois, Chicago.

\* Science, N. S., vol. xli, No. 1044, p. 34.

# ART. XXXII.—Contributions to Sardinian Petrography: I. The Rocks of Monte Ferru ; by HENRY S. WASHINGTON.

Introduction.—A considerable number of chemical analyses have been made in past years of the igneous rocks of Sardinia which were collected in 1905 and are still unpublished. As there seems to be no immediate prospect of making the additional analyses needed for the rather complete study of Sardinian lavas which was originally contemplated, it has been decided to publish those already made, along with the proper descriptive matter, so as to make them adequately available to petrographers. The rocks of Monte Ferru will be first described, then those of the recent small cones, and finally the lavas of the early sheets. I have to thank Prof. J. V. Lewis for the photographs of the trachyte.

#### MONTE FERRU.

Bibliography.-The volcano of Monte Ferru was often mentioned and its main characters were well described (according to the science of his day) in La Marmora's classic and monumental work on Sardinia.\* Twenty years later Doelter published brief descriptions of its geology + and lavas, t with some analyses and a geological map.

Subsequently Bertolio§ gave a brief description of a few of the rocks. The short notices of Zirkel and Rosenbusch appear to have been based entirely on Doelter's work. The first modern description of the volcano is found in two papers by Dannenberg, who gives a geological map. In two more recent papers T Deprat discusses very briefly the structure of the volcano and the general chemical characters of its lavas. though, unfortunately, he does not communicate the new analyses which he made. The most important part of the volcano is covered by the Santu Lussurgin and Bosa sheets (Folio 206, III and IV) of the Italian military map, scale 1:50,000.

Topography and geology.—The volcano of Monte Ferru is situated at about the center of the west coast of Sardinia, midway between the towns of Bosa on the north and Oristano on the south and 40 km. north of Monte Arci. The area covered by its lava is at least 700 square kilometers. Its greatest

\* A. de La Marmora, Voyage en Sardaigne, Description Géologique, 2 vols., Turin, 1857. † C. Doelter, Denkschr. Ak. Wiss. Wien, xxxviii, p. 193, 1877.

t C. Doelter, op. cit., xxxix, p. 41, 1878. § S. Bertolio, Boll. Com. Geol. Ital., 1896, p. 190.

A. Dannenberg, Sb. Preus. Ak. Wiss., 1903, p. 853; Neues Jahrb., Beil. Bd., xxi, p. 1, 1905. ¶ J. Deprat, C. R., cxlv, p. 820, 1907; C. R., cxlvi, p. 702, 1908.

#### 514 Washington—Contributions to Sardinian Petrography:

altitude, 1050 m., is reached at the summit of Monte Urtigu,\* near the southern end of the exposure of the trachytic mass, and about 4 km. west of the town of Santu Lussurgiu. The small cluster of flat-topped peaks, of which this is slightly the highest, is at the headings of three caldera-like valleys, the general extent of which is indicated on Dannenberg's map. The largest is on the north with the town of Cuglieri near its mouth. Somewhat smaller is that of the Ghizo region in the southwest, and still smaller is that in the southeast, near Santu Lussurgin. These valleys reveal very clearly the internal structure of the mass.

According to Dannenberg, eruptions began in the Miocene with the ejection of rhyolitic or trachytic tuffs, while Deprat considers these tuffs to be pre-Miocene and antedating the Ferru volcano. I made no special observations on this point, but am inclined to agree with the latter view. Over these tuffs were extruded trachytic lavas, which seem to have been highly viscous and to have formed a huge dome at least 1000 m. high, the lava forming but few true flows. This extrusion was seemingly not accompanied by any extensive amount of tuffs or loose material, though some small secondary cupolas were formed. This trachytic core of the mountain was quite uniform in character, but there are masses of phonolite or phonolitic trachyte, which seem to be rather schlieren in the trachyte than flows.

After a repose of unknown duration there followed, apparently with few lavas of intermediate composition, a prolonged outpouring of basalts, which seem to have issued, not from craters, but from fissures which penetrated the trachytic mass. These basalts are somewhat varied in character, one type forming flat tables which cover the trachytes in some of the higher parts of the mountain. These were followed by extensive sheets which covered the lower slopes and extended far over the surrounding plain. There seems to have been a paucity of scoria and ash accompanying these basaltic outflows, as was the case with the trachytes.

There ensued a long period of complete repose, during which probably the three large calderas were formed, presumably by erosion after preliminary explosions. Volcanic activity reawoke feebly and for a short time with the outpouring of small flows of peculiar and, for this volcano, aberrant lavas, the analeite basalts of Scano and Ghizo, and a biotite-augite rock of Monte Commida.

Monte Ferru, then, is essentially composed of a large domal core of very uniform trachyte, passing locally into phonolite,

\* This is the spelling on the Italian map. Doelter renders it Urtica, and Dannenberg Urticu. The accent is on the second syllable.

covered with a thick mantle of basalt, which extends far beyond the boundaries of the trachytic mass, and a few very subordinate, final and aberrant types. In its general structure, therefore, it much resembles the neighboring Monte Arci, though here the salic core is largely of rhyolite.\* There are at the present day no hot springs or solfataric activity, so that the volcano may be regarded as definitely extinct.

#### Trachyte (Pulaskose, I. 5. 2. 3).

Cuglieri type.—Though the trachytes of Monte Ferru are rather uniform, yet.it will be convenient to refer them to two types, which differ notably from each other. The first is markedly porphyritic and, at least in part, earlier than the second type, and much less abundant. It is the sanidineplagioclase trachyte of Doelter, and the porphyritic type of Deprat, while Dannenberg does not seem to discriminate between the two. I found it well developed below Cuglieri, specially at a mill (molino) 3 km. from the town along the road, at the second small round area of trachyte on Dannenberg's map. It also occurs near the Serbatoio, on the road from Cuglieri to Santu Lussurgiu, and at a few other localities. Doelter describes it from near the iron mines in the southwestern part of the volcano, a locality which I did not visit.

Megascopically it is dopatic with many stout tables or equant individuals of feldspar, and some black augites, which lie in a pure light gray, compact, aphanitic groundmass. Microscopically it is holocrystalline. The feldspar phenocrysts are mostly of soda-orthoclase, with fewer of oligoclase-andesine, and the subhedral augite phenocrysts are brownish-green and somewhat corroded on the borders. The highly predominant feldspars of the groundmass are stoutly prismatic or almost equant and do not show fluidal arrangement. The greater part is soda-orthoclase, quite commonly in Carlsbad twins, but there is considerable andesine. No quartz is visible. The augites of the groundmass are small, greenish-gray anhedra, and there are some magnetite grains. No biotite or hornblende was seen.

Sennariolo type.—This type is by far the most abundant and it forms the greater part of the trachytic dome. It is usually massive, but in places columnar and somewhat platy structures are found. No vesicular forms were observed. Megascopically it is extremely dense, compact, and fine-grained, with a dull luster and often subconchoidal fracture. It is generally a pure gray, varying from rather dark to almost white. The type is almost absolutely perpatic—quite without

\* Cf. H. S. Washington, this Journal, xxxvi, p. 577, 1913.



F1G. 1. Trachyte. Sennariolo. Parallel nicols.

FIG. 2.



FIG. 2. Trachyte, Sennariolo. Crossed nicols.

phenocrysts of any kind, though a few specimens show very rare (not more than 1/2 per cent) small  $(1/2^{mm})$  crystals of black augite or still fewer feldspar phenocrysts.

The microscopic characters are, in general, quite uniform. The rock is composed of very small thin laths of alkali feldspar, mostly untwinned, with some small anhedra of a colorless or pale greenish-gray diopside-augite, with extinction up to 40°, and fewer small magnetite grains, in a colorless, isotropic, glassy base. The feldspar laths generally show fluidal arrangement, but are occasionally divergent. Neither quartz nor andesine could be detected in these trachytes, but a few showed a very small amount of nephelite, revealed by staining, showing them to be transitional to the phonolitic trachytes. Small crystals of blue noselite are very rare, and these were not found to be as abundant in my sections as the descriptions of Doelter and Deprat would lead one to expect. Neither hornblende nor biotite are present, except for a few crystals of the latter in the trachyte of Punta sa Chidanza.

*Chemical Composition.*—The chemical composition of both types may be discussed together. Two analyses made by me of a typical specimen of each are given in Table I, along with analyses of similar rocks for comparison.

			•			
	$\mathbf{A}$	В	С	D	Е	$\mathbf{F}$
SiO,	58.43	61.07	57.01	55.11	61.62	60.20
Al Ó,	18.58	19.47	20.81	20.90	18.11	20.20
Fe O .	3.00	2.50	4.13	6.11	2.36	1.58
FeÖ	1.22	0.71	n.d.	n.d.	1.28	1.01
MgO	0.13	0.46	1.23	1.21	0.26	0.39
CaO	3.20	1.45	2.91 -	3.54	1.44	1.96
$Na_2O$	4.78	4.84	5.92	5.31	5.77	4.75
K.O	5.82	7.07	6.30	7.52	7.60	5.57
$H_{2}O +$	0.94	0.96	1.41	1.04	0.78	3.00
H <sub>0</sub> O –	1.63	0.42		~ -		
TiO <sub>2</sub>	1.11	0.69	n.d.	n.d	0.87	0.51
$ZrO_2$	0.24		~ -			
$P_2O_5$	0.13	0.04	trace	trace	0.13	n.d.
SO,	0.11				Cl 0.15	
MnO	0.09	trace	trace	trace	trace	n.d.
BaO	0.14			·		
SrO	0.06					
	99.97	99.68	99.72	100.74	109.67	99.47

## TABLE I.

Analyses of Trachytes.

A. Trachyte (I". 5. 2. 3). Molino, near Cuglieri, Monte Ferru. H. S. Washington analyst.

## 518 Washington-Contributions to Sardinian Petrography:

B. Trachyte (I. 5. (1)2. 3). Sennariolo, Monte Ferru. H. S. Washington analyst.

C. "Sanidine-plagioclase trachyte." Miniera, Monte Ferru. C. Doelter analyst; Denkschr. Ak. Wiss. Wien, xxxix, p. 51, 1878. D. "Sanidine-augite trachyte." Near Sennariolo, Monte

Ferru. C. Doelter analyst, op. cit., p. 54.
E. Trachyte obsidian (I". 5. 1. 3.). Monte Rotaro, Ischia.

E. Trachyte obsidian (1. 5. 1. 3.). Monte Rotaro, Ischia. H. S. Washington analyst, this Journal, viii, p. 289, 1899.

F. Phonolitic trachyte (I. 5. 2. 3"). Lusclade, Mont Dore, Auvergne. Pisani analyst. Michel-Levy and Lacroix, C. R., cxlviii, p. 1723, 1909.

The two types are much alike, the only differences of note, and these not very great, being in silica, lime and potash. The preponderance, both actual and molecular, of ferric over ferrous oxide may be noted. They resemble quite a number of analyses of trachyte and syenite from other localities, two of which are given for comparison. Doelter's analysis (C) of the Cuglieri type much resembles mine (A) in its main features. His analysis of the Sennariolo type differs markedly from mine, his silica being much lower, and his iron oxide, magnesia, lime and soda higher. This is the more remarkable, as the type is an unusually uniform one microscopically and both specimens came from very nearly the same locality.

The norms calculated from my two analyses are as follows:

	A	В
Q	2.04	2.52
Or	34.47	42.26
Ab	40.35	40.87
An	11.95	7.23
С		1.13
Di	0.62	
Ну		1.20
Wo	1.63	
Mt	0.93	0.23
Il	2.13	1.37
Hm	2.56	2.40
Ap	0.34	

These place both rocks in pulaskose, that from Cuglieri being intermediate toward monzonase, symbol I''. 5. 2. 3, and that from Sennariolo being transitional toward phlegrose, symbol I. 5. (1)2. 3. Microscopic examination alone, without chemical analysis, would lead one surely to consider the Sennariolo type as heralkalic.

*Mode.*—The texture of these rocks is such that a satisfactory measurement of the modes by Rosiwal's method is impractica-

ble. They may, however, be approximately calculated from the norms, the glass base in B being assumed to carry the quartz and andesine. To the modal augite is assigned a little normative anorthite, ilmenite and hematite. The results are as follows:

	A	В
Quartz	2.0	2.5
Or, Ab,	62.0	73.0
Ab An	26.0	16.0
Augite	5.0	3.5
Ores	5.0	5.0
	100.0	100.0

It will be seen that the mode of the Cuglieri rock is strictly normative, while that of the other would be so were it holocrystalline.

#### Trachytic Phonolite (Phlegrose-beemerose).

Occurrence.—The trachytes of the Sennariolo type pass by imperceptible gradations, chiefly in the nephelite content, into what may be considered to be phonolites, though in most of them the amount of nephelite is so small and the transition so gradual that, as a whole, they had best be called trachytic phonolites. On this account Dannenberg did not distinguish between the trachytes and the phonolites on his geological map, though Deprat considers that Dannenberg has underrated the importance of the latter. My observations led me to believe that the phonolites are of comparatively slight importance, and they would appear to be, in general, schlieric patches in the trachytic mass, distinguished by only very slight differences in composition, rather than distinct flows, radically different in character from the trachytes.

Among prominent localities may be mentioned the summits of Monte Oe and Monte Tinzosu near Santu Lussurgiu, where they overlie trachyte but without discontinuity; a small hill near Cuglieri west of Castel Ferru, with fine columnar structure; and a ridge west of Punta sa Chidanza, marked 872 on the map (206, III).

Description.—Megascopically these rocks are extremely finegrained and compact, looking much like the densest quartzites, and often showing well-marked conchoidal fracture. The color is dark gray, usually greenish or brownish, and often with a slightly greasy or silky luster. They are almost absolutely aphyric, the only phenocrysts present being very rare feldspars, 5 to 10<sup>mm</sup> in diameter. In some cases a flow texture is well developed, this being especially fine at Monte Tinzosu.

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, NO. 233-MAY, 1915.

## 520 Washington—Contributions to Sardinian Petrography:

On the whole, except for the greasy luster in some specimens, they closely resemble the trachyte of the Sennariolo type.

In thin section also these rocks are very similar to the Sennariolo trachyte. Small laths of alkali feldspar make up most of the rock, but these are usually rather larger and not so well defined as in the trachyte. There are many small  $(.02 - .10^{\text{mm}})$ prismoids of pale green ægirite-augite, with the usual, though faint, pleochroism. The presence of these rather readily distinguishes the two rocks, as in the trachyte the small pyroxenes are almost colorless or only slightly greenish gray. Magnetite grains are rare and there is no soda-lime feldspar. No noselite was seen in my sections, though one analysis indicates that it is present, and both Doelter and Deprat speak of it as a constant constituent. Between the feldspar laths is a weakly birefringent base of nephelite, which is not easily discernible and is best revealed by staining. In a few specimens, as in that from the hill below Castel Ferru, the nephelite forms very small, sharply defined, equant individuals. All the phonolites seem to be holocrystalline.

Chemical Composition.—An analysis was made of the phonolite of Monte Tinzosu, which was regarded as most typical, and of one from the small hill west of that on which stands the Castello Ferru mentioned above. The latter is incomplete, as only the main constituents were determined for comparison with Doelter's analysis. The amount of ZrO, is assumed to be that in the other phonolite, the alumina being corrected for it.

	A	В	С	D
SiO.	60.43	59.47	53.95	61.07
Al,Ô,	18.35	19.25	23.82	19.47
Fe <sup>O</sup> ,	1.64	1.92	2.68	2.50
FeO	0.91	0.94	n.d.	0.71
MgO	0.17	0.52	0.52	0.46
CaO	1.41	1.66	0.99	1.45
Na <sub>2</sub> O	6.12	6.86	10.03	4.84
К,О	8.68	6.89	5.79	• 7.07
$H_{2}O + \dots$	0.62)	1.0.9	1.00	0.96
H_O	0•34 ∫	1.20	1.09	0•42
TiO	0.36	0.66		0.69
ZrO <sub>2</sub>	0.21	(0.20)		
P,O,	trace			0.04
SO,	0.22		trace	
Cl	none	~ -		
MnO	0.16		trace	trace
BaO	0.08			
SrO	0.02			
	99.75	99.65	99.70	99.68

#### TABLE II.

#### Analyses of Phonolites.

A. Phonolite (I(II). 5(6). 1.3). Monte Tinzosu, Monte Ferru. H. S. Washington analyst.

B. Phonolite (I". (5)6. 1. 3(4). Hill near Castello Ferru, Monte Ferru. H. S. Washington analyst.

C. Phonolite. Hill near Castello Ferru. C. Doelter analyst. Denkschr. Ak. Wiss. Wien, xxxix, p. 62, 1878.

D. Trachyte. Sennariolo, Monte Ferru. H. S. Washington analyst. Cf. p. 515.

The two analyses are very similar, except that the alkalies differ slightly. Both of them are also much like the analysis of the Sennariolo trachyte, though in these the soda is markedly higher, this difference involving the modal content in nephelite.

Doelter's analysis is much lower in silica and higher in soda. He does not mention the exact locality where his specimen was obtained, but it is probable that it comes from the same locality as that analyzed by me—a small hill (592 on the map, 206, IV), west of the castle and about one kilometer and a half southeast of Cuglieri along the fourth class road. This shows well-developed columnar structure, the lava resting on tuffs, giving a fine exposure, and one from which a specimen would certainly be taken by any geologist. If this is so the differences between Doelter's and my figures are hard to explain, as the mass is apparently very uniform in character. It may be noted that the differences here are much the same as those between Doelter's and my analyses of the Sennariolo trachyte.

The norms of the two rocks are as follow:

	A	В
Or	51.71	40.59
Ab	25.94	37.20
An		0.28
Ne	10.65	1 <b>1·3</b> 6
Ac	4.62	
Ns	0.24	
Di	3.35	2.81
Wo	1.28	1.39
Mt		1.39
Il	0.68	1.22
Hm		0.96

These place the Tinzosu rock (A) in phlegrose, transitional to beemerose, I(II). 5(6). 1. 3, while the other, B, is in beemerose, transitional to miaskose and phlegrose, with the symbol I''. (5)6. 1. 3(4). They both indicate that the amount of nephelite present is not great—a fact fully in accord with their close similarity to the true, nephelite-free trachytes. It may also be noted that the presence of normative acmite in A, while it is absent in B, is in harmony with the fact that the pyroxene of the former, as seen in thin sections, contains decidedly more aegirite than that of the latter rock. The designation of trachytic phonolite is fully justified by the analyses and their norms.

## Basalt (Camptonose).

The basalts of Monte Ferru are divided by Doelter into olivine-free and olivine-bearing varieties. Dannenberg and Deprat, on the other hand, lay no stress on the presence or absence of olivine, and refer them to two groups: andesitic basalts, gray, rather coarse-grained and with feldspar phenocrysts, which form tabular masses on the higher parts of the mountain; and basalts proper, dark and fine-grained, without feldspar phenocrysts, which form the flows on the lower flanks of the cone and extend far beyond in all directions. The former issued from large dikes, with a general north-south trend, which are met with in the central parts of the volcano; and the latter from more irregular dikes lower down on the flanks. The reader may be referred to Dannenberg\* for descriptions of these occurrences.

I have made only two analyses of these rocks, which are much alike, and several more are needed for their proper study. Practically all the basalts collected by me carry more or less olivine, and these differ chiefly in the size of the feldspar laths of the groundmass. I have but few specimens of the "table-basalts" of Dannenberg. These are rather light in color and show feldspar phenocrysts, in accordance with the distinction made by Dannenberg and Deprat. But, on the whole, the difference between them does not seem to me to be of great petrographic significance, so that, in the absence of sufficient analyses and of a more detailed study of their various occurrences, it seems to be advisable at present to make no marked distinctions and to describe them together.

Description.—The basalts vary in color from a rather light to a very dark gray. They are all fine-grained, some, especially those forming the dikes, being very dense and aphanitic. They are only rarely vesicular, but never scoriaceous. In the lighter colored specimens, as from near Monte Entu and Nuraghe Sylvanis, there are some phenocrysts of feldspar (from 2 to 5<sup>mm</sup> in diameter), and in the specimen from the latter place are also phenocrysts of black augite and olivine, these rocks being almost dopatic. Nearly all the basalts, however, are almost or quite perpatic, small phenocrysts of augite or olivine being rare.

In thin section they are seen to be fairly uniform. Plagioclase, with an average composition of labradorite, about

\* Dannenberg, Neues Jahrb., B. B., xxi, p. 38, 1905.

Ab<sub>1</sub>An<sub>1</sub>, is most abundant. There are some euhedral, much twinned, phenocrysts of this, especially in the andesitic type, but for the most part it forms the usual groundmass laths, with divergent arrangement, and varying in size from very small and thin to coarse individuals up to  $1^{mm}$  long. In any one specimen they are of about uniform size. In the andesitic basalts (as from Punta Arancola and Nuraghe Silvanis), the groundmass feldspars are mostly equant and anhedral, rather than lath-shaped.

In most cases pyroxene is the next most abundant mineral. This is also quite colorless in the thin section, none of the crystals showing even a tinge of green. It is of two kinds. Monoclinic diopside is rather abundant in short, stout prismoids and anhedral grains giving extinction angles up to about 35°. Enstatite is less common, but often present, in euhedral to subhedral crystals, giving thick laths with equal ends, and with parallel extinction. There is little apparent difference in the birefringence of the two. Both pyroxenes, but especially the diopside, also form the usual small anhedral grains of the groundmass.

Olivine is almost always present, its amount being sometimes as great as that of the pyroxene, and in rare cases (as in the basalts near Seneghe), it almost entirely replaces the latter. Again, as in some of the dikes, its amount is small or it may rarely be quite wanting. It forms small sharply euhedral phenocrysts, not occurring in the fine groundmass, giving the common lozenge-shaped sections. Many of these are more or less corroded and embayed, though generally with the angles left sharp, and are occasionally reduced to skeletons or anhedral grains. The olivines nearly always have a border of light yellow iddingsite, some of the crystals being entirely colored, but nearly all the basalts are very fresh.

Magnetite grains are abundant, and small apatite prisms are fairly common. Neither orthoclase nor nephelite could be detected. The groundmass between the larger crystals is nearly always holocrystalline, made up of minute feldspar laths, and granules of pyroxene and magnetite, with often a colorless somewhat birefringent, apparently feldspathic base. Only two specimens, from the great flows northwest of Sennariolo, are distinctly vitreous. Interstitial between the divergent and rather coarse plagioclase laths, these show considerable colorless glass, which looks gray through the presence of much globulitic dust, and with considerable magnetite in grains or dendritic forms.

*Chemical Composition.*—Two analyses have been made by me of these basalts. The first, (A), is from a flank flow at a point along the highway about 4 km. west of Cuglieri. The second, (B), is from a prominent dike, about 5 km. south of Cuglieri, cutting trachyte in the steep eastern face of Monte Tuvonari, near "510" on the map (206, IV). This dike is vertical, about one meter and a half thick, striking N. 20° W., and with finely developed, transverse columnar structure—standing up like a wall of polygonal masonry. It has not altered the trachyte at the contact.

With them are given analyses made by me of three other Sardinian basalts, C representing the basalts of Monte Arci, D one of those of the recent small cones, and E one of the Tertiary sheet basalts. A silica determination of an andesitic basalt from above Fontana Figu gave 50.20 per cent.

#### TABLE III.

#### Analysis of Basalts.

	$\mathbf{A}$	В	С	D	E
SiO	52.40	52.20	52.79	53.48	49.00
Al, Ó,	15.26	13.20	16.45	13.59	15.63
Feo	0.74	1.29	2.74	1.78	4.03
FeO	8.33	7.91	6.44	8.30	5.00
MgO	7.45	8.71	5.56	5.88	7.86
CaO	7.33	7.95	6.51	7.20	8.16
Na <sub>0</sub>	3.54	3.20	3.64	4.38	3.93
K, Ö	0.99	1.01	1.21	1.02	2.60
$H_{0} + \dots$	0.29	1.68	1.02	0.79	0.13
H_0	0.06	0.29	0.21	0.11	0.18
TiO	3.12	2.00	2.64	2.52	3.25
P.0.	0.49	0.24	0.39	0.59	0.63
MnÖ	0.08		0.06		
NiO	0.06		0.18		
	100.14	99.68	99.84	99.64	100.40

A. Basalt ("III. 5. 3. 4"). Flow. Near Cuglieri, Monte Ferru. H. S. Washington analyst.

B. Basalt (III. 5. 3. 4"). Dike. Monte Tuvonari, Monte Ferru. H. S. Washington analyst.

C. Basalt (II". "5. 3. 4"). Flow. Uras, Monte Arci. H. S. Washington analyst, this Journal, xxxvi, p. 589, 1913.

D. Basalt ("III. 5. (2)3. 4(5)). Flow. Monte Austida. H. S. Washington analyst.

E. Basalt ((II) III. 5". (2)3. 4). Sheet. Tres Nuraghes, S. E. of Bosa. H. S. Washington analyst.

The two analyses are very much alike. This is to be expected, as the dike is evidently a feeder for one of the series of flows to which the other basalt analyzed belongs. The only noteworthy differences are the somewhat higher alumina and

## I. The Rocks of Monte Ferru.

slightly lower magnesia and lime of the flow, which makes it a little more salic, a feature expressed by its symbol. A striking character of both is the great preponderance of ferrous over ferric oxide (in marked contrast to the trachytes and phonolites), as well as to a less extent that of soda over potash. They both greatly resemble the Arci basalt and some of those of the recent cones. The resemblance is less close with the sheet basalt, the difference in the amounts of silica and potash and the relations of the iron oxides being marked.

The norms of the two Monte Ferru basalts are :

	A	В
Q	0.48	
Or	6.12	6.12
Ab	29.87	27.25
An	22.80	18.35
Di	7.88	15.48
Hy	24.28	23.62
OÍ		0.65
Mt	1.16	1.86
Il	5.93	3.80
Ap	1.34	0.67
<u> </u>		

These norms place both rocks almost centrally in camptonose, the symbol of A being "III. 5. 3. 4," and that of B being III. 5. 3. 4".

Mode.—It is scarcely practicable to measure the modes of many of these basalts, partly because of the complexity of their texture and partly because of the small size of many of the mineral individuals. For the two rocks analyzed, however, modes may be reckoned approximately from the norm, checked as regards most of the minerals by study of their thin sections. These yield the following figures, which can be regarded as, at best, but rough approximations:

	A	В
Quartz	5	4
Ab,An,	57	50
Pyroxene	21	32
Olivine	10	8
Ores	6	5
Apatite	1	1

The presence of quartz, even though in small amount, in these rocks along with olivine, and when it is not visible in the thin section, will doubtless be surprising. Its modal presence is, however, made necessary by the considerable amount of actual olivine in the rock, while the norm shows only hypersthene or but a trace of olivine. The crystallization

of olivine from the magma liberated a certain amount of silica. which would otherwise have formed metasilicate rather than orthosilicate with the magnesia and ferrous oxide. The quartzbasalts described many years ago by Iddings and Diller \* are well-known cases of the simultaneous presence of olivine and quartz. Another instance may be found in the sheets of diabase which form the Palisades in New Jersey, where the olivine has apparently settled to the bottom of the liquid mass, forming a layer of olivine diabase, while the bulk of diabase "is somewhat quartzose." +

Though the quartz is not actually visible in these Ferru basalts, possibly because of the fine-grained character of the interstitial groundmass, to which final stage of consolidation it would belong, yet the comparison of the norms and modes show that it must be present-forming an occult mineral, to use a term recently introduced.<sup>‡</sup> It may be remarked that this matter of occult minerals is one which has been much neglected, but which is of much theoretic importance in the interpretation of igneous rocks, and one for the study of which the idea of the quantitative classification will be of great utility.

In recent papers Bowen and Andersen§ have clearly shown, by physico-chemical study of the systems: MgO-SiO, and diopside-forsterite-silica, that at a high temperature, that is an early stage of the crystallization, olivine separates out, due to dissociation of the molecule MgSiO, into Mg,SiO, + SiO, and its relative insolubility. If the cooling be slow enough this olivine will be gradually resorbed, the equation being reversible. But if it be too rapid, part of the olivine will remain, leaving an excess of silica in the magma, which must crystallize as quartz or form a hypersilicic glass according to circumstances. The embayed, corroded, and skeletal forms of the olivine phenocrysts in the basalts here described are fully in harmony with this interpretation, as well as is the gradual transition from olivine-rich to olivine-free basalts of what must be, judging from the microscopical examination, much the same chemical composition. The common presence of enstatite in these basalts is, of course, to be expected on this hypothesis.

### Analcite-basalt. (III. 5-6. 2-3. 5).

Small flows of what was formerly believed to be leucitebasalt, but in which the so called leucite has been shown to be

\*J. P. Iddings, this Journal, xxxvi, p. 208, 1888; U. S. G. S., Bull. 66, 1890. J. S. Diller, U. S. G. S., Bull. 79, 1891. †J. V. Lewis, N. J. Geol. Surv., Ann. Rep. (1907), p. 731, 1908. ‡J. P. Iddings, Igneous Rocks, II, p. 19, 1913. § N. L. Bowen and O. Andersen, this Journal, xxxvii, p. 487, 1914.

N. L. Bowen, this Journal, xxxviii, p. 207, 1914

analcite,\* formed the final products of eruptive activity. They are met with near Scano, on the northeastern flank, and form part of a ridge south of this village, called Binzale Prunu. There is also an exposure at a locality called Ghizo, west of Monte Urtigu, and Dannenberg mentions and maps another at Spelunca, south of Ghizo, which I did not see. As these rocks, with similar ones from near Bonorva, are fully described in the paper cited, a brief description must suffice here.

These lavas are dark gray to black, very dense, compact, and with aphanitic groundmass. The rock from Scano carries nodules of augite and granular olivine, but shows few true phenocrysts of augite, olivine and biotite. Those of Binzale Prunu, Ghizo and Spelunca show many large plates of a bronzy biotite, and a few phenocrysts of olivine and augite. The specimens from about Scano are very fresh, but those from Ghizo are badly weathered.

Microscopically the small phenocrysts of augite and olivine are not prominent and offer no features of special interest. The biotite tables are brown, with an axial angle  $2E = 40^{\circ} - 45^{\circ}$ , and a refractive index  $\gamma_{na} = 1.65 - 1.655$ , as determined by Dr. Merwin, resembling some from Mount Vesuvius. There are many small isotropic areas of a mineral which resembles leucite, showing similar inclusions, but with a refractive index of 1.502, determined by Dr. Wright. Analysis of the portion of the rock soluble in warm dilute hydrochloric acid vielded the figures Na<sub>2</sub>O = 2.66 and K<sub>2</sub>O = 0.12 in percentages of the rock, showing that the supposed leucite is in reality analcite. The amount of water yielded by these very fresh rocks is also in harmony with this interpretation. This analcite is regarded as primary and it is suggested that its occurrence will explain the apparent anomaly of supposed leucites in other fresh rocks high in soda and low in potash.

The microgroundmass is formed of many very small prisms of augite and grains of olivine and magnetite in colorless glass. There is no feldspar present.

The chemical composition is represented by two analyses of the Monte Ferru rocks, with one of that of Bonorva.

Silica is rather low, and titanium decidedly high, and there seems to be a noteworthy amount of nickel. The most striking feature—when the presence of "leucite" is considered—is the small amount of alkalies and the dominance of soda over potash. The high amount of water, in view of the freshness of the rocks, is also noteworthy.

Doelter's analysis is obviously faulty, especially in the high \*H. S. Washington, Boll. Soc. Geol. Ital., xxxiii, p. 147, 1914; Jour. Geol., xxii, p. 742, 1914.

TABLE IV.				
	A	В	С	D
SiO,	44.85	44.37	46.54	42.30
Al Ô,	12.55	11.36	12.68	18.22
Fe O	3.33	7.23	3.41	17.30
FeO	5.30	3.49	5.29	n.d.
MgO	10.27	9.28	10.09	6.66
CaO	8.32	8.50	8.00	11.01
Na <sub>o</sub> O	4.77	3.62	5.11	1.31
K.Ó	0.72	0.74	1.64	2.93
HO+	2.01	3.28	2.35	0.55
H <sub>0</sub> –	0.92	1.95	0.25	
TiO,	5.07	5.21	3.98	
$P_{a}O_{b}$	1.17	0.99	0.91	trace
MnÖ	0.02			trace
NiO	0.23			
	99.60	100.07	100.25	100.28

A. Analcite basalt (III. (5)6. 2. 5). Scano, Monte Ferru. H. S. Washington analyst, this Journal, xxii, 748, 1914.

B. Analcite basalt (III. 5. (2)3. (4)5). Monte Columbargiu, Monte Ferru. H. S. Washington analyst, loc. cit.

C. Analcite basalt (III. 6. 1(2). 4). Bonorva, Sardinia. H. S. Washington analyst, loc. cit.

D. "Leucite basalt." Scano, Monte Ferru. C. Doelter analyst. Denkschr. Akad. Wiss. Wien, xxxix, 80, 1878.

 $Al_2O_3$ , partly due to non-separation of TiO<sub>2</sub> and P<sub>2</sub>O<sub>3</sub> and in part probably to the incomplete separation of MgO from  $Al_2O_3$ . The iron oxides are almost certainly too high, and the two are not separately determined. It seems probable that his alkalies have been interchanged.

The norms of these rocks are as follows :

	$\mathbf{A}$	В	С
Or	4.45	4.45	15.59
Ab	28.30	31.44	15.98
An	10.56	11.95	3.61
Ne	6.53		14.62
Di	17.93	15.12	23.79
Hy		5.00	
Oľ	12.18	7.84	10.21
Mt	2.32		4.87
II	9.73	9.45	7.60
Hm	1.76	7.23	
Pf		2.18	
Ap	2.69	2.35	2.02

These place the Scano rock (A) in the subrang with the symbol III. (5) 6. 2. 5, which has been called scanose.\* The

\* H. S. Washington, C. R. xii Cong. G. Int., 231, 1914.

Columbargiu rock (B) is in ornose with the symbol III. 5. (2) 3. (4) 5. The Bonorva rock (C) has the symbol III. 6. 1(2). 4, the name pilandose being assigned to this subrang.<sup>\*</sup> The symbols of these subrangs show clearly the highly sodic character of these rocks, and support the view that the supposed leucite is really analcite.

The olivine and augite nodules in the Scano basalt are described in the paper cited, and only their analyses need be given here, for the sake of completeness. The analyses by Doelter here, also, are clearly very faulty.

	A	В	С
SiO,	41.24	50.13	43.77
TiO	0.10	1.91	
Al <sub>2</sub> Ó <sub>3</sub>	0.21	7.08	
Fe O	0.48	1.10	0.61
$\operatorname{Cr}_{2}^{\circ}\operatorname{O}_{3}^{\circ}$	$\mathbf{nil}$		
FeO	8.36	4.41	24 <b>·9</b> 0
MnO	trace	0.02	
NiO	0.21	0.05	
MgO	49.90	13.73	29.21
CaO	nil	20.06	trace
Na <sub>2</sub> O		1.88	
K <sub>2</sub> O		0.22	
H <sub>2</sub> 0		0.11	
	100.62	100.73	98.49

A. Olivine. Nodule in analcite basalt. Sp. gr. = 3.307 at 20°. Scano. H. S. Washington analyst, op. cit., p. 746.

B. Augite. Nodule in analcité basalt. Scano. H. S. Washington analyst, op. cit., p. 747.

C. Olivine. Nodule in "leucite basalt." Scano. C. Doelter analyst, op. cit., p. 78.

Geophysical Laboratory,

Carnegie Institution of Washington, Washington, D. C., January 26, 1915.

\* H. S. Washington, Jour. Geol., xxii, 751, 1914.

# ART. XXXIII.—The Estimation of Pentavalent Vanadium by Means of Sodium Thiosulphate; by G. O. OBERHELMAN.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxvi.]

As is well known, standardized sodium thiosulphate in excess may be employed under certain definite conditions as a reducer of ferric chloride, the amount of the thiosulphate which disappears by transformation to tetrathionate (determined by the idiometric determination of the excess) serving as the measure of the ferric salt reduced. In this process, originally proposed by Scherer,\* and studied by many investigators, there are three chief sources of error which may appear, according to conditions: viz., incompleteness in the reduction of the ferric salt, decomposition of the thiosulphate by the action of free acid, and progressive oxidation by the action of the air. Nortont has shown that these sources of error may be made to disappear by the use of a sufficient excess of sodium thiosulphate, by regulation of the time of action, and by attention to the concentrations of free acid, thiosulphate, and the ferric salt. According to Norton's procedure the volume of the solution should be at least 400cms for each 0.1 grm. of iron oxide present, the quantity of free hydrochloric acid present should not exceed 1<sup>cm<sup>3</sup></sup> of the strongest aqueous acid to each 400<sup>cm<sup>3</sup></sup> of solution, the excess of N/10 thiosulphate should amount to at least 15<sup>ems</sup>, and this excess should be determined by titration with N/10 iodine as soon as the color brought out in the solution before reduction due to the addition of a drop of potassium sulpho-cyanide solution has been discharged. Oudermannst has recommended the introduction of cupric sulphate as a catalyzer, to hasten the process of reduction, but Norton found this procedure unnecessary.

This paper is the account of a successful attempt to adapt a similar process of reduction by sodium thiosulphate to the determination of vanadic acid (in the course of work the account of which will be published later) under conditions in which the ordinary modes of determination are impossible or inconvenient. It has been found that the action of reduction may be made to proceed regularly in the sense of the expression

$$V_2O_6 + 2Na_2S_2O_3 + 2HCl = V_2O_4 + Na_2S_2O_6 + 2NaCl + H_2O.$$

The amount of vanadium present may be measured by the difference between the amount of standard thiosulphate introduced and the amount of that reagent remaining, as determined

<sup>\*</sup> Gel. Anzeig. k. Bayrisch, Acad., Aug. 31, 1859.
† This Journal, (4), viii, 25, 1899.
‡ Zeitschr. anal. Chem., ix, 362.

by titration with standard iodine; but in this case (unlike that of the reduction of the ferric salt) the presence of a catalyzer is necessary to bring about the reduction of the vanadic acid, and the concentration of the free hydrochloric must be slightly larger than that indicated by Norton as applicable in the reduction of the ferric salt. When considerably larger amounts of hydrochloric acid are present the thiosulphate is decomposed with the liberation of sulphur dioxide, which, of course, entirely vitiates the process.

On the introduction of thiosulphate into a solution of ammonium vanadate containing a little copper sulphate and slightly acidified, the golden yellow changes to green and finally to a pure blue which indicates reduction of the vanadium to the tetravalent state. With iron it is necessary to introduce a little sulphocyanide as an indicator of complete reduction. With vanadium no outside indicator is necessary. When the solution has become a pure blue it is only necessary to add starch, with enough potassium iodide (0.1 to every 100<sup>cm³</sup> of solution) to bring out a sufficiently delicate end-point,\* before proceeding with the titration by iodine.

Certain experiments showed plainly that with a certain amount of copper sulphate and hydrochloric acid present the rapidity of reduction depends largely upon the concentration of the acid. It was found that to bring about complete reduction within a reasonable time as much as 1.5<sup>cm<sup>3</sup></sup> of the (32%) acid should be present in every 400<sup>cm<sup>3</sup></sup> of solution and that this concentration of acid does not cause appreciably, at ordinary temperature and during the period of reduction, a secondary decomposition of sodium thiosulphate (resulting in the liberation of sulphur dioxide) provided the excess of this reagent does not exceed the equivalent of 75 cm3 of the N/10 solution in the 400<sup>cm<sup>3</sup></sup>.<sup>+</sup> In the quantitative tests of the process detailed below the concentrations of acid and thiosulphate were kept within these safe limits. Moreover, since copper sulphate and potassium iodide react at sufficient concentrations with the liberation of iodine according to the expression

# $2CuSO_4 + 4KI \rightleftharpoons Cu_2I_2 + 2K_2SO_4 + I_2$

it is plain that in the reduction of vanadic acid by the thiosulphate the amount of copper sulphate used as a catalyzer should be kept, if possible, well within the maximum, which may be present without setting up in appreciable degree the reactions by which iodine is set free. The following table contained the results of experiments made to discover the amount of copper sulphate which may be present in a solution of 400<sup>cm³</sup>

\* Hale, Am. Chem. Jour., xxviii, 938.

† Compare Norton, this Journal, (4), vii, 287, 1899.

## Oberhelman—Pentavalent Vanadium.

or a little more in presence of  $1.5^{\text{cm}s}$  of 32% hydrochloric acid and potassium iodide in varying amounts. The starch reaction was observed after a little more than the lapse of time which would occur in the titration of the excess of thiosulphate by iodine in the vanadic acid determination.

#### TABLE I.

The Action of Copper Sulphate upon Potassium Iodide with Liberation of Iodine.

CuSO <sub>4</sub> .5H <sub>2</sub> O grm.	$\mathrm{HCl}(32\%) \ \mathrm{cm}^3$	KI gm.	${f Volume\ cm^3}$	Starch reaction
0.0100	1.5	0.4	410	None
0.0100	66	0.8	420	None
0.0100	66	1.2	430	None
0.0200	66	1.2	440	None
0.0300	66	1.2	450	None
0.0300	66	1.6	460	None
0.0300	66	2.0	400	Blue
0.0300	٤٥	2.4	400	Blue
0.0200	"	2.4	400 ·	None
0.0100	66	2.4	400	None

From the results given in Table I it would appear that in presence of  $1.5^{\text{cm}^3}$  of (32 per cent) hydrochloric acid in the water solution of approximately  $400^{\text{cm}^3}$  there is no appreciable liberation of iodine when so much as 30 milligrams of the copper sulphate and 1.5 grm. of potassium iodide are present. When, however, even smaller amounts of the copper salt and iodide are present during the reduction of vanadic acid by the thiosulphate taken in slight excess ( $2^{\text{cm}^3}-5^{\text{cm}^3}$ ) an appreciable over-use of thiosulphate appears.

In studying the conditions for the quantitative estimation of vanadium, the solutions used were made from ammonium vanadate and standardized by means of the Holverscheit method (Inaug. Diss. Berlin, 1890), according to which the vanadate is treated with potassium bromide and hydrochloric acid and the liberated bromine determined by absorption in a solution of potassium iodide and titration of the liberated iodine. The thiosulphate solution, approximately N/10, was standardized against N/10 arsenite made from twice sublimed arsenic trioxide. The amounts of copper sulphate were restricted to a maximum of 10 milligrams in a volume of 400cm<sup>3</sup> and the iodide to about 0.1 grm. for every 100<sup>cm<sup>3</sup></sup> of solution. Qualitative experiments showed that the reduction of the vanadic acid might be considerably accelerated by the presence of an excess of the comparatively insoluble cuprous iodide, used as the catalyzer in place of copper sulphate, but the quan-

532

titative tests indicate that the reduction is not complete and that the addition of cuprous iodide to solution charged with a sufficient amount of the copper sulphate is without apparent effect. The experiments of Table II show the effects due to variation in the amount of the catalyzer under conditions otherwise similar.

#### TABLE II.

Reduction in Presence of	f an	Excess of '	Thiosulphate	amounting to
$2^{\text{cm}3} - 5^{\text{cm}3}$ of the N	/10	Solution in	a Volume of	400 <sup>cm3</sup> .

V2O5	V205	HCl	$CuSO_{4.5}H_{2}O$	KI	Volume
taken	found	(32%)	marm	arm	cm <sup>3</sup>
grm.	gim.	CIII	mgrm,	grm.	400
0.1283	0.1260	1.2	T	0.42	400
0.1283	0.1555	1.5	*	0.42	400
0.1955	0.1942	1.5	3 *	0.42	400
0.1955	0.1950	1.2	5 *	0.42	400
0.1955	0.1952	1.5	7 *	0.45	<b>40</b> 0
0.1955	0.1957	1.5	8 *	0.42	400
0.1955	0.1958	1.5	8 *	0.45	400
0.0977	0.0982	1.5	8 *	0.42	400
0.0977	0.0982	1.5	8 *	0.42	400
0.0977	0.0983	1.5	8 *	0.45	400
0.1955	0.1966	1.2	10 *	0•45	400
0.1955	0.1957	1.5	5	0.4 +	400
0.1955	0.1957	1.5	5	0.4 +	400
0.1955	0.1957	1.5	5	0.4 +	400
0.1955	0.1955	1.5	5	0.4 +	400
0.0977	0.0980	1.5	5	0.4 +	400
0.0977	0.0979	1.5	5	0.4 +	400
0.0977	0.0980	1.5	5	0.4 +	400

\* Cuprous iodide also present in suspension.

The results obtained are below the theory when cuprous iodide was the only catalyzer, fairly good when cupric sulphate was also present in amounts varying from 5 mgrm. to 10 mgrm., and very close to theory when cupric sulphate present to the amount of 5 mgrm. was the only catalyzer. The progress of the reduction was, however, rather slow and the expedient of increasing the excess of thiosulphate in order to accelerate the action was tried. At a volume of  $400^{\text{cm}3}$ , however,  $1.5^{\text{cm}3}$  of the 32 per cent hydrochloric acid will liberate from the equivalent of  $15^{\text{cm}3}$  of N/10 thiosulphate enough sulphur dioxide to be recognized by the odor. In the following experiments, therefore, the total volume of the solution was doubled, with corresponding increase in the concentration of acid and iodide, while the excess of N/10 thiosulphate was placed at  $15^{cm^3}$ .

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Reduction in	Presence of an	Excess of Thiosulph	ate amounting to
15°m3	of the N/10 So	lution in a Volume	of 800 <sup>cm3</sup> .

V₂O₅ taken grm.	V2O5 found grm.	HCl (32%) cm <sup>3</sup>	CuSO <sub>4</sub> .5H <sub>2</sub> O mgrm.	$\begin{array}{c} {\rm Excess \ of} \\ {\rm N}/10{\rm Na_2S_2O_3} \\ {\rm cm^3} \end{array}$	KI grm. present	Volume cm <sup>3</sup>
0.0967	0.0965	3	10	15	0.8	800
0.0967	0.0967	3	10	15	0.8	800
0.1935	0.1932	3	10	15	0.8	800
0.1935	0.1937	3	10	15	0.8	800
0.3870	0.3866	3	10	15	0.8	800
0.3870	0.3876	3	10	15	0.8	800

In these experiments, obviously excellent, the rapidity of the process was much increased by the limited increase in the concentration of the thiosulphate. The results seem to justify the conclusion that, if the conditions are carefully controlled, pentavalent vanadium may be rapidly and accurately estimated by direct reduction with sodium thiosulphate and titration of the excess.

According to the procedure recommended, the vanadate solution is brought to a volume of  $800^{\text{cm}s}$  or  $400^{\text{cm}s}$ ; 10 mgrm. or 5 mgrm. (respectively) of copper sulphate, CuSO.5H,O, and  $3^{\text{cm}s}$  or  $1.5^{\text{cm}s}$  (respectively) of hydrochloric acid (32 per cent) are added; N/10 thiosulphate is slowly run in, with constant stirring, until an excess of  $15^{\text{cm}s}$  or  $7.5^{\text{cm}s}$  (respectively) is present; the solution is allowed to stand until its color has become a pure sky blue; potassium iodide to bring the amount up to 0.1 grm for each  $100^{\text{cm}s}$  of solution is added; and the excess of thiosulphate is titrated with N/10 iodine in the presence of the starch indicator. The vanadium blue interferes but slightly with starch-blue end point.

When the amount of vanadate to be determined is not approximately known, a preliminary determination in which the copper sulphate is used to the amount of 20 mgrm. will quickly give the information required for the proper adjustment of the thiosulphate in an exact analysis to follow.

534

T. C. Brown—Development of the Mesenteries. 535

## ART. XXXIV.—The Development of the Mesenteries in the Zooids of Anthozoa and its Bearing upon the Systematic Position of the Rugosa; by THOMAS CLACHAR BROWN.

For more than half a century the systematic position of the Paleozoic corals designated as Madreporaria rugosa by Milne-Edwards and Haime, and Tetracoralla by Hæckle has been repeatedly discussed. Many writers have considered them to be absolutely distinct from the modern stony corals and actinians. Others have considered them as very closely related to the modern forms; for example, Ogilvie \* would derive the various groups of Mesozoic and later Zoantharians directly from as many different groups of Paleozoic forms, giving as her chief reason for doing so the similarity in the microscopic structure of the skeleton or corallite. Duerden, on the other hand, approaching the subject from the developmental standpoint and basing his conclusions upon the mode of addition of new mesenteries in the zooid and the addition of new septa in the corallite, holds the opinion that the rugose or tetrameral corals are most closely allied to the Zoanthids among living forms.<sup>+</sup> It has been suggested several times that the Tetracoralla were derivatives of hexameral forms, and that the tetrameral plan was superimposed upon an original hexameral form. ‡

The object of the present paper is to call attention to the structure and development of a number of recent Anthozoa and to point out the probable bearing of these facts upon the interpretation of the corallites of Paleozoic species.

It seems to have been taken for granted by many workers on modern Anthozoa that a great unbridged gap separated the Alcyonaria (Octocoralla, Hæckel) from the Zoantharia (Actiniaria, Madreporaria, etc.). The Alcyonarian zooids have eight mesenteries, never more, and eight tentacles which are branched or pinnate. As a rule, when they build a skeleton it is composed either of horny material, or of spicules of carbonate of lime, or of a combination of these two. When a hard skeleton is formed with calvees for the zooids, with septa-like ridges within, these septa-like structures or pseudosepta bear no relation to the intermesenterial spaces.

The Zoantharian zooids, on the other hand, have six or more mesenteries, and six or more simple unbranched tentacles.

\* M. M. Ogilvie, Phil. Trans. London, vol. clxxxvii, p. 83 ff, 1896. † J. E. Duerden, Ann. Mag. Nat. Hist., vol. ix, p. 381, 1902; vol. x, pp. 96, 382, 1902; vol. xi, p. 141, 1903; vol. xvii, p. 356, 1906; Biol. Bull., vol. vii, 1904; vol. ix, 1905. ‡ R. Ludwig, Palæontographica, vols. x and xiv. L. F. de Pourtales, Ill. Cat. Mus. Comp. Zool., vol. iv, 1871. J. E. Duerden, loc. cit.

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, No. 233.-MAY, 1915. 35



FIG. 1. Diagram showing a transverse section in the stomodæal region of a typical Alcyonarian zooid.

Fig. 2. Diagram of a transverse section through the stomodæal region of Edwardsia.

FIG. 3. Diagram showing the order of introduction of the first six pairs of mesenteries in the genera Actinia, Sagartia, and Bunodes, after Bourne.

FIG. 4. Diagram showing the order of introduction of the first six pairs of mesenteries in the genera *Rhodactis*, *Halcampa*, and *Manicina* after Bourne. FIG. 5. Diagram of *Aiptasia diaphana*, after Bourne.

FIG. 6. Gonuctinia prolifera, after Bourne.

When skeletal structures are formed these are composed of plates (sclerites) of carbonate of lime, and the septa within the corallites always bear a direct relation to the intermesenterial spaces.

There is at least one modern genus which seems to almost bridge the gap between these two widely separated divisions of the Anthozoa, namely Heliopora. Moseley \* has clearly shown that this is an Alcyonarian with eight complete mesenteries, and Bourne has further shown that in this type the calcareous skeleton is built up in precisely the same way as in the scleractinian or stony corals by a layer of cells derived from the ectoderm and calleda clicoblasts. In all the Alcvonaria except *Heliopora* the calcareous skeleton consists of spicules, each spicule forming as the entoplastic product of a cell. + Hence in so far as the origin and minute structure of the skeleton is concerned there is no great unbridged gap between Alcvonaria and Zoantharia.

A section across the stomodæal region of an Alcvonarian zooid shows that the arrangement of internal structures is simple and definite. These are shown diagrammatically in fig. 1. The zooid is clearly bilaterally symmetrical with the axis of symmetry coinciding with the long axis of the stomodæum. A ciliated stomodæal groove (the sulcus) is located at one side of the stomodæum. Eight complete mesenteries extend from the outer wall to the stomodæal wall and each of these bears a muscle "banner" (cross section of a longitudinal muscle band) on that side which is toward the sulcar side of the zooid. This is the simplest type of complete Anthozoan zooid; occasionally imperfect or modified individuals may show fewer parts but this is the typical plan in all complete and perfect individuals. Attention is called to the fact that this zooid is built on the plan of eight or two times four, not on the plan of six.

Among the Zoantharia or typical hexameral zooids the simplest form is represented by the modern genus Edwardsia, a type which does not build a skeleton. Figure 2 shows that this form is bilaterally symmetrical; a ciliated groove is located at either side of the stomodæum, the sulcus at the lower (ventral) and the sulculus at the upper (dorsal) side. The muscle banners on the four axial mesenteries (the directive mesentric couples) are turned away from one another and away from the axis of symmetry; those on the other four mesenteries are turned toward the sulcar side of the zooid. The cross section of this zooid differs in only two particulars from that of an Alcyonarian; there are two ciliated grooves in the stomodæum

\*H. N. Moseley, Phil. Trans. London, vol. clxvi, p. 91 ff, 1876. +G. C. Bourne in "A Treatise on Zoology," Lankester ed., Anthozoa, pp. 79-80.











FIG. 7. Zoanthus, after Bourne. I-VI the first six pairs of mesenteries; 7-9 couples added later.

FIG. 8. Cerianthus, based on the work of Boveri and Bourne. Numerals and figures indicate the order of development of the mesenteries.

FIG. 9. Hypothetical section across a young Streptelasma profundum showing the original eight mesenteries; the beginnings of the corallite are indicated by the shaded part of the figure. FIG. 10. View looking into the calyx of an adult Streptelasma profundum;

FIG. 10. View looking into the calyx of an adult *Streptelasma profundum;* (republished from the Ann. N. Y. Acad. Sci., vol. xix, p. 55). The tertiary septa are greatly exaggerated in apparent size because of the sloping walls of the cup. These really extend but a small fraction of an inch from the wall in toward the center of the cup.

FIG. 11. Hypothetical cross section of a zooid to fit the cup shown in fig. 10. I, I, etc., are the eight primary mesenteries. It is possible that all of the mesenteries reached the stomodæum. The dorsal member of each couple is represented as incomplete because the tertiary septa, assumed to have developed in the exocoeles, are always short and do not appear till late in the life of the individual. instead of one, and the muscle banners on the sulcar couple of mesenteries are turned away from the axis of symmetry instead of toward it. The tentacles in this type are simple as in other Zoantharians, not branched or pinnate as in the Alcyonaria. Nevertheless, the underlying eight-fold structure is very evident; furthermore complex Zoantharian zooids with a few exceptions pass through a stage in their development which corresponds to the adult condition in *Edwardsia*. This has been called the Edwardsian stage.

Great emphasis has been laid upon the fact that the muscle banners on the sulcar directive mesenteries in the Zoantharia are turned away from the axis of symmetry while in the Alcyonaria they are directed toward this axis. A study of the early stages in Zoantharian zooids, and of the order of introduction of the mesenteries in these, indicates that there are always eight primary mesenteries corresponding to the eight mesenteries of *Edwardsia*, but that the position of the muscle banners upon these mesenteries, the particular order of their introduction, and their final position in the zooid, are features which are not constant. A few examples will illustrate these points.

In such genera as Actina, Sagartia and Bunodes, investigations of the early stages of development have shown that the first eight mesenteries to develop correspond to the Edwardsian mesenteries, and that they have the muscle banners similarly placed. The order of appearance of these mesenteries is indicated by the numerals in fig. 3. The first pair appear on either side of the stomodæum and divide the cavity of the zooid into two unequal parts, a smaller sulcar and a larger asulcar space. The second pair is introduced, one on either side of the asulcar end of the axis of symmetry; these are the asulcar (dorsal) directives. The third pair is introduced in a corresponding position at the sulcar end of the axis; these are the sulcar (ventral) directives. The fourth pair is introduced, one on either side of the stomodæum between the first and second pairs. After a short pause the fifth and sixth pairs are added, one in each of the sulcar and middle lateral chambers, making the typical twelve of the hexameral forms. These twelve mesenteries form six couples; two of these, the sulcar and asulcar directives, have the muscle banners turned away from each other. In the other four couples formed by the fourth and fifth, and first and sixth mesenteries on either side of the stomodæum, the muscle banners are turned toward one another. The spaces enclosed within any one of these couples is called an entocoele; the spaces between the couples are called exocoeles. It can be clearly seen that these genera pass through an eight-mesenteried stage in the course of their development, and the mesenteries of this stage correspond exactly with those of *Edwardsia*.

## 540 T. C. Brown—Development of the Mesenteries

In such genera as *Rhodactis*, *Halcampa*, and *Manicina* a course of development is followed which is indicated in the diagram, fig. 4. This differs from the preceding figure only in the order of appearance of two pairs of the first eight mesenteries. The asulcar directive mesenteries are the fourth to appear instead of second as in the preceding examples.

In fig. 5 is shown the order of appearance of the mesenteries in *Aiptasia diaphana*. Here the eight first mesenteries appear in exactly the same order as that illustrated in fig. 4, but the muscle banners on the first pair of mesenteries to appear are located on the ascular instead of on the sulcar side of these mesenteries. Furthermore, the fifth and sixth pairs of mesenteries appear almost simultaneously in the space between the first and second pairs; as a result that pair which probably corresponds to the sixth appears on the ascular side of mesentery number one instead of on the sulcar side. Additional couples of mesenteries are introduced as indicated in the figure.

In Gonactinia prolifera a condition occurs in which there are sixteen mesenteries present as indicated in fig. 6. Eight of these are complete and extend from the outer wall to the stomodæum; these correspond exactly with the eight mesenteries in *Edwardsia*. The other eight are all incomplete; two pairs of these correspond to the fifth and sixth pairs of mesenteries in the normal actinian and form couples with two of the complete pairs; the other two pairs form couples in the asulcar exocoeles.

A consideration of these figures shows very clearly that the order of appearance of the eight primary mesenteries is not constant; that the position of the muscle banners on these primary mesenteries is not constant (e. g., position of muscle banners of first pair of fig. 5, compared with the corresponding pair in figs. 2, 3, 4); and that the point at which the later mesenteries are introduced is not constant (compare the sixth pair in figs. 5 with the corresponding pair in figs. 2, 3, 4).

Lacaze Duthiers pointed out long ago that the first two pairs of mesenteries in modern Zoantharia appear soon after one another, and that there is then a pause before the third pair appear. The fourth pair succeeds the third pair rapidly and a longer pause ensues. Finally the fifth and sixth pairs appear almost simultaneously. Thus in the early development the factor four is the dominant factor, not six as is generally assumed. This prominence of the factor four in the early development of typical hexameral forms, and the prominence of the Edwardsian stage in the development of all of these forms, have led the writer to believe that all Anthozoa are derived from forms with an original tetrameral plan, and that upon this original tetrameral plan a radially symmetrical hexameral plan has been superposed in the case of the Mesozoic and later Zoantharians. This original tetrameral, or, more correctly, bilateral symmetry has been retained unmodified by the Alcyonaria and the Paleozoic Rugosa.

The importance of this underlying bilateral symmetry becomes more evident when such aberrant types as the Zoanthids and Cerianthids are taken into consideration.

The Zoanthids are forms which do not build skeletons; the order of development of their mesenteries is shown in fig. 7. The first eight or Edwardsian mesenteries develop exactly as they did in those forms illustrated by fig. 4; they differ only in that the fourth pair remains incomplete, i. e., does not reach the wall of the stomodæum. The fifth pair always and the sixth pair generally remain incomplete. Additional mesenteries are added in couples at only two points, in the sulcolateral exocoeles adjacent to the third mesentery on either side. Eech couple consists of a complete or macromesentery and an incomplete or micromesentery. The complete mesentery is always located on the sulcar side and the incomplete mesentery on the ascular side of the couple.

In the Cerianthids a very different course of development is found; this is shown in fig. 8. The first four pairs of mesenteries that appear have been compared with the first four or Edwardsian mesenteries of *Halcampa*, but the ciliated groove between the third pair seems to be a sulculus, not a sulcus; hence the axial direction is really reversed. The remaining mesenteries are added in a peculiar way; the fifth pair is introduced in the space between the fourth; the sixth pair in the space between the fifth, and so on. Therefore, after the first four pairs, mesenteries are added in pairs and at only one point in the zooid.\* Duerden has shown that the mesenteries are introduced in a similar manner in certain of the zooids of Porites.

The foregoing discussion shows that in a great many (perhaps most) of the Zoantharia, a resting stage occurs when only eight mesenteries have been formed. If at this stage of the development a corallite or skeleton should be formed it evidently would have only four septa and later septa would be added in accordance with the mode of addition of the mesenteries, since in all Zoantharia with skeletons the septa are known to arise in the intermesenterial spaces.

It has already been shown that a stage does occur in the Paleozoic Rugosa when only four septa are present.<sup>+</sup> Fig. 9

\*In fig. 8, and the description here given I have followed the figures of

arve by Boveri and description here given 1 have followed the lightes of agree with S. J. Hickson, Camb. Nat. Hist., vol. i, p. 368, fig. 163 (3), 1909. †C. E. Gordon, this Journal, (4), vol. xxi, pp. 109–27, 1906. R. G. Car-ruthers, Ann. Mag. Nat. Hist., (7), vol. xviii, pp. 356-63, 1906. T. C. Brown, this Journal, (4), vol. xxiii, pp. 277-84, 1907; Ann. N. Y. Acad. Sci., vol. sin pp. 45, 27, 1000. vol. xix, pp. 45-97, 1909.

has been drawn to show the probable condition at this stage in the development of such a type as *Streptelasma profundum* from the Middle Ordovicic. Additional mesenteries were evidently added in both the counter and cardinal quadrants of the Rugosa as they are in the sulcar lateral exocoeles of the Zoanthids as suggested by Duerden. Fig. 10 is a view looking down into the cup of an adult specimen of *Streptelasma profundum*, while fig. 11 shows the hypothetical arrangement of the mesenteries in the stomodæal region of an adult zooid of this species. The apparently perfect radial symmetry possessed by many adult forms among the Rugosa (e. g., *Streptelasma corniculum* and *S. rusticum*) is a character acquired late in life and is in no way connected with the early development of the individual.

As a result of the studies here briefly summarized, and of others not yet completed, the writer has arrived at the following conclusions:

1. All Anthozoa, Paleozoic, Mesozoic, and Modern, are derived from one common stem form in which the zooids were bilaterally symmetrical and probably had eight mesenteries.\*

2. One branch from this common stem, arising early in the Ordovicic, leads up to the modern Alcyonaria (Octocoralla). To this grand subdivision probably belong all such genera as *Columnaria*, *Favosites*, *Heliolites*, *Syringopora*, etc., which are either without septa, or have apparent septa (pseudosepta) or septal spines which bear no direct relation to the soft parts of the zooid in either number or position.

3. Another branch from this common stem, likewise arising early in the Ordovicic, embraces the typical tetrameral corals of the Paleozoic—the Rugosa, having eight primary mesenteries and four primary septa, with secondary septa inserted in the four primary exocoeles in a unilateral pinnate manner, and with tertiary septa inserted late in life in the secondary exocoeles. This branch of the Zoantharia became extinct, in North America at least, at the close of the Paleozoic.

4. Another branch from the common stem gave rise to the Mesozoic and later Zoantharians—Actinians, Scleractinians, Zoanthids, and Cerianthids. All of these pass through an eight-mesentery (Edwardsian) stage in their development, but the great majority of them acquire a later secondary radial symmetry. The particular mode of arriving at this six-fold symmetry varies greatly in the different subgroups.

Bryn Mawr College, Bryn Mawr, Pa.

\*Compare G. C. Bourne, "A Treatise on Zoology," E. Ray Lankester editor, Anthozoa, pp. 55-56.
## ART. XXXV.— The Use of the Roentgen Ray in Paleontology. Skiagraphy of Fossils; by RICHARD M. FIELD. With Plate VIII.

#### THEORY OF SKIAGRAPHY.

In the spring of 1914, while studying some fossil brachiopods in the paleontological laboratory of Harvard University, the idea occurred to the writer of using the Roentgen rays as a means for investigating the internal or hidden structures of fossils. The wonderful strides which have been made in diagnosis and medical research during the past few years are well known to the physician, the recent progress of whose knowledge of such concealed and intricate processes as digestion, bone diseases, and all sub-surface phenomena of the human body is largely due to the means which the ray affords for direct observation of the processes at work and the structures of the diseased and fractured tissues. With the advent of skiagraphy (X-ray photography) came the possibility of retaining an accurate and permanent picture of the structure to be examined. The clearness with which the ray will skiagraph even minute details upon the X-ray, or modified, photographic plate, is indeed amazing.

The writer believes that this method of investigation has been little appreciated by others than those of the medical profession. Why should not the scientist make use of skiagraphy for investigating inorganic as well as organic structures? The paleontologist may ask the following questions :—

1. Will the X-ray penetrate those inorganic substances which cause petrifaction ?

2. If penetration is effected will a skiagraph result which faithfully reproduces the hidden structure of the petrifaction to be examined ?

With these questions in mind the writer made a hasty survey of English, French and German literature to see what investigations had been made along these lines.

As early as 1895 Professor Roentgen had examined, by means of the fluoroscope, a sheet of zinc composed of small plates soldered laterally together with solders of different metallic proportions. The different lines of shadow caused by the difference in solders were visible evidence that a new means had been detected for discovering flaws and chemical variations in metals. The writer was at first unable to discover whether more had been done in developing the use of the Roentgen ray for determining inorganic structures. Mineralogists are aware of the interesting discoveries of Laue and Friedrich\* and the recent masterly application of these results,

\*"Interferenzerscheinungen bei Roentgenstrahlen und die Raumgitter der Krystalle"; von W. Friedrich, Zeit. für Kryst. u. Min., vol. lii, p. 58, 1913.

543

by Dr. W. H. Bragg of the University of Leeds, to the discovery of the molecular structure of crystals. Such investigations, although of great importance in themselves, are of little service in solving the problem at hand. Bragg deals with crystallized, not composite, mineral structures. Unfortunately it was not until his own experiments had been performed that the writer became aware of the work of Bruhl, Doelter and Branco, the latter having made somewhat extensive experiments as late as 1906. Branco's results are particularly interesting and well worth attention. The writer believes, however, that his paper has been read by few, if any, paleontologists in this country, and it is largely for this reason that the following communication is presented.

In 1896 Bruhl\* had asked the question: "Can the X-ray be projected through the sedimentary rocks, and if so, what will be the degree of the intensity of the penetration in the different clastic rocks"? His experiments showed that "mineralized fossils wholly or half buried in the rock might be discovered."

C. Doelter<sup>+</sup> experimenting in 1896 arrived at the general conclusion that certain minerals were more impervious to the ray than others. He states that :—

1. A comparison can not be made between the "durchlässigkeit" (degree of penetration) and the thickness (under 1 centimeter).

2. A comparison can not be made between the chemical composition and the degree of penetration.

3. Twinning does not affect the degree of penetration.

Doelter experimented with a large group of minerals. The following table is compiled from a few of his examples :

Substance	Thickness	Degree of penetration		
Amber	1 · 1 <sup>mm</sup>	Easily penetrated /		
Jet	1.2	"	"	
Graphite	2.9	66	"	
Kaolin	2.2	"	"	
Opal	2.2	Penetrated		
Quartz	2.6	66 <sup>1</sup>		
Plagioclase	2.6 - 2.7	"		
Gypsum	2.2	Penetrated	with	difficulty
Chalk	2.7	66	66	۳ ،
Aragonite	2.9	"	" "	"
Marcasite	5.3	Impenetral	ole	

\*" Uber Verwendung von Roentgenschen X-strahlen zu paleontologischdiagnostischen Zwecken," Verhandl. Berlin. Physiol. Gesellsch., Archiv für Anat. und Physiol. p. 547, 1896.

† "Verhalten der Mineralien zu den Roentgenschen X-strahlen," Neues Jahrb. Min., II. pp. 87-106, 1896.

Another interesting table is to be found in vol. 50 of the International Library of Technology, page 71. In this table the transparencies (penetrabilities) of the various minerals and substances are compared with that of water. Only the figures for water, glass and the metals are given below :

Substance	Specific gravity	Transparency
Water	1.00	1.000
Aluminium	2.67	<b>·3</b> 80
Glass	2.70	·340
Tin	7.29	·118
Zinc	7.16	·116
Iron	7.78	.101
Nickel	8.51	.095
Copper	8.92	·084
Silver	10.24	.070
Lead	11.39	.055
Mercury	13.59	.044
Gold	19.63	.030
Platinum	21.53	·020

From these tables we learn at a glance that a large number of inorganic substances may be distinguished from each other by means of the Roentgen apparatus, and the intensity of their shadows registered by skiagraphy.

Doelter's table is interesting in that it shows the carbonaceous substances to be the ones which are the most easily penetrated by the ray. On the other hand, the metallic sulphides are the most impenetrable. Again, gypsum, chalk and aragonite are penetrated with more difficulty than kaolin, quartz and plagioclase. Obviously, the different effects of the ray on the sulphides of the metals, marcasite and pyrite, from those upon calcite, aragonite and quartz, are of especial interest to us in connection with the investigation of structures in fossils. If we now turn our attention to the mineral composition of fossils and fossiliferous rocks, we see at once the possibility of determining, by means of the ray, not only the presence of fossils hidden in the rocks, but also, which is more important, we should be able to discover the internal structures of the fossils themselves, when such structures have been preserved. As has already been stated, Branco,\* inspired by Doelter's earlier work, made numerous experiments with both vertebrate and invertebrate fossils. His well-illustrated paper proves without doubt the possible application of skiagraphy to fossil diagnosis. Many of Doelter's experiments have been independently proved by the writer. Moreover, the writer's experiments with brachiopods were especially productive of interesting results and it is in the study of this class of invertebrate fossils,

\* "Die Anwendung der Roentgenstrahlen in der Palaeontologie." Abhand. Berlin. Akad., 1906.

545

as well as because of certain results obtained through the use of newer and hence more powerful and accurate apparatus, that the writer is able to add something to the previous work on this subject. None of the writer's investigations could have been possible had it not been for the kindness, generosity and skill of Dr. Walter James Dodd, who for years has devoted his energies to the development and manipulation of the Roentgen apparatus. About thirty skiagraphs were taken at Dr. Dodd's laboratory. All the fossils used in the experiments were selected from the collections belonging to the Laboratory of Paleontology at Harvard University.

#### TECHNIQUE.

The writer does not feel justified in entering into a discussion of the general methods of skiagraphy. The subject is complex and its practice requires the knowledge and experience of the expert who has learned to manipulate his appara-Much remains to be learned regarding the best methods tus. for the skiagraphy of inorganic substances and experiments carried on by the paleontologist in connection with the physicist should yield the best results. As stated elsewhere in this paper, the best skiagraphs can only be obtained by one having an intimate knowledge of the nature of the petrifaction. The physicist knows the limits and possibilities of his apparatus and the paleontologist is needed to select the material for the experiments and to interpret the results. Working together, the physicist and the paleontologist should be able to develop the technique of the skiagraphy of fossils just as the surgeon and the physicist have worked such wonders in skiagraphy of the human tissues. Any apparatus that will give a 6 to 10 inch spark can be used for skiagraphing fossils. In making the plates used for illustrating this article the penetration was raised from 7 to 10 Benoist, which is equivalent to from 70,000 to 100,000 volts and 50 milleamperes. Experiments showed that for specimens of low density (comparative) more contrasty skiagraphs could be obtained by using an intensifying screen and lower voltage, say 50,000 to 60,000, the exposure in this case being  $\frac{1}{4}$  second. No exposures were made of over one second duration. The special photographic plates which are used for organic investigation were found to work equally well for the skiagraphy of fossils. When placing the fossil on the plate care should be exercised to have the structures to be discovered nearest the plate and farthest from the source of the rays.

#### EXPERIMENTS IN SKIAGRAPHY OF FOSSILS.

In the preliminary experiments it was discovered that a pencil of rays having an intensity of 6 Benoist could easily

penetrate specimens of such rocks as shale, sandstone and limestone at least 2 centimeters thick. It was also found upon examining the skiagraphs that the surface inequalities of the specimens had been faithfully reproduced. This discovery led to experiments with rocks which bore merely the print of an organism, such as the moulds of striated brachiopods and of the cephalon and pleura of trilobites in a sandstone. As had been expected from the first experiment, the resulting skiagraphs showed the surface details almost as clearly as if they had been photographed. Having determined that the ray would penetrate and record upon the X-ray plate the graphs of the common sedimentary rocks up to at least 2<sup>cm</sup> in thickness, the next problem was to determine if the X-ray would bring out on the X-ray plate some petrified organism which was partially exposed on the surface of a sedimentary rock. It had already been discovered that inequality of surface was skiagraphed upon the X-ray plate by the penetrating ray. It was therefore natural to suppose that the slightly elevated form of any fossil preserved upon the surface of a thin section of rock would be skiagraped upon the plate when subjected to the penetrating ray, no matter if the fossil itself were composed of the same material as the rock which partly enveloped it. But what would be the fate of that portion of the fossil which remained hidden? Experiment shows that it will be registered when the fossil is composed of a substance whose density is greater or less than that of the matrix in which it lies. Physicists agree that theoretically the ray penetrates with an intensity which is indirectly proportional to the atomic weight of the substance treated. This fact has long been recognized by users of the Roentgen apparatus who protect themselves from the ray by means of a thin lead screen (see table on previous page). In the early days of experimentation with the X-ray no protection was afforded the eyes of the operator from the rays, which emanated from the tube in all directions. Recently it has been discovered that a shield made of glass which has a high percentage of lead added to the melt during its manufacture partially prevents the escape of the rays except within the limited direction required.

In the latter case we have a solid solution of nearly the same transparency as ordinary glass but which has had its density increased by the addition of an element of high atomic weight, thus rendering it much more impenetrable to the ray. (It is not certain whether the lead oxide is held in solution or suspension.) Bearing these facts in mind we should expect to discover the clearest definition of structure on the skiagraph when the mass to be penetrated is made up of compounds whose elements show the greatest differences in atomic weights. As we shall see later, we are dealing, in practice, with difference in density as well as difference in atomic weight, the closeness with which mineral particles are bound together and the amount of foreign matter which they (the crystals) occlude during their crystallization having an important effect on the degree of the penetrability of the mass. Few, if any, petrifactions have a uniform density throughout.

For the next experiment the writer selected a specimen of Triarthrus becki from the Utica shale of Rome, N. Y. This well-known species of trilobite is found in this locality as a pseudomorph of pyrite whose iron content causes it to be much more impervious to the ray than the highly carbonaceous shale in which it is embedded. A section of the shale 3<sup>mm</sup> in thickness was prepared (see fig. 9) placed upon the X-ray plate in the same position as shown in the figure and subjected to the rav. The results obtained are illustrated in figures 10 and 11. Unfortunately it is impossible to get the same amount of detail in the reproduction as in the original skiagraph. In the original skiagraph a close examination shows certain covered portions of the trilobite to be revealed. As shown in the accompanying figure the left antenna and the entire border of



Diagrammatic sketch made from skiagraph of the specimen of *Triarthrus becki* shown in fig. 9 of Plate viii, x 2. On comparison with the specimen, it may be seen that the skiagraph brings out the outline of the trilobite and several appendages which are buried in the matrix. the shield are outlined in the skiagraph, while they are not shown in the photograph. Fig. 9 also serves to illustrate the effect which the ray has on the shale itself. The black spots represent segregated material, probably pyrite, more impervious to the ray than the bulk of the shale. It will also be noticed in the same illustration that the inequalities in surface are faithfully reproduced. This experiment alone does not prove, however, that the X-ray will discover all fossil structures of a subsurface nature. Organisms which are replaced by the heavy metallic sulphides are quite rare as compared with the number of calcareous and siliceous forms. What is more, it is unusual to find fossils where different parts have been replaced by minerals of distinctly different atomic weights, as, for instance, in

the Atrypa reticularis with calcarcous valves and pyritic spires, or in certain fossils with calcarcous valves and siliceous spires. Also in both these cases investigation of the internal structure is readily permitted by dissolving the cover with hydrochloric acid. Paleontologists have been bothered for

some time in their investigation of the internal structures of brachiopods where valves, spires, brachial supports, hinge teeth, have all been preserved by the same mineral, usually calcite or its allied form, aragonite. Attempts have been made to section brachiopods in which the internal structure has been preserved, and by a number of such sections to discover the form of the brachial support, form and location of the spires, etc. . . \* Such a method is not only tedious but also difficult to interpret in the attempt to delineate the true structures. Obviously, if a method could be evolved for depicting the internal structure of a brachiopod without a preliminary preparation of the specimen, such a method would be of distinct value to the paleontologist in his determination of genera. Figs. 6, 7, 8, show the first attempt to prove that the X-ray will determine structure, under favorable conditions, when the replacement of both valves and spires has been by siliceous material. Fig. 6 represents the photograph of the actual specimen with pedicle valve removed to show the spires and air space. Figs. 7, 8, are reproductions of the actual results obtained in the skiagraph. The spires are seen to be clearly distinguished from the shadowy outline of the brachial valve through which they have been projected by the ray. Obviously then, the ray will distinguish between siliceous spires and siliceous valves under favorable conditions. Will the ray distinguish between spires and valves under less favorable conditions, namely, under the conditions in which fossil brachiopods are usually found ? Figs. 3, 4, 5 show the duplication of a skiagraph in which the spires are found to be faithfully delineated within the shadows of both valves. Owing to the added thickness of the pedicle valve and want of air space between the spires and the valves the graph is less distinct than in 7, 8, but still plainly recorded on the X-ray plate. It is, therefore, possible to discover, by means of the Roentgen apparatus, the internal structure of a fossil brachiopod when the said structure is entirely hidden from sight. The fossils selected for this experiment were composed of a mineral which is penetrated with more difficulty than calcite or aragonite (see table on previous page), thus the above statement holds good for calciferous replacements.

#### Conclusions.

The writer's experiments have led him to believe that in the majority of cases where internal structures are present in fossils they may be discovered by means of the X-ray. Slight differences in density are bound to arise, due to the varying conditions of replacement by crystallization, between the sub-

<sup>\* &</sup>quot;Internal characteristics of some Mississippian Rhynchonelliform shells," Geol. Society of America, vol. xxi, pp. 497-516. Also by the same author, "Genera of Mississippian loop-bearing Brachiopoda," Jour. of Geol., vol. xix, No. 5, 1911.

## 550 R. M. Field—Roentgen Ray in Paleontology.

stances which form the interior and exterior portions of the petrifaction. Slight as these density differences may be, we have seen that they will be registered in the skiagraph. Undoubtedly, such conditions as the presence of air space between structures and great difference in density between the internal and external structural substances afford the most favorable opportunity for obtaining good results. However, when we realize that the physician is now able to distinguish not only between bone and muscle tissues but also between the inner and outer layer of the epidermis, it would seem possible for the paleontologist to develop the X-ray method to a high stage of usefulness.

The best results are obtained by studying the original skiagraph as shown in the exposed and developed X-ray plate, for even a print loses greatly in detail. When an enlarged photograph of the original skiagraph is made, a print taken from this and the result used for illustrative purposes, it can be readily seen that a great deal of the original detail will be lost.

In getting "results" in the skiagraphy of inorganic just as of organic substances, a great deal depends on the ability of the investigator to interpret what he sees. Owing to the present rapid increase in number of Roentgen apparati the expense of making skiagraphs of fossils should be relatively nominal. When we consider the number of small fossils which can be crowded on a  $10 \times 10$  photographic plate and skiagraphed in a few seconds, we realize the value of this method of investigation to the biologist and paleontologist.

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#### EXPLANATION OF PLATE VIII.

1. Print from original skiagraph of *Cleiothyridina devonica*, showing lack of preservation of internal structure.

2. Reproduction of skiagraph of Spirifer oweni, showing internal structure.

3. Photograph (enlarged) of *Cleiothyridina sublamellosa* with both valves in place.

4. Reproduction of skiagraph of same specimen.

5. Print from original skiagraph.

6. Photograph (enlarged) of *Cleiothyridina sublamellosa* with spires exposed.

7. Reproduction of skiagraph of same specimen.

8. Print from original skiagraph.

9. Photograph of Triarthrus becki in shale.

10. Reproduction of skiagraph of same specimen.

11. Print from original skiagraph.

(NOTE.) In the original skiagraphs the denser portions of the fossils are shown by the denser shadows. When a print is made directly from the skiagraph, as shown in figs. 5 and 8, the lights and shadows are naturally reversed. The dark central circles shown in figs. 4 and 7 have nothing to do with the internal structure of the fossil but are the result of the diffusion of the rays, causing a supplementary illumination on the X-ray plate. The two fine, hair-like, black lines in fig. 7 are due to scratches on the original skiagraph.

# Am. Jour. Sci., Vol. XXXIX, May, 1915.



























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## ART. XXXVI.—A New Ordovician Eurypterid; by Ellis W. Shuler.

DURING the summer of 1914, the writer collected fossils from the Bays sandstone at various points along Walker Mountain in southwestern Virginia. The collection at Lyons Gap yielded a few Eurypterid fragments. This is one of the best known localities for collecting in the Bays sandstone. Prof. J. J. Stevenson visited the locality in 1884 and secured a number of fossils among which were "Ambonychia radiata" and "Rhynconella capax" (= Orthorhynchula linneyi), and since that time it has been visited by a number of other geologists. These facts are mentioned because the Bays sandstone formation is for the most part unfossiliferous in Walker Mountain. The fossiliferous localities are limited to the southwestern section of the mountain along a band about twenty miles in length.

At Lyons Gap the fossil-bearing bed is about ten feet in thickness and occupies approximately the middle of the Bays formation, ninety feet below the Clinch sandstone. The point, however, of separation of the Bays sandstone from the Sevier shales below is a somewhat arbitrary one. The bed is an argillaceous sandstone which has a pronounced brick red color. It seems worthy of note that the bed carrying marine fossils is distinctly redder than the non-fossiliferous part of the sandstone. The southwestern section of the Bays sandstone along Walker Mountain, carrying the fossiliferous horizon, is also, on the whole, a deeper red than the section along the mountain to the northeast, which is practically barren of fossils.

#### Stylonurus (Ctenopterus)? alveolatus sp. n.

The Eurypterid fragments consist of parts of four post-oral limbs; a part of the telson spine with the impression of two abdominal segments, and a fragmentary carapace.

The best preserved fragment is that belonging to the second or third endognathite, fig. 4. It consists of three segments, all of which, after making allowance for mashing due to the conditions of preservation, show a distinct dorsi-ventral flattening. The articulation of the joints is such as to permit flexing movements downward and backward, an arrangement which suggests an adaptation of the limb to swimming. The individual segments are distinctly elongated, being on the average twice as long as wide. The lengths of the successive segments beginning with the proximal one are:  $16^{\text{mm}}$ ,  $16^{\text{mm}}$ , and  $20^{\text{mm}}$ . The corresponding widths are:  $10^{\text{mm}}$ ,  $8^{\text{nm}}$ , and  $6^{\text{mm}}$ .

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 233.—May, 1915. 36

#### 552 E. W. Shuler-New Ordovician Eurypterid.

The posterior margin of the proximal joint is supplied with two prominent spines or flattened bristles, the larger of which occupies the distal corner. This is the largest spine preserved. It has a length of  $41^{\text{mm}}$ . The width,  $2^{\text{mm}}$ , is fairly uniform along its whole length. In common with the other spines it originates in a projecting alveolar process or ring-like swelling of the integument at the base, which from its unusual development, is a significant characteristic of this species. The smaller





FIGS. 1-6. Stylonurus (Ctenopterus) alveolatus sp. n.

Figure 1. A part of the telson spine with the impression of two abdominal segments. Figure 2. Moulds of the tubercles on a fragment of the carapace ( $\times$  2). Figure 3. Endognathite probably belonging to the first pair of post-oral appendages. Figure 4. Endognathite belonging to the second or third pair of post-oral appendages. Figure 5. Undetermined fragment of an appendage. Figure 6. A fragment of a joint from the walking leg. All figures except figure 2 natural size. The specimen represented in figure 4 is to be considered the holotype of the species.

spine has a measured length of 14<sup>mm</sup>. The broken jagged ends indicate that the spines were originally much longer.

The adjacent segment shows four alveolar processes with parts of three spines preserved. Again the distal corner was occupied by the largest spine. All spines have been lost from the third segment but five alveolar processes are seen, the distal one being the larger. The alveolar processes in all the segments have a distinct serial arrangement along a median line. The pronounced flattening of the bristles or spines gave a much enlarged paddle-like surface to the whole endognathite.

The anterior margins of the segments show a smooth arcuate curve without dentition. The joints show the expected thickening around the articulating surfaces.

The second appendage, fig. 3, also shows three segments. These are shorter and more robust than the joints of the appendage just described. They do not show spines, though this may be due to the conditions of preservation. The fragment is probably a part of the first endognathite. The measurements, beginning with the proximal joint, are as follows: length,  $8^{mm}$ ,  $7^{mm}$ ,  $7^{mm}$ ; the corresponding widths are:  $4^{mm}$ ,  $2 \cdot 5^{mm}$ ,  $2^{mm}$ .

A part of the telson spine with the impression of the last two abdominal segments is shown in fig. 3. The posterior segment has a length of  $16^{\text{mm}}$ ; the second has a length, estimated from the curvature of the mould, of  $19^{\text{mm}}$ . A number of measurements of *Stylonurus* and other Eurypterida showed a rather constant ratio between the length of these two segments and the total length of the individual. This ratio was approximately one to eight. While no special stress is laid on such a ratio, it is interesting that this would indicate that the complete specimen was  $280^{\text{mm}}$  long (about eleven inches).

Fig. 6 represents what appears to be a segment of one of the walking or balancing legs, typical of *Stylonurus*. It has a length of  $30^{\text{mm}}$ , but this probably does not represent the total length of the segment. The width at the proximal end is  $4^{\text{mm}}$ ; at the distal end,  $2 \cdot 5^{\text{mm}}$ . Fig. 5 shows a fragment of an unidentified limb.

The fragment of the carapace shows the mould of one of the compound eyes, two depressions questionably identified as ocelli, and the impression of a rough tubercular surface. The supposed ocelli lie well back behind the compound eye and the general appearance is more that of *Eusarcus* than *Stylonurus*. The state of preservation is, however, such as to preclude a definite identification or exact description. Fig. 2 shows an enlarged view ( $\times$ 2) of the tubercular moulds.

This merostome has been provisionally referred to *Ctenopterus*, a sub-genus of *Stylonurus*, on account of the long flattened segments of the endognathite; the lack of serrations on the segments such as is found in *Eurypterus*; the presence of the long joint belonging probably to the walking leg or balancer, characteristic of *Stylonurus*; and the long broadened spines or bristles which are especially characteristic of the subgenus *Ctenopterus*. It has been given the specific name *alveo*- *latus* in recognition of the very pronounced development of the alveolar processes surrounding the spines.

The endognathites figured above are in many respects similar to those figured by Clarke and Ruedemann (N. Y. State Museum Memoir 14, 1912, Vol 2, p. 541) under the name Stylonurus (Ctenopterus) multispinosus. This species possesses elongated joints fringed with spines along the posterior margin. While there is a difference in the general shape of the joints the chief distinction between the species multispinosus and alveolatus is in the prominent development of the alveolar process and the unusual size of the distal spine in the specimen from the Bays sandstone. Stylonurus (Ctenopterus) multispinosus Clarke and Ruedemann occurs in the Pittsford shale of the Middle Silurian. It is interesting to find an Ordovician species so strikingly similar to a form which comes from a much higher horizon in the Silurian.

Dr. Bassler and others have correlated the Bays sandstone with the Lorraine of New York. Dr. A. W. Grabau has made it the equivalent of the late Maysville and Richmond. The general character of the fossils collected with the Eurypterid fragments certainly establishes a correlation with the Upper Ordovician, and probably Maysville rather than Richmond.

In the "Table of the Geologic Distribution of the North American Species of Eurypterids at Present Known" (N. Y. State Bull., Memoir 14, 1912, p. 431), representatives in the Ordovician have been reported from the Normanskill shale, the Schenectady beds, and the Utica. One species has been reported from the Richmond.

The bionomic interest of the find lies in the association of the fragments with a typical marine fauna. One of the joints was found resting against a specimen of one of the most abundant of the Bays brachiopods. Such an association falls in line with the general occurrence of Ordovician Eurypterid remains with those of marine organisms. The delta-like and near-shore character of the Bays sediments is evident. But though the fragmental character of the Eurypterid remains indicates transportation and a consequent breaking up of a complete exoskeleton, the occurrence at Lyons Gap gives no indication that this took place in a fresh water stream rather than in surf along the shore. On the whole, the find seems to confirm Laurie's suggestion that *Stylonurus* possessed purely littoral habits.

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# ART. XXXVII.—A New Mosasaur from the Ft. Pierre; by F. B. LOOMIS.

JUST west of the Black Hills in Wyoming there stretches from southeast to northwest a great belt of black shales of the Ft. Pierre age. The scarcity in them of both invertebrate and vertebrate fossils has caused these beds to be neglected, not to say shunned; for the abundance of alkali in the shales makes camping in the region a dubious pleasure, However on the high ground west of Edgemont, near the heads of the small streams, some vertebrates have been found, the first by the American Museum of Natural History, which however were in such hard concretions as to make their preparation and study impractical, and again by the Amherst College expedition of 1903, these latter being in the shales and in a fair state of preservation. This collection was made at the head of Mule Creek, 20 miles due west of Edgemont, and contains a fair fauna of both invertebrates and vertebrates, the most interesting of which is a set of mosasaur bones belonging to a new species and represented by practically all parts of the skeleton.

The invertebrates occurred in concretions at the same locality and horizon and are useful in determining the age of the horizon. I give the list of shells found which are typically Ft. Pierre species:

Inoceramus sagensis var. nebras-	Protocardia rara E & S
censis Owen	Callista deweyi M & H
Inoceramus crispii var. barba-	Callista peplucida M & H
bini Morton	Anisomyon subovulatus M & H
Yoldia ventricosa M & H	Entalis? paupercula M & H
Nuculana ? equilateralis M & H	Vanikoro ambigua M & H
Pteria linguiformis E & S	Aporrhais biangulata M & H
Pteria nebrascana E & S	Fasciolaria? flexicostata M & H
Chlamys nebrascensis M & H	Heteroceras?cochleatum M & H
Syncyclonema rigida M & H	

Beside the invertebrates there occurred a series of vertebrates which in their generic features resemble a Niobrara fauna, but they are specifically different though the preservation is not sufficiently good to use them to make new species. In their preservation there was some crushing, and the cracks filled with gypsum, later expanding so that delicate bones are usually distorted and very difficult of preparation.

556	F. B.	Loomis-Neu	Mosasaur	from the	Ft.	Pierre.
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Elasmobranchii	Corax	represented	by	2 teeth and three strings of vertebræ.
Teleostomi	Portheus	"	"	one pair of lower jaws.
	Ichthyodectes	66	66	18 strings of vertebræ, by portions of the tail, and by the dentale and maxilla.
	Saurocephalus	66	"	2 crushed skulls.
	Empo	66	"	skull bones and vertebræ.
	Pachyrhizodus	۰ ،	"	vertebræ.
Reptilia	Platecarpus	66	"	many parts of skeletons.
	Elasmosaurus	"	"	1 paddle and part of a second.

The mosasaurs were far the most abundant fossil and the best preserved. We found one skeleton with a complete skull followed by 23 vertebræ and their ribs all in place, a second consisting of a disassociated skull, 7 anterior vertebræ and a scattered front paddle, a third consisting of parts of the skull and 56 vertebræ from the mid-body to the middle of the tail, another consisting of the front paddle practically all the phalanges being in place, and a dozen less important specimens, one a considerable part of the posterior paddle. These are the basis of the new species to be described. They were all found within 100 yards of each other not varying in horizon more than 10 or 15 feet.

#### Platecarpus brachycephalus sp. nov.

I take as the type the disassociated skull, No. 389 in the Amherst Collection, and as a cotype the complete skull No. 398. To what these give, I add data and drawing from some of the other material from the same place and level.

The first question raised is as to the genus of the form. The following table gives the most salient features by which the mosasaur genera are subdivided.

In the brevity and width of the skull, the small number of teeth in the maxilla, the Amherst specimens resemble Brachysaurus, but in the shape of the humerus, in the fact that the suprastapedial process of the quadrate is not coosified with the base of the quadrate behind, and in the fact that the chevrons of the caudal vertabræ are free and articulated to the centra, it resembles Platecarpus. In the major and in a number of minor features the form is intermediate in character between the Ft. Pierre genus Brachysaurus and the Niobrara genus Platecarpus, but I consider it nearer to Platecarpus as its differences from Platecarpus are mostly in degree, while those from Brachysaurus are positive ones and mark a wider diver-

					and and a second s
Genera	Horizon	Praemaxillo- nasals	Maxilla	Quadrate	Caudal vertebræ
Clidastes	Niobrara to Ft. Pierre	Rostrum sharp, of mod. length: median ridge separate teeth	15–16 teeth	small : suprastape- dial process long but not fused.	7 pygals: chev- ronsfused: tail broadened.
Tylosaurus	Niobrara	Rostrum very large and long: smooth below	13 teeth	medium: suprasta- pedial process small, not fused.	6 pygals: chev- rons artic- ulated.
Mosasaurus	Niobrara	Rostrum me- dium size and short : median groove.	14 teețh	medium : suprasta- pedial process short, not fused.	
Brachysaurus	Ft. Pierre		11 teeth	moderately large : suprastapedial pro- cess long and fused.	chevrons fused :
Platecarpus	Niobrara to Ft. Pierre	Rostrum small, obtuse, and short : smooth below.	12 teeth	large : suprastape- dial process large, not fused.	5 pygals: chev- rons artic- ulated.
Amherst specimen	Ft. Pierre	Rostrum small, obtuse, and short: median ridge behind teeth.	11 teeth	large : suprastape- dial process very large, not fused.	5 pgyals: chev- rons artic- ulated.

gence. I have therefore placed this in the genus Platecarpus\* though I realize that it represents an intermediate relationship.

Platecarpus has a couple of rather doubtful Ft. Pierre species, ? P. latispinis Cope, based on one cervical and five dorsals, peculiar in the considerable length of the diapophyses, and of a size about 25 per cent larger than P. bachycephalus: and P. tectulus Cope, based on a number of cervical and dorsal vertebræ of unusually small size. The Amherst material can not be associated with either of these.

The skull as a whole is remarkable for its extreme brevity and width. As found it is crushed from above downward, to which is due the abnormal position of the jugal bones (see fig. 1). The nares are well forward, short and relatively wide. The orbits are short and wide. The exoccipital region is prolonged considerable back of the condyle, much further than

\*I use the term Platecarpus for this genus as the one in common use. Hay, in his Bibliography of Fossil Vertebrates of North America 1902, uses Marsh's name, Lestosaurus. The priority is dependent on the final determination of dubious types, which has not yet been done. See Williston, Univ. Geological Survey of Kansas, vol. iv, p. 178.

usual. The total length of the skull from the snout to the occipital condyle is  $510^{\text{mm}}$ .

The premaxillæ are fused to each other and to the nasals, and are characteristically short and blunt, making a very short rostrum in front of the four teeth, which they carry. On the ventral surface there originates a median carina just behind



FIG. 1. Top view of the skull of the cotype. 1/6 nat. size. f, frontal; j, jugal; l, lacrymal; mx, maxilla; n, nasal; p, parietal; pf, prefrontal; pmx, praemaxilla; psq, presquamosal; q, quadrate.

the teeth, which does not project between them, but is continued backward onto the vomers. Between the nares the fused nasals make a moderately wide septum, which however in the middle of the span is narrowed for a short distance to about  $10^{\text{mm}}$ .

The vomers are wide and fill in the anterior part of the space between the maxillæ. The sutures about the vomer are not clear, but the species is peculiar in that the palatal vacuity (which is usually in two parts, a smaller anterior and a larger posterior) is so reduced that only the posterior portion remains open.

The maxillæ are heavy bones and each carry but 11 teeth, (a very small number for any mosasaur) which are the typical acrodont, striated, conical teeth, compressed toward the points from the inside toward the outside: These teeth like those of the lower jaw are rather slender, and from 25 to 30<sup>mm</sup> long. All eleven need not be on the jaw at once, for the replacement is of the typical reptilian type in which there is a tendency for each alternate tooth to be in some stage of replacement, in which case even the bony base on which they are situated may be for the time eliminated.

The prefrontal is short and wide and extends about half way along the external margin of the naral opening, as is typical in Platecarpus. The lachrymal is of small size and bounds the anterior external side of the orbit.

The frontals are fused into a broad roofing bone, extending from the nares back almost to the parietal opening. There is little distinctive about this bone, except that on either side is a groove beginning shortly behind the naral opening, extending backward obliquely toward the median line, then turning sharply outward and dying out near the orbit about opposite the parietal foramen.

The parietal is not so bounded that the outline can be made out, but it has a fair-sized parietal foramen. The preservation of the back of the skull does not permit describing the sutures of such bones as the postfrontal, the presquamosal, postorbital, or exoccipital.

The jugal makes a short arch, which in the specimen found extends laterally; but this is doubtless due to crushing, the normal position of the bones being under the orbit, in which case there is nothing unusual about this bone.

The quadrate is very characteristic, first in its large size as compared with the rest of the skull. Its lower articular surface for the mandible is rather small, and expanded on the outer side. The body of the bone projects forward and swings in an almost complete circle around the auditory meatus, the suprastapedial process being very large, its distal end almost reaching the base of the quadrate; but there remains a narrow and well marked opening between the end of the process and the base of the bone, which distinguishes the form from Brachysaurus where the process is coosified with the base of the quadrate. On the external face of our quadrate the margin of the upper articulation projects laterally, making a rim which extends clear around to the base, in front being developed into a thin plate. The immediate border of the meatus is also

raised in a low rounded ridge, so that between this and the external rim there is a shallow channel. On the inner surface the margin of the meatus is beveled and the external edge rounded. The large oval stapedial pit is situated very high up (see fig. 2) as in Brachysaurus and Platecarpus, lying at the upper end of the meatus notch.



FIG. 2. The quadrate from the inner side showing the stapedial pit. 1/2 nat. size.

The lower jaw is unusually long and fairly slender, and carries in my specimen 7 teeth with places for four more, making a total of 11 teeth for the dentale. This bone projects a short distance in front of the first tooth and extends back so as to make over half of the mandible. Externally it is ornamented with longitudinal striæ. The splenial (presplenial) is exposed externally only below the posterior end of the dentale. The articulare is large and extends from the rear of the dentale back beyond the articular fossa. In this species is found but very little of the articular fossa, that being carried mostly by the supra angulare. This latter bone is unusually large, covering almost all the space back of the dentale and above the

articulare, while the coronoid is only a small bone making a low process. In all these features the mandible resembles that of Platecarpus.

For determining the vertebræ specimen No. 388 aids greatly with its 23 vetebræ in place. On this specimen the first long

FIG. 3.



FIG. 3. The mandible from the outer side. 1/6 nat. size. a, articulare; c, coronoid; d, dentale; sa, supra angulare; sp, splenial.

rib (i. e. probably reaching to the sternum) is on the eighth vertebra. Then follow 10 long ribs, after which the ribs are much shorter. The specimen with 56 vertebræ begins in the middle of the long ribs. There are twelve with short ribs and clearly five which are noncostiferous (at this point the series is disarranged). Following this are 24 anterior caudals with chevrons, then a break of several vertebræ, followed by 14 caudals from well down in the tail. Williston gives the vertebral formula for Platecarpus as 7 cervicals, 22 dorsals, 5 pygals and 80? caudals = 115? for the full series. With the above, the Amherst specimens agree; so that if restored the form, *Platecarpus brachycephalus* would appear just about as does *P. coryphæus*<sup>\*</sup> and would be about 15 feet long.

In the cervical series, the atlas consists of three small nodular pieces, of which two are preserved. The intercentrum is a tiny bone with three principal faces, of which the two upper articular ones are slightly concave, while the ventral one is convex with a slight median prominence for muscular attachment. Only one lateral piece is present which is distorted by the infiltered gypsum, but seems to be normal to the genus. The rest of the cervicals have suffered in preservation so that the ends of the spines and processes are crumbled and partly gone. On the axis the odontoid is a separate element, and is a three-sided nodule with a rounded convex anterior surface and

\* Williston, Univ. Geol. Survey of Kansas, vol. iv, plate LXXII.

with concave faces on the rear and anterior sides. The axis has a stout nodular hypophysis below and heavy transverse processes. The posterior articular end of the centrum is concave and almost circular in outline. The remaining cervicals are similar in shape, except that the centrum is convex in front and concave behind and the hypophyses are progressively smaller. Each carried a small rib on its transverse process.

The dorsal vertebræ have no hypophyses. The transverse processes are short and heavy, and from the anterior of each process a heavy ridge extends forward continuing into the prezygapophysis. The spines are of moderate height and each



FIG. 4. A dorsal vertebra (6) 1/4 nat. size. FIG. 5. A caudal vertebra (8) 1/4 nat. size.

about as broad (antero-posteriorly) as the length of the centrum. The postzygapophyses are small and situated above the neural canal on the spines. Each pair is close together, making the interlocking of the vertebræ very close. The neural canal is remarkably small.

The pygal vertebræ<sup>(</sup> (noncostiferous) number five, have no hypapophyses, very large transverse processes, weak zygapophyses and strong spinous processes.

On the caudals the transverse processes at the anterior end grow progressively smaller toward the rear and soon disappear. On the ventral side are chevrons which are free and articulated with the lower surfaces of the centra. In the anterior regions the caudals are robust, but toward the rear become more and more flattened from side to side.

Length of the cervical series (7)	$260^{\mathrm{mm}}$
Length of the dorsal series (22)	1265
Length of the pygal series (5)	250
Length of the caudal series $(25 = 1050^{\text{mm}})$	
estimated	2200
Length of the skull	510
0	

 $4485^{\text{mm}} = \text{about 15 feet.}$ 

The ribs are single headed and simple. Their varying length give an idea of the size of the body as follows:

Cervica	l rib	3	$54^{ m mm}$	Dorsal	rib	6	$420^{mm}$
"	"	4		"	"	7	370 +
"	"	5	116	66	"	8	408
"	"	6	132	66	"	9	370
"	66	1	475	66	"	10	350
Dorsal	rib	1	320	66	"	11	202
"	"	<b>2</b>	330	66	"	12	175
66	"	3	350	٤٢	"	13	160
"	"	4	410	"	"	14	155
"	"	5	390 +	"	"	15	140

The ossified portion of the scapula has the distal articular end greatly thickened, its rounded roughened surface showing two faces, both convex, the one for the coracoid, the other for the humerus. The neck is strongly constricted; the anterior margin is the shorter, and deeply concave; the posterior border is longer and less concave; the proximal border is rogose and highly convex. The bone as a whole is flat and moderately thin.

The coracoid is larger than the scapula but like it a fanshaped bone. The articular end is not as swollen as that of the scapula, and it presents two surfaces, the one for the scapula, the other for the humerus. The anterior margin is short and slightly concave; the posterior margin longer and much more concave; the inferior border is convex, and about a fourth of the way from the front has a deep notch as seen in the figure (fig. 7). I do not find beside this a coracoid foramen as is typical for Platecarpus.

The humerus is remarkable for its distal width, being actually greater than the height of the bone (exaggeration of Platecarpus). The proximal end is only slightly convex, the articular surface being greatly thickened opposite the pectoral process. The distal end makes nearly a half circle, the articular surfaces for the radius and the ulna being thick-

ened, between which two surfaces the humerus is pinched into relative thinness. The radial border of the humerus is the shorter and is so concave as to be almost a notch; the ulnar border is slightly longer and not quite so concave. A strong



FIG. 6. The right scapular from the outer side. 1/4 nat. size.



FIG. 7. The left coracoid from the outer side. 1/4 nat. size.

pectoral process rises a little to the radial side of the humerus and extends three-fourths of the length of the bone; the cartilaginous surface extending about to the middle of the humerus. This is the most strongly developed pectoral process I have seen recorded, being an exaggeration of the large one typical of Platecarpus.

The radius is the larger of the forearm bones. Its proximal end is greatly thickened opposite the middle of the inner

side, so that in an end view the articular surface is broadly triangular. The distal end is rounded and but slightly thickened. The anterior border is the longer, both it and the posterior border being moderately concave.

The ulna is the small forearm bone, its upper end being considerably but uniformly thickened. Distally the articular surface is divided into two parts which meet each other in an obtuse angle.

One of the specimens which was found was an approximately



FIG. 8. The anterior paddle seen from the inner surface. 1/6 nat. size.

complete paddle with 6 carpal bones, the metacarpals and phalanges all in place. In fig. 8 these carpals are drawn as they were found, except that the sixth, which lay above the one marked  $\times$  and was like it including the notch, has been omitted as being either an extra, or at least out of place. All these carpals are probably too far toward the radial side. It is unusual for Platecarpus to have more than four carpals, but it is apparently a feature of this species. The metacarpals are

not greatly differentiated though the first is slightly larger than the others. The phalanges are those typical of the genus. We have two paddles to judge from, and they would seem to indicate that the formula was 4 6 6 6 4. This allows for one lacking on the first digit in my drawing, and for three lacking on the fourth and fifth digits.

The hind limb material is not as abundant or perfect as the front limb. I have no ilium or ischium. A femur, which must belong to this form as no other mosasaurs were found here, is a large flattened bone, expanded both proximally and distally. The articular ends, however, are only moderately thickened. The tibia is considerably the larger bone of the



FIG. 9. The hind limb showing the femur, tibia, fibula, tarsals, and four metatarsals. 1/6 nat. size.

two in the fore leg. It has the ends much thickened and expanded. The fibula differs from what would be expected, being very short, the ends thick and expanded, the inner border concave, and the outer c o n v e x and much t h i n n e d.

In the tarsus three bones were ossified, two larger and one tiny. This again is more ossification than is characteristic of Platecarpus. Four metatarsals were found with this specimen, all of generally uniform size, except that the fifth is expanded proximally as is typical.

Throughout the preceding description the figures are carefully drawn to scale, so that relatively few measurements have been given. I think it entirely safe to take others from the figures.

Amherst College.

FIG. 9.

# ART. XXXVIII.—Growing Crystals for Measurement; by JOHN M. BLAKE.

WHEN we have soluble salts to work upon we can, by proper treatment, grow crystals that are nearly symmetrical and complete in their parts, and that have the correct proportional development of planes belonging to the species. We do not as a rule, have this advantage with mineral species. We have to take the crystals as we find them. It is comparatively rare that complete crystals are found, and very often, the individual crystals are crowded together, so that, besides losing one end of each crystal, we have more or less distortion of form, and miss the correct proportioning that free-growing, suspended crystals should assume.

It is with the object of drawing attention to the importance of using free-grown crystals for the study of the laws that govern all crystal development, that this is written. Such crystals can easily be grown from solutions.

There are questions in regard to crystal-growth and development that seem important to test by experiment, and although some work has been done in this direction, the field appears worthy of further exploration. Some methods for growing will be given. Individual efforts in this direction will doubtless suggest improvements in apparatus.

The solutions of all salts can become supersaturated. The maintenance of this condition in proper degree has an important influence on the quality of the crystals obtained. It means a reserve of material which may require some time to deposit, and there are certain limits of saturation within which this reserve material will act selectively to the extent that it will favor our growing crystal without forcing other and undesirable crystals to start in growth. We have to wait for diffusion to take place to bring the material to the place it is wanted, and diffusion is slow through the bulk of the solution.

Control of temperature is of the first importance in gaining and maintaining the proper degree of supersaturation. If we cool a hot saturated solution, and the salt is being deposited rapidly, a crystal suspended in it will have an upward current flowing from it of solution that has become lighter from loss of deposited material. On the contrary, if we suspend a crystal in an under-saturated solution, a current of dense solution will flow downward from the crystal as it slowly dissolves. During a very rapid deposition of material there will be a lively commotion from the ascending currents. It

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 233.—May, 1915. 37 is important to work within limits which will not give rise to noticeable currents during the deposit, since these currents tend to cause irregular action on the parts of a growing crystal, and may be expected to result in a loss of symmetry. We wish to allow the natural forces that govern crystal growth, unrestrained action, since the correct proportional development of the planes should be one object of our measurement.

The most familiar examples of artifical crystals are produced by allowing saturated solutions to cool. Thus, very beautiful large crystals are grown in the manufacture of salts on a large scale, where the bulk of the solution is large, and the cooling occupies considerable time. But these crystals, since they are grown in groups, or attached to a support, have no chance to complete their form.

The writer had some success in working this cooling method while using limited quantities of solution. This solution was placed in bottles which were suspended in a large cask filled with hot water. The cask was packed in sawdust in a large containing box. The crystals to be grown were suspended in these bottles. This bulky apparatus might be replaced by a smaller reservoir with a source of heat regulated by an adjustable thermostat.

Two other plans will be mentioned which can be made to give good results. The first is to fill a large test tube with saturated solution, and support it in an inclined position. This position is taken to prevent particles of salt from falling upon the growing crystal. A small crystal is cemented to a wire or splint, and supported centrally toward the bottom of the tube. Next, a thimble made of fine brass wirecloth may be pushed down the mouth of the tube an inch or more, and the supply of material for growing is supported on this wirecloth, or, instead, the material may be retained in a cloth bag. Heat is supplied to the upper part of the tube by a thin strip of sheet copper one quarter of an inch wide, one end of which is to be bent around the tube, and sprung on so that it can be slipped up and down, and retain its position.

The upper part of this strip, close to the tube, is twisted one quarter turn, and also bent so that its surface takes a horizontal position. A gas flame turned very low supplies heat to the strip, and by adjusting the distance along the strip the amount of heat supplied to the tube may be varied. This distance may, at times, be five inches or more. This apparatus can give a steady, constant growth to a crystal, and has given good results.

A second apparatus, which gave more freedom for suspending and removing the crystal, was made of a half-pint tumbler having tapering sides. A copper wire was bent and tied into

a hoop which could be crowded down one inch from the top of the tumbler. Cotton cloth was stitched upon this hoop, and a one-half inch hole hemmed in its center. This formed a shelf to support the feeding material, while the crystal to be grown was hung by a thread to a wire placed across the hole. The heat was supplied by a resistance element consisting of two feet of No. 35 resistance wire doubled on itself, and wound spirally around a copper wire. The two ends were soldered to thicker wires for connecting. These wires were then varnished and inclosed in a small rubber tube with only the thicker connecting wires projecting from one end. Both ends of the rubber tube were cemented, to exclude water, and the tube was then bent into a circular shape to be stitched to the lower side of the cloth shelf, but, first, the connecting wires together with one end of the rubber tube were brought up through the cloth shelf, a hole being made for this purpose. The top of the rubber tube was made to stand a trifle below the top of the tumbler, while the wires passed out over its edge. The mouth of the tumbler was covered with a glass plate. Heat was obtained from a small six volt door-bell transformer connected to the street current.

Another successful plan was tried later. This was to wind the resistance wire around the outside of the test tube, or the neck of a long, wide-mouth vial, and coat the wire with varnish to prevent short circuit. The material for growing was suspended in a small cloth bag, and the vial was tilted so that the growing crystal would swing free from the sides.

This apparatus was used for growing crystals for measurement, and for experiments on supercrystallization of isomorphous salts. Also, some experiments were made to produce planes that are not of frequent occurrence, but which actually belonged to the species under treatment. For instance, a sphere of the salt was ground and polished, and was then grown a short time. This gave every plane a chance to assert itself, and the peculiar change the polished sphere took on after a very short growing treatment was very interesting. The light could be flashed from the fine step-like surface growth, and when mounted for measuring, the zone system of measurement which the writer advocated many years ago, could not very well fail to bring out the full complement of planes. See this Journal, May, 1866.

This experiment led to a possible explanation for the occasional finding of rare and exceptional planes which might be formed when crystals have been rapidly and partially dissolved, but certain rounded surfaces were still left; and this solution was followed by a cooling, and a deposit of the salt which might result in developing the rare planes. It should be understood that the carefully grown crystals often lack these rarer planes, but by the careful growing we obtain the correct proportions as a whole. Some of these planes would be represented on a drawing as a very narrow plane, while on the actual crystal this part might have a sharp edge with no trace of a plane. Our carefully grown crystal can be filed off and made round on the edges, and then grown again for a short time to brighten the surfaces, and then the rare planes can be looked for.

Further, it should be noted that the distortion which results from the crowding of growing crystals, for the reason that it gives rise to an unequal distribution of growing material, will often cause the broad development of planes which may be narrow or absent in the carefully grown, suspended individuals. To give such planes unnecessary prominence on a drawing that is designed to show a naturally proportioned crystal would be incorrect. If the drawing was for the purpose of merely showing the position and intersection of the planes, it would be admissible.

As a rule, a system of weeding out will have to be followed to prevent useless growth from absorbing too much of our growing material. That is, if we aim to produce large crystals.

When a crystal is taken from a solution, it should be blotted off at once with absorbent paper in order to preserve its brilliancy. Before returning it to a fresh growing solution, it should be dipped in water for a short time to insure that no abnormal growth can take place from unobserved nucleii that may be adherent.

It is desired to awaken interest in the subject, and to give a partial idea of what we may hope to accomplish by such experiments, and also to suggest that the habits acquired by working over incompletely developed crystals may at times lead us to overlook some things that may be of importance. In growing crystals with this object in view, the highest success will be likely to follow a slow, constant and uninterrupted deposition, together with the necessary careful control of temperature.

New Haven, Conn., February 15th, 1915.

## ART. XXXIX.—The Primary Analcite of the Crowsnest Volcanics; by J. D. MACKENZIE.

THE writer recently published a description of some analcitebearing pyroclastics which occur in southwestern Alberta,\* and interpreted the nature of the analcite as primary. In the light of the facts of the occurrence as fully described in the publication referred to, it was not thought necessary to consider the hypothesis that the analcite might be secondary.

However, in a recent number of this Journal+ a review questions the writer's conclusions and suggests that what is now analcite may have been originally leucite, and that it has become converted to analcite by sodium solutions, through a process the possibility of which is suggested by Lemberg's experiments. The reviewer's questions are principally based on a misinterpretation of the conditions of deposition of the pyroclastics as described, and also to an inferred doubt that primary analcite could form under the conditions of eruption.

It is the intention of the present note to show: (1) that under the conditions described there is no reason to suppose the conversion of the analcite to be probable; (2) that the possibility of conversion is doubtful, even with conditions such as the reviewer imagined; and (3) that it is quite possible for analcite to form under the conditions described.

(1) In the article under consideration<sup>‡</sup> the writer, when summarizing the conditions of deposition of the Crowsnest volcanics, stated that :

> "... the area they now cover was occupied by a shallow sea probably of fresh water . . . .

the evidence for this conclusion being given elsewhere in the article. It might have been better to have used the term "lake" instead of "sea," and a further ambiguity is introduced two lines below by the word "submarine"; this should be "subaqueous." Despite these inaccuracies of statement, it seems clear from the context that the volcanics were described as having been deposited in fresh water. However, the evidence for the character of the water is not conclusive, and it may have been brackish, or salt; nevertheless it was more probably fresh, and was so described. Thus, the assumption by the reviewer of "solutions of sodium salts" is not justifiable from the writer's description, and the evidence in hand

<sup>\*</sup> Geol. Surv. Canada, Mus. Bull. No. 4, Geol. Series No. 20, Nov. 19, 1914. † Vol. xxxix, p. 222, February, 1915. ‡ Op. cit., p. 13.

indicates no reason to suppose conditions favorable for the conversion of leucite to analcite to have been present.

(2) Supposing, however, that the pyroclastics were deposited in salt water, we may critically inquire into the possibility that the present analcite represents converted leucite.

Lemberg's experiments\* clearly show that finely-powdered leucite is converted into analcite by treatment with solutions of sodium salts. This reaction, it is indicated, may take place even with rather dilute solutions and at relatively low temperatures. While these experiments are significant, the extent to which they may be called upon to explain analcite occurrences in igneous rocks is problematical.

In the case under consideration the analcite phenocrysts are euhedral trapezohedrons up to one inch in diameter, and form 50 per cent of the volume of the rock. Fifty per cent of the remainder are composed of smaller analcite phenocrysts and analcite in the groundmass. The analysis of the phenocrysts shows that the analcite is in a high state of purity.

The large trapezohedrons in thin section are quite homogeneous, with the analcite cubic cleavage well developed, proving that they are single individuals. That this condition resulted from a conversion of leucite to analcite seems inconceivable. Lemberg's experiments, carried out on finely-powdered material, throw no light on the mechanism of the change. Whether it is a molecular exchange, or merely a substitution of sodium for potassium atoms with the taking on of a molecule of water, we can only surmise. In either case, the conversion would proceed from the exterior of the crystals inward, and it is altogether unlikely that the conversion would have been so complete in every case as to leave no trace of the original leucite. Supposing a replacement by equal volumes to have taken place, it is probable that a granular aggregate of analcite would replace the original leucite, a tendency which would be accentuated by the fact that leucite generally is composed of twinned layers.

If, instead of replacement by equal volumes, the molecules of analcite be supposed to take the place and orientation of the original leucite molecules, an increase of volume of about 10 per cent would result, with accompanying distortion, an effect that has not been observed.

The analcite-bearing rocks are, as described,<sup>+</sup> very slightly altered. This is a strong argument for the primary character of the analcite, and the writer would refer to Pirsson's wellstated argument in maintaining the primary nature of the analcite in some of the basalts from the Highwood mountains.<sup>‡</sup>

\*Zeitschrift der deutschen Geol. Gesellsch, xxviii, pp. 535, et seq., 1876.

<sup>†</sup> Op. cit., p. 28.

<sup>‡</sup> Jour. Geology, vol. iv, p. 686, 1896.

The statements there made are strikingly applicable to the analcite rocks of the Crowsnest volcanics. In particular it is not reasonable to suppose the complete transformation of leucite to analcite could take place in the presence of the easily altered nephelite, and the latter remain unaffected, and the same argument applies to the ægirite and ægirite-augite. Both nephelite and ægirite, in fact, according to Brögger,\* may alter to analcite, and if conditions were favorable for the complete transformation of leucite into that mineral, surely the nephelite, ægirite, and ægirite-augite would not remain unaffected.

Washington also, in discussing the primary nature of the analcite<sup>+</sup> in some basalt flows of Sardinia, presents a similar line of arguments, and in view of these, and the facts and reasons stated above, the possibility that the blairmorites of the Crowsnest volcanics were originally leucite rocks seems to be highly improbable.

(3) Finally, the possibility of primary analcite forming in eruptive lavas remains to be considered. From the character of the analcite-bearing rock (op. cit., p. 20) it is quite apparent that the analcites did not form in lavas "undergoing explosion" as suggested in the review.

Plainly, one-inch analcites could not form in a lava "undergoing explosion" unless we assume a virtually instantaneous growth of the crystals. The obviously intratelluric nature of these phenocrysts meets the objection that the pressure in the magma was not sufficient for their formation.

In order that analcite may form in a magmatic solution, it is necessary, so far as the water is concerned, that when the crystallization temperature of the mineral is reached, the pressure on the magma must be in excess of the partial pressure of the (gaseous) water at that temperature. It may be well to point out that the amount of analcite forming in a given case is not proportional to the pressure, but to the amount of water present. That the necessary pressure was realized in the magma chambers feeding the Crowsnest volcanoes is made evident by the nature of the blairmorite described. It is not a rock crystallized wholly under surface conditions, and on the face of it, the first generation of analcite phenocrysts formed *before* and not during explosion. This intratelluric nature of these phenocrysts necessitates their formation under pressure-obviously enough for analcite to form.

While it is not necessary in the case of the blairmorite to assume the actual formation of analcite in lavas undergoing eruption, such a thing is by no means impossible. The above

> \*Zeitschrift Kryst. Min., vol. xvi, pp. 223-333, 1890. †Jour. Geology, vol. xxii, pp. 749-750, 1914.

postulated conditions of partial pressure of the water vapor might conceivably be realized under surface conditions, so that even there analcite could form.

Some of the Sardinian basalts recently described by Washington<sup>\*</sup> are examples of rocks consolidating at the surface and containing analcite, though it is possible that here, too, the mineral is intratelluric in origin. The shackanite of Daly<sup>+</sup> may be also mentioned in this connection.

With the facts of the original paper in mind, and their further explanation here given, the primary nature of the analcite of the Crowsnest volcanics can not be open to any reasonable doubt.

Massachusetts Institute of Technology, Boston, Mass. March 15, 1915.

> \* Jour. Geology, vol. iv, pp. 742-753, 1914. † Geol. Surv. Canada, Mem. 38, p. 411, 1912.

# ART. XL.—New Genera of Permian Reptiles; by S. W. WILLISTON.

AMONG the new genera of Permian vertebrates represented by material in the collections of Yale and Chicago Universities there are two presenting such peculiar characters as to justify their present description. A third new genus of reptiles from New Mexico is represented by parts of two skulls and will be described later. Two distinctive genera of small amphibians from New Mexico, of new and peculiar types, are also represented in the Chicago collections by skull and limb bones.

#### Glaucosaurus megalops, gen. sp. nov.

The type and only known specimen of the present genus and species is an incomplete skull of small size discovered by Mr. Paul Miller on Mitchell Creek, Texas, in the same horizon as that of the type of *Broiliellus*, that is, from the lower part of the Texas beds. The same horizon has also yielded five specimens of *Pantylus*. numerous specimens of different species of *Captorhinus*, *Theropleura*, etc., none of which has ever been detected in the uppermost deposits.

The skull (fig. 1) had been fossilized complete, but, when found, the lower posterior part and much of the roof of the occipital and parietal region were gone. Enough remains, however, to indicate approximately the contour of the quadrate region.

The skull is remarkably narrow and high, reminding one of the general shape of the chameleons. It has a high, thin, nose-like face, very much like that of *Edaphosaurus*, with the external nares near the pointed end, and separated by a narrow bar of bone. There are two teeth on each premaxilla, of small size, and fifteen on each maxilla, the latter increasing a little in size as far as the twelfth; the last two are smaller. Some of the teeth have been injured on the outer side in preparation, showing a hollow cavity, but their outlines are visible in nearly all. They are rather obtusely rounded at the extremity, the front ones more acute. They appear to be acrodont, but are, in all probability, protothecodont. They are not cuspidate. The most peculiar character of the skull, one that dis-

The most peculiar character of the skull, one that distinguished it from the skulls of other known genera, is the relatively enormous size of the orbits, their greater diameter being nearly equal to one-half the whole length of the skull, and considerably more than the length of the face in front of them. In life they looked nearly directly outward, with a

## 576 Williston—New Genera of Permian Reptiles.

slight inclination forward. The mandibles have a considerable depth posteriorly, but are thin, and can have only a single row of teeth. Back of the orbits the thickened, smooth border of the anterior inferior angle of the temporal opening is apparent. The structure here was probably much like that of *Edaphosaurus*, the lower bar broader and the quadrate in all probability not descending so low. Above, posteriorly, only the impressions of the roof bones with clinging fragments are preserved. The region here is similar to that of *Edaphosaurus*.





FIG. 1. Skull of *Glaucosaurus megalops*, from side and from above. Natural size. No. 603, University of Chicago.

The orbital margins are rather prominent, and the frontal region between them is concave. The sutures, so far as they have been made out, are shown in the drawings.

In the general shape of the skull *Glaucosaurus* seems to resemble *Tetraceratops* Matthew, from the Permian of Texas, but the genus differs markedly in the absence of rugosities for nasal and frontal horns, and especially in the teeth. Moreover, the orbits are much larger. Two or three genera of Permian reptiles from Texas are yet known only from skeleton bones, and there is a possibility that some one may eventually be found to be identical with the present, but, upon mature consideration, I believe that the probability is very slight.

One wonders what the habits of this creature, with such extraordinary eyes, could have been. Possibly it was crepuscular in habit, and probably a rock climber. That the genus must be classed with the so-called "Pelycosauria" or Theromorpha is evident, but closer relationships among the extraordinary diversity of the American reptiles can at present be but a mere speculation.
#### Chamasaurus dolichognathus gen. sp. nov.

Although the type and only known specimen of the present genus consists of the left mandible, lacking its posterior end, the characters it presents are so peculiar that they will justify its description.

The specimen was accidentally discovered in the matrix of dark reddish brown sandstone enclosing a type specimen of *Limnoscelis*, from the Permian or Permo-Carboniferous of New Mexico. The type specimen is No. 827 of the Yale Museum collections. The mandible (fig. 2) is especially note-

FIG. 2.



FIG. 2. Left mandible of *Chamasaurus dolichognathus*. Twice natural size. No. 827, Yale University.

worthy because of its slenderness. That it does not belong to an amphibian is evident from the teeth, which are closely set, flattened, and thecodont or protothecodont, characters unknown among the amphibians. The slight but distinct rugosities of the mandible are cotylosaurian rather than pelycosaurian, though this character is not unknown among the zygocrotaphous reptiles. Twenty-five teeth are preserved, the most of them perfectly. The first four or five, the sixteenth and the twenty-third are injured on their outer sides, but show for the most part their shapes. In front of these teeth there are alveolar emarginations for two more, which have been represented in the drawing by dotted outlines, making twenty-seven as the entire number. The teeth are very closely placed, almost touching each other at their bases. They are smoothly and gently convex on the outer side, from one and a half to more than two times as long as wide. They are rather acute and longer anteriorly; more obtusely pointed posteriorly. They are evidently inserted in a single row.

Sixty-two described genera of American Permian or Permo-Carboniferous amphibians and reptiles are at the present time recognized as presumably valid. A few of these are yet known only from incomplete or fragmentary material, and will not be securely established until more is known of them. About fifteen genera are now known from practically complete skeletons. In the Chicago collections forty-four distinct genera have been recognized, with two or three additional, more or less doubtful, described ones. Omitting the few doubtful genera there are to-day in the collections not less than sixty distinctly differentiated genera from the Permian deposits of Texas, Oklahoma, Kansas, New Mexico, Illinois and Pennsylvania, distributed about equally among the Amphibia, Cotylosauria and Theromorpha. They have been classified under at least twenty-three families, and ten larger groups.

As regards the distribution of these genera, twelve are known only from New Mexico, two from Oklahoma, two from Illinois, and two from Pennsylvania. Four genera are more or less doubtfully common to New Mexico and Texas, and four to Illinois and Texas. The four genera supposed to be common to New Mexico and Texas are Eryops, Aspidosaurus, Edaphosaurus and Diadectes, but it is probable that some of these, if not all, will be found to be distinct when more thoroughly known. The four genera common to Illinois and Texas are Lysorophus, Diplocaulus, Cricotus and Clepsydrops, the first three almost certainly; the last doubtfully the same. Not a trace of any one of these has been detected in New Mexico, of the first three not even their families, though it is possible that Chenoprosopus may be allied to Cricotus. Some of the most common genera in Texas are utterly unknown in New Mexico, notably Dimetrodon, Captorhinus, Labidosaurus, Diplocaulus, Lysorcphus and Trimerorhachis, and only the first of these is replaced by an allied form, Sphenacodon, so far as we know; while Theropleura of Texas is represented by the closely allied but distinct Ophiacodon; Diadectes, Diadectoides and Chilonyx by Nothodon, Animasaurus and Diasparactus; Zatrachys by Platyhystrix, etc. The genus Limnoscelis has no known allied form. Not a single one of all these American genera has been recognized elsewhere, though I am convinced from the examination of European specimens, as also from Huene's studies, that some of the known European forms are allied, possibly belonging in identical genera. Especially have I seen a part of a spine in the museum at Halle which I could not distinguish from the peculiar ones of *Edaphosaurus*; and long-spined, dimetrodont forms seem also to occur there. Broom and Watson have urged the relationships of some of the south African types with certain ones of America, and their arguments are persuasive; nevertheless, the relationships of the South African forms do not seem to be as close as do some of the European Permian genera. Perhaps, after all, as Case has urged, we are dealing chiefly with generalized rather than genetic characters.

That deposits no thicker than those of Texas and New Mexico should have already yielded so extraordinarily rich a

#### Williston—New Genera of Permian Reptiles. 579

fauna of amphibians and reptiles-and the end is not vet; that the local faunas of regions so little remote as those of Texas and New Mexico, though closely allied, should show such distinct generic differences, suggest that the world's fauna of reptiles at least, in early Permian times was richer in genera and species than it has been at any succeeding epoch in geological history. Divergence was limited by primitive characters, for evolution had not gone far enough to affect the more fundamental ones, but no other known epoch of approximately equal duration has yielded so extensive a fauna of cold-blooded airbreathing animals as has the Lower Permian of America. Of the genotypes, or specimens upon which the accepted described genera have been based, thirty are preserved in the collections of the American Museum, eighteen in the collections of the University of Chicago, six in those of Yale, four at Munich, and the remainder at the universities of Oklahoma, Kansas, Michigan and the Carnegie Institute.

# ART. XLI.—The Radium Content of Water from the Gulf of Mexico; by STEWART J. LLOYD.

The growing recognition of radium as an important factor in geological processes\* has led to a multiplication of analyses of rocks and soils, of springs and of river waters for that element. Our greatest reservoir of radium, the ocean, containing at a minimum estimate one thousand tons of the metal, has however received but little attention from investigators. It is much to be desired that determinations of the radium content of sea water from many different localities should be made, in order that some definite knowledge may be acquired as to the actual quantity contained in a unit volume, or if the content varies from place to place or from time to time, that we may learn definitely the extent of this variation and upon what it depends. The present paper contains, in addition to a brief statement of what has already been done in this field, the result of an examination of the water of the Gulf of Mexico, an area not hitherto covered.

The radium content of sea water has so far been measured by three scientists, Joly, Eve, and Satterly. The first<sup>+</sup> made determinations on waters from the Irish coast, from the North and South Atlantic, the Mediterranean, the Black Sea, the Arabian Sea, and the Indian Ocean, twenty-four in all. His results varied from  $38.0 \times 10^{-12}$  grams radium per liter of water to  $4.0 \times 10^{-12}$  grams, with a mean of 17.0. Quantities of water not exceeding 3,000<sup>cc</sup> were taken, evaporated to half the original bulk, acidified with hydrochloric acid and boiled to drive off the emanation. Save that the quantity of material used was rather small, and the percentage error correspondingly large, no particular fault can be found with his method.

Evet has measured on two separate occasions the amount of radium in water from the North Atlantic. His first result (1907) gave  $0.3 \times 10^{-12}$  grams radium per liter; the second (1909), to which he attaches much more weight, gave  $0.9 \times$ 10-12 grams.

Satterly§ examined in 1911 three waters from the coast of England, obtaining an average value of  $1.0 \times 10^{-12}$ .

Through the kindness of Mr. Truman Smith of Mobile, Ala., a sample of water from a point in the Gulf of Mexico about two hundred miles due south of Mobile was obtained. Seven

\* T. C. Chamberlain, Jour. Geol., xix, 673.

+ Phil. Mag. 1908, xv, 385, 1908; ibid., xvi, 190, 1909; ibid., xviii, 396, 1909. Radioactivity and Geology, page 46.
+ Phil. Mag. xiii, 248, 1907; ibid., xviii, 102, 1909.
§ Proc. Camb. Phil. Soc. xvi, 360, 1911.

and one-quarter liters of this water were evaporated down to 750<sup>cc</sup> whereby, of course, an abundant solid residue was obtained. Five cc. of redistilled, concentrated hydrochloric acid were added during the evaporation. Contrary to the general opinion the presence of a precipitate does not necessarily impair the accuracy of the determination,\* especially when several successive readings are made on the same sample.

The measurements were made in the usual type of vacuum electroscope with amber insulation. The transfer of the emanation from the flask containing the evaporated sea water to the electroscope was made essentially by McCoy's method,+ except that the emanation was collected over a warm saturated solution of sodium chloride. For standardizing the electroscope, Joachimsthal pitchblende containing 46.2% of uranium was employed. It was dissolved in nitric acid, diluted until 250<sup>cc</sup> contained amounts of radium of the same order of magnitude<sup>‡</sup> as the sample of sea water, and kept for thirty days before using in order to ensure the presence of the maximum amount of emanation. Following Rutherford it was assumed that one gram of uranium is in equilibrium with  $3.4 \times 10^{-7}$ grams of radium. Heinemann and Marckwald§ have recently obtained the value 3.328 for this constant, but the degree of accuracy of the present measurements is not sufficient to make it worth while to depart from the former value.

Three successive determinations on the same sample gave respectively 1.4, 1.75, and  $1.65 \times 10^{-12}$  grams radium per liter. As the first reading in such cases is usually low, the mean of the last two was taken, and 1.70 assumed to be the correct result. This figure is in comparative agreement with those of Eve and of Satterly, and disagrees radically with that of Joly, as is evident from the accompanying table :

Grams Radium per liter of sea water.

Joly	17.	Х	$10^{-12}$
Eve (1907)	0.3	X	$10^{-12}$
Eve (1909)	0.9	X	$10^{-12}$
Satterly	1.0	X	$10^{-12}$
Lloyd	1.7	X	$10^{-12}$

It is difficult to account satisfactorily for the extraordinary discrepancy between Joly's results and all the others. Α repetition of his work on the waters which gave him the highest figures, notably those from the Irish coast  $(34 \times 10^{-12})$ 

\* J. Phys. Chem., xiv, 476, 1910.

- + J. Am. Chem. Soc. xxvii, 402, 1905.
- ‡ Randall, Trans. Am. Electrochem. Soc., xxi, 496, 1912. § Jahrbuch Radioakt. und Elektronik, x, 299, 1913.

and from the equatorial region of the Atlantic  $(38 \times 10^{-13})$  would be of great interest.

If we exclude Joly's results and the earlier one obtained by Eve, we obtain as an average value for the radium content of a liter of sea water,  $1.2 \times 10^{-12}$  grams. This would correspond to a total amount of radium in the sea slightly exceeding 1400 tons.\* As the amounts of radium found in river waters are by no means sufficient to maintain this quantity of radium in the ocean, we must postulate the presence in the latter of an amount of uranium approximately sufficient to maintain the radium at its present value. To do this, since one gram of uranium is in equilibrium with  $3.4 \times 10^{-7}$  grams of radium, will require almost 4,200,000,000 tons of uranium, which may, therefore, be taken as the amount of uranium contained in the ocean. No attempt has so far been made to determine directly the uranium content of sea water, though the result would be of considerable interest. One hundred liters should contain, if the above figures are correct, from three to five tenths of a milligram of uranium, an amount of the same order of magnitude as that of gold in sea water.

Department of Chemistry, University of Alabama.

> \* Joly, Radioactivity and Geology, p. 48. † Clarke, Data of Geochemistry, p. 111, 1911.

# ART. XLII.—The Mobilities of Ions in Air; by E. M. WELLISCH.

#### 1. INTRODUCTION.

It is a well-known result of experiment that over a wide range of pressures the mobility (k) of the ion varies inversely as the pressure (p) of the gas through which the ion is moving. For the positive ion in air the law pk = constant has been verified down to a pressure of 1<sup>mm</sup>; Todd\* made several determinations at still lower pressures and found that below  $1^{mm}$  the value of the product pk showed a marked increase over its normal value. The case of the negative ion in air has been studied by a large number of experimenters who all agree in stating that the product pk increases when the pressure is reduced below about  $10^{cms}$ . Kovarik<sup>+</sup> detected an increase when the pressure was as high as 20<sup>cms</sup>. This result indicates a simplification in the nature of the ion as the pressure is reduced. Prof. Townsend drew attention to the necessity of thoroughly drying the gas employed in the experiments; it was then found that in a dry gas at low pressures the velocities of the negative ion reached very large values indicating that at least for part of its career it was in the electronic state. As a result of numerous experiments undertaken in conjunction with his students Prof. Townsend arrived at the conclusion that the velocity (v) of the negative ion should be expressed in general as a function of the electric field (X) and

the pressure (p) in the form  $v = f\left(\frac{X}{n}\right)$  indicating that the

nature of the ion depends in general on the field and the pressure. At the higher pressures v was directly proportional to

for moderate field strengths; this indicates that the negap

tive ion remains unaltered in character over this range of pressures. But although the results obtained by numerous experimenters were in accord as far as the general nature of the variation in the value of pk was concerned, a close examination of the actual values obtained revealed such discrepancies as to raise at least the presumption that some residual disturbing factor had not been eliminated or even detected.

The experiments which are described here were undertaken to throw further light on this phenomenon; the present paper must be regarded as merely a brief account of the results obtained in this connection as much of the data needs further

> \* Todd, Phil. Mag., ser. 6, xxii, p. 791, 1911. +Kovarik, Phys. Rev., xxx, p. 415, 1910.

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXIX, NO. 233.-MAY, 1915. 38

583

## 584 E. M. Wellisch—Mobilities of Ions in Air.

elaboration and the experiments are being continued in other directions.

#### 2. EXPERIMENTAL METHOD AND PROCEDURE.

Method.—The method employed to determine the mobilities of the ions was that devised by Franck and Pohl.\* In this method the ions are produced in the region above a gauze



FIG. 1.

and under the action of a steady field are drawn to the gauze; some of the ions diffuse through the meshes and come under the influence of an alternating electric field which is established between the gauze and a parallel electrode connected to an electrometer. If the frequency of alternation of the field be kept constant and the current which is conveyed to the electrometer be determined for different values of the alternating field, the mobility of the ion under the given conditions can in general be estimated by means of certain formulae given later.

Vessel.—The vessel employed in these experiments (fig. 1) consisted of a brass cylinder  $(10^{cms} \text{ in diameter})$  divided into two compartments by a brass partition containing a circular

\* Franck and Pohl, Verh. Deuts. Phys. Ges., ix, p. 69, 1907.

aperture 3<sup>cms</sup> in diameter. In the upper compartment was a copper plug on which was a deposit of polonium which had been kindly prepared for me by Professor Boltwood; this plug was placed near the circumference of the partition and extreme care was taken that all the radiation was confined to the upper compartment. A circular electrode A (4<sup>cms</sup> in diameter) was situated about 3<sup>cms</sup> above the aperture and was in metallic contact with the case of the vessel. The lower compartment contained the gauze electrode insulated by a thin ebonite ring from the partition. The gauze consisted of brass wire '77mm thick with  $6\frac{1}{2}$  meshes to the cm. Two cms. below the gauze was the electrode e connected to the electrometer; surrounding this electrode was a guard ring which was metallically connected to a guard screen (W) consisting of a gauze cylinder mounted on a circular plate. Both the ring and the screen were connected to earth by means of the guard tube shown in the diagram. The object of the screen was mainly to prevent disturbing effects which might arise as a result of the rapid changes in potential undergone by the case of the vessel. The insulation consisted throughout of ebonite.

Four brass tubes admitted of connection between the vessel and other apparatus; through one of the tubes the air was admitted after passage through glass tubes containing  $P_2O_5$ , CaCl<sub>2</sub>, and glass and cotton wool. Pressures above 2<sup>cms</sup> were read on a mercury gauge one limb of which was evacuated ; pressures below 2<sup>cms</sup> were ascertained by means of a McLeod gauge. Both a Fleuss and a Töpler pump were used for purposes of evacuation. By means of the cylinder and reservoir containing mercury of which a sketch is given in the diagram the air was passed several times through a tube containing  $P_2O_5$ ; in this way any traces of water vapor could be removed before observations were made.

The Commutator. — The commutation of potential was effected by means of the principle employed by Langevin in his experiments. This is illustrated in fig. 2. The two potentials  $V_1$  and  $-V_2$  under consideration were connected across the terminals of a large metal resistance R. The commutating device consisted of a circular brass disc with a number of equally spaced slots cut at regular intervals along its periphery; these slots were filled with vulcanized fiber which was made flush with the curved surface of the disc. Brushes consisting of bent copper strips were mounted at regular intervals on a circular frame close to the disc. Mounted on the same shaft as the commutating disc, and in metallic connection with it, was a collector ring consisting of a brass disc  $4\frac{1}{2}$ <sup>cm</sup> in diameter. The commutator was placed between that end of the resistance connected to the gauze and the point whose potential was V,

## 586 E. M. Wellisch—Mobilities of Ions in Air.

(K in diagram); between the commutator and V, was a potentiometer device consisting of a tray of cells (v) joined to the terminals of a Wolff potentiometer (r). In the steady state when the brushes are not in metallic contact with the commutator the potential of K is  $-V_2$ ; when the brushes are in contact with the disc the potential of K is readily deducible by an



application of Kirchhoff's laws; if x denote the potential at K we deduce

When the commutator is in action the potential of K should vary sensibly between x and  $-V_2$  provided we maintain satisfactory relations between the frequency of commutation and the resistance R. We shall revert to this point later on, but at present the assumption will be made that the potential of the gauze is given by x and  $-V_2$  alternately, the former potential lasting for a fraction f of the total time. This fraction can be determined experimentally. Under these conditions it is easy to deduce the expression for the mobility (k) of the ion under consideration after a series of experiments has afforded the value of the critical potential  $(V_0)$  which is just sufficient to bring the ions over to the electrode e. If n be the number of complete alternations per second and d the distance between the gauze and the electrode, we obtain

$$k = \frac{d^2 n}{f \mathcal{V}_0} = \frac{4n}{f \mathcal{V}_0} \text{ for } d = 2.$$

In all the experiments described in this paper the ions were drawn to the gauze by a potential of 20 volts applied to A and the case of the vessel; this potential is denoted by a and is of course of the same sign as that of the charge carried by the ion whose mobility is under consideration.

Diagram of Connections and Experimental Method.—The complete diagram of connections is exhibited in fig. 3, and



needs little explanation. As is shown in this diagram two commutating discs were employed; one of these (2) which was  $9^{\text{cm}}$  in diameter had 20 fiber segments whereas the circumference of the other (1) ( $6\frac{1}{2}^{\text{cm}}$  in diameter) was half fiber and half metal. Four brushes were used on commutator 2 in order to ensure good contact; the collector ring had two brushes and commutator 1 of course only one. The motor was worked generally on 110 volts which afforded approximately 42 revolutions per second. The speed counter was attached permanently to the system and the time for 5000 revolutions was observed several times during the course of a series of read-

587

ings. The motor maintained a very constant speed and the error in the determination of the frequency was less than 1 per cent.

The double-throw switch f in fig 3 was employed to throw either commutator into action; g was employed to short circuit either commutator. The double-pole, double-throw switch S, when thrown to the right, completed the connections as exhibited graphically in fig. 2. When thrown to the left, connection was made with a subsidiary potentiometer system (b); it will be seen from fig. 3 that in this position the quadrants of the electrometer can be commutated in potential between zero and any convenient potential read off on the potentiometer. This device afforded a thoroughly reliable indication as to the nature of the contact between the brushes and the commutator: excellent contact was indicated by the electrometer needle assuming a definite position, and the slightest irregularity in contact was shown by a corresponding unsteadiness of the needle. Moreover, this device was employed to ascertain the value of f, the fractional duration of contact; f is obviously the ratio of the potential assumed by k when the switch q is in turn opened and closed. f was of course approximately  $\frac{1}{2}$  in most cases but owing to wear in the brushes was often slightly greater, especially when commutator 2 was employed. A third use of the potentiometer device was to enable the electrometer needle to be so adjusted in taking observations that the zero of the instrument was also the midpoint of the range of deflections over which the current was estimated; this point is of especial importance when the gauze was at a small potential.

For convenience in manipulation, a table was prepared of the potentials assumed by the gauze for different values of  $\rho$ ,  $V_1$ ,  $V_2$  and R. v was always chosen equal to 40 volts and r was always 15,000 ohms. This was effected by means of formula (1) which for the purpose was put in the following form :

$$x = \mathbf{V}_{1} + \left[\frac{\rho v}{r} - (\mathbf{V}_{1} + \mathbf{V}_{2} + \frac{\rho v}{r}) \left\{ \frac{\rho(r-\rho)}{\rho(r-\rho) + \mathbf{R}r} \right\} \right]$$
  
=  $\mathbf{V}_{1} + c \text{ (say)}$  (2)

The calculated values of c for various values of  $\rho$  and  $V_1 + V_2$  were then tabulated and the value of x under any desired conditions could be quickly obtained.

The correctness of the results furnished by this formula was experimentally verified by reading directly the potentials on a Kelvin multicellular electrostatic voltmeter; the smaller potentials (below 2 volts) were read off directly on the electrometer, which had a sensibility of  $180^{\text{mm}}$  per volt. In all the instances employed the agreement was excellent. Use was also made of the electrostatic voltmeter to ascertain that the conditions in operation admitted of an effectively instantaneous establishment of the withdrawing potential  $-V_2$ through the resistance R. It was found that with the highest speed of commutation employed the value R = 200,000 was sufficiently small to ensure exact mobility determinations in practically all measurements. R was chosen to be 50,000 ohms, so that a large factor of safety was provided for.

The switches S, f and g were manipulated when observations were being taken in such a way that the electrode e was practically at zero potential when the (advancing) potential (x) was established on the gauze; no induction correction was therefore necessary.

For large current values readings were taken with the capacities B and C added to the electrometer system; the capacity was then increased  $17\frac{1}{2}$  times.

Throughout the experiment the potential  $V_2$  was always chosen considerably greater numerically than x in order to ensure the complete withdrawal from the field of any ions which failed to reach the electrode e during an alternation.

The temperature was throughout approximately 20° C.

## 3. Experimental Results.

For each pressure employed, a complete curve was in general obtained expressing the current registered by the electrometer as a function of the "advancing" potential x. The alternations of potential assumed by the gauze were so extremely rapid that no sign of unsteadiness on the part of the electrometer needle was noticeable, the current being measurable with the same ease as if produced by a direct field.

As the pressure of the air was reduced, there was relatively little reduction in the value of the ionization current passing between the gauze and the electrode e; the diminution of the ionization produced in the region above the gauze at the lower pressure was to a large extent compensated by the increased rate at which the ions diffused through the gauze. The current, for example, was 5.32 in arbitrary units when the pressure was  $121.5^{\text{mm}}$ ; under otherwise identical conditions, the current was 2.28 at a pressure of  $8.09^{\text{mm}}$ . At the lowest pressures employed when the mean free path of the ion was of the order of the distance between the meshes of the gauze the ionization current decreased rapidly with diminishing pressure.

In fig. 4, there are shown typical curves giving the relation between the electric current and the "advancing" potential under various conditions. These curves were produced to cut the axis of potential and in this way the critical potential  $V_{\alpha}$ 

## 590 E. M. Wellisch—Mobilities of Ions in Air.

was determined; e. g., with  $p = 121 \cdot 5^{\text{mm}}$  we get  $V_0 = 46 \cdot 0$ volts. The speed counter indicated 10,000 revolutions in 229.2 seconds and f was exactly equal to  $\frac{1}{2}$ . The mobility of the positive ion is given by  $k_1 = \frac{4n}{fV_0} = 7 \cdot 59$  cm/sec at a pressure of  $121 \cdot 5^{\text{mm}}$ . Assuming pk = constant, we deduce K = 1.213 as the mobility corresponding to a pressure of  $760^{\text{mm}}$ .



At the higher pressures, the curves obtained were all of the type shown in fig. 4; but the curve obtained in the case of the negative ion at lower pressures was of an essentially different character, especially when the rapid alternations of commutator 2 were employed. Such a curve is shown in fig. 5, corresponding to a pressure of  $12 \cdot 22^{mm}$ ; this curve is typical of many others which were obtained under various conditions. The curve is readily seen to be compounded of two simple curves, e. g., the curve E, which is obtained by a free prolongation of the initial part of the experimental curve, when compounded with the curve I is equivalent to the original curve. That the curve E is at least in part due to electrons is shown by the fact that it cuts the potential axis so near to the origin, in other

FIG. 4.

words, the electrode e begins to receive a negative charge with a very small potential applied to the gauze. Moreover, the curve E is exactly the type which we would expect to obtain if it were due to a single constituent, i. e., if the electric charges which correspond to it were carried by a carrier of a definite nature. This point is borne out by a reference to the curve of fig. 6 which gives the relation between the current due to positive ions and potential of the gauze, when the latter



is direct (i. e. there are no alternations). The potential in the antechamber was as usual 20 volts, the pressure was  $17.39^{\text{mm}}$  and the current was measured with the capacities B and C added to the system. This was the type of curve obtained in all cases when a direct field was employed; the continued upward slope of the curve at the higher potentials is due to the fact that as the potential is increased a larger number of ions are pulled out from the region above the gauze. The curve E of fig. 5 is thus exactly of the nature which we would expect to arise from a single type of carrier and may in consequence be regarded as being due entirely to free electrons. The curve marked I is similarly due to a single type of carrier, but one which moves with a smaller mobility; for this reason, this

FIG. 5.

carrier is regarded as the negative ion. It is easy to calculate the mobility of this ion from the experimental curve; the portions of this curve corresponding to the ions and the electrons are produced to meet and the abscissa of the point thus obtained is obviously the critical potential corresponding to the ionic current. In the case under consideration, we deduce  $V_0 = 27.2$  volts. The experimental data were:  $p = 12.22^{\text{mm}}$ ; 100,000 alternations in 203.8 secs; f = .57. We obtain



 $k_2 = 125.6$  cm/sec and K = 2.02. This is practically the same as the value of K obtained for the negative ion in dry air at the higher pressures; other determinations gave still closer results. We are consequently led to the conclusion that the negative ion corresponding to the conditions of the curve of fig. 5 is exactly the same ion as is obtained at the higher pressures.

The current of negative electricity is thus due partly to electrons and partly to ions; the electrons traverse the whole distance between the electrodes without attaching themselves to neutral molecules; the ions are of exactly the same nature as those which are produced at the higher pressures. All the curves corresponding to the negative ion at pressures below 8<sup>cm</sup> were of the same type as that exhibited in fig. 5. A set of curves obtained is shown in fig. 7; the frequency of field alternation was practically the same for each of these curves and consequently a comparison can be readily instituted between



FIG. 7.

them. In order to avoid undue complication, the points from which the curves were drawn are not given, but in every case the curve was drawn smoothly through a large number of points. For purpose of illustration, the actual observations from which curve C (p = 1.69) was drawn are recorded below.

V <sub>2</sub> volts	x volts	Rate	$v_2$ volts	x volts	Rate
-120	$\begin{array}{c} 104 \cdot 0 \\ 92 \cdot 5 \\ 80 \cdot 0 \\ 63 \cdot 2 \\ 55 \cdot 0 \\ 50 \cdot 1 \\ 46 \cdot 3 \\ 40 \cdot 0 \\ 34 \cdot 4 \\ 29 \cdot 5 \\ 25 \cdot 0 \\ 24 \cdot 0 \\ 23 \cdot 0 \\ 22 \cdot 0 \\ 21 \cdot 0 \\ 20 \cdot 1 \\ 19 \cdot 2 \\ 18 \cdot 4 \end{array}$	$\begin{array}{c} 6\cdot10\\ 6\cdot02\\ 5\cdot95\\ 5\cdot26\\ 5\cdot08\\ 4\cdot90\\ 4\cdot76\\ 4\cdot47\\ 4\cdot13\\ 3\cdot88\\ 3\cdot50\\ 3\cdot40\\ 3\cdot31\\ 3\cdot23\\ 3\cdot20\\ 3\cdot09\\ 3\cdot00\\ 2\cdot91\\ \end{array}$	-120	$\begin{array}{c} 17.5\\ 16.7\\ 15.9\\ 14.3\\ 13.6\\ 12.9\\ 12.2\\ 11.5\\ 10.2\\ 9.0\\ 7.91\\ 6.9\\ 5.0\\ 3.4\\ 2.14\\ 1.13\\ .73\\ .42\end{array}$	$\begin{array}{c} 2.80\\ 2.73\\ 2.65\\ 2.49\\ 2.42\\ 2.35\\ 2.25\\ 2.17\\ 2.07\\ 1.96\\ 1.84\\ 1.77\\ 1.59\\ 1.49\\ 1.33\\ 1.07\\ .82\\ .47\end{array}$

The small circles drawn in the diagram refer to the points from which the mobilities of the negative ions were obtained in the manner previously described. The experimental data relating to these curves are as follows :

Curve	Pressure mm.	Critical Potential V <sub>0</sub> Volts	f	Time for 100,000 alternations sec.	k2 cm/sec	K cm/sec
A	.39	1.75	·592	117.1	3300	1.695
В	.87	4.0	·559	118.3	1512	1.73
C	1.69	7.5	.553	117.5	821.2	1.83
D	2.80	11.5	•545	114.6	557.0	2.05
$\mathbf{E}$	5.92	25.0	.500	114.4	279.8	2.18
$\mathbf{F}$	8.09	35.0	$\cdot 539$	116.3	182.3	1.94
G	12.12	52.5	•543	116.4	120.5	1.92
H	22.6	90.0	.564	118.4	66.2	1.98
K	62.0		•565	121.3		

The lowest pressure employed for the case of the negative current was  $15^{mm}$ ; the curve was of the general type and gave a normal mobility value for the ion. In none of the curves is there evidence of an intermediate

or transition stage in the nature of the negative carrier; it is

either an electron or an ion. At first sight the presence of the bend in that part of each curve where the ions begin to appear might be construed as evidence of the presence of carriers intermediate in nature between the electron and the ion. Against this view, however, is the fact that a similar bend occurs in the curves for both the positive and the negative ions at the higher pressures. This is shown in the curves of fig. 4. The three curves which correspond in that figure to the three higher pressures were obtained with relatively small frequencies of alternations. They all exhibit this characteristic bend, which is in all probability due to a distortion of the field in the neighborhood of the gauze ; as a result of this some ions arrive slightly ahead of the main body and thus appear to have greater mobility. The curve corresponding to  $p = 62^{\text{mm}}$  is interesting as affording an illustration of the advantages which arise from the higher resolving power obtained by using large alternation frequencies; the curve K of fig. 7 shows that at least part of the bend in the corresponding curve of fig. 4 must be due to electrons.

For pressures below  $1^{\rm mm}$  the values of the critical potential  $(V_o)$  were of necessity small and consequently the observation error was proportionately large; it is however safe to conclude from the experimental results that the value of pk for the negative ion is the same at the lowest pressures employed as at one atmosphere, showing that the nature of the negative ion remains unaltered over a range of pressures from one atmosphere down to  $15^{\rm mm}$ . The mean value of K for the negative ion came out as 1.93, which is higher than is usually assigned.

The curves of fig. 7 show not only that the negative carriers consist of electrons and ions, but that the proportion of electrons increases with diminishing pressure. It must be remembered, however, that these curves give information only with regard to the relative number of electrons and ions which constitute the current between the gauze and the electrode e. This is not the same as the relative number of electrons and ions produced in the antechamber owing to the unequal rate of diffusion through the gauze. A rough estimate which was made showed that at a pressure of  $12 \cdot 2^{mm}$  the ions were still at least 80 per cent of the total number of carriers produced, and even at the lowest pressure ( $\cdot 15^{mm}$ ) were still over 50 per cent.\*

The mobility of the positive ion was determined at various pressure intervals from 1 atmosphere down to  $\frac{1}{20}$  mm. At the lower pressures where the error of observation in the value of  $V_o$  was relatively large, the mobilities were also determined by a method which was suggested to the writer by Professor \*See footnote p. 598. Erikson of the University of Minnesota. The mobility is given by

$$k = \frac{d^2 n}{V} \cdot \frac{i}{fi - i'}$$
 where V is

a potential near  $V_o$ ; *i'* is the current corresponding to the potential V when the alternating field is employed; *i* is the current corresponding to the potential V directly applied. There was no evidence of any anomalous behavior and over the whole range the product pk remained unaltered, indicating that the nature of the positive ion in thoroughly dried air remains the same over this range of pressures. The mean of a series of determinations was found to be 1.23 cm/sec per volt/cm, which is lower than is usually given.

To sum up, the experimental results indicate that the positive ion remains the same in nature over the whole pressure range employed; the negative carriers, however, consist, in general, of two kinds, electrons and ions, the former increasing in number relatively to the latter with diminishing pressure. In the present experiments the electrons came into evidence at pressures below 8<sup>cm</sup>, but it is probable that they exist in small numbers at much higher pressures and that they would be detected by more sensitive measuring instruments.

There is no evidence of any transition stage in the nature of the ion; the electrons appear to travel freely through the molecules of the gas without attaching themselves and the ions manifest a similar behavior. The negative ion remains the same in nature over the whole pressure range employed.

#### 4. BRIEF DISCUSSION OF RESULTS.

As mentioned in the introduction, many observers have undertaken a determination of the mobility of gas ions at relatively low pressures. They all arrived at the same general conclusion, viz., that the product pk increases in the case of the negative ion when the pressure is reduced below about  $10^{\rm cm}$ ; this result was interpreted as denoting a progressive diminution in the size and mass of the ion as the pressure is reduced. Professor Townsend and his students showed that at low pressures when the gas was thoroughly dried the negative ion tended to assume the electronic state; the velocity of the negative ion was

expressed in the general form  $v = f\left(\frac{X}{p}\right)$  which implies that

the nature of the ion is determined by the field as well as the pressure. In his recently published treatise\* (pp. 120, 121) Professor Townsend sums up the results of a large number of experiments by stating that the negative ion consists in general

\* Electricity in gases, Oxford, 1915.

596

of a cluster of molecules grouped round a charged nucleus, that for a certain range of forces and pressures there is a transition stage in which the average mass diminishes from that of a group of molecules to that of an electron; and finally when the value of  $\frac{X}{p}$  exceeds 2 (X being measured in volts/cm and p in mm) the negative ions in dry air are all in the electronic state.

The present series of experiments confirms the view that in dry air the tendency is for the negative ions to assume the electronic state as the pressure is reduced but in other respects they lead to a view of the mechanism which is radically different from the foregoing. The chief point of difference lies in the result that the negative carriers in general consist of two distinct kinds, electrons and ions. There is accordingly no justification for introducing the terms mobility or velocity as applied to the negative carriers at the lower pressures where the percentage of electrons is appreciable; all attempts to determine the velocities under these conditions rest upon a fictitious method of averaging which appears to be unjustifiable.

If, however, care be taken to distinguish between the electron and the ion, it is found that the latter has a distinct mobility so that its velocity is expressible in the form  $v = k \frac{X}{p}$ ; there appears to be no necessity for introducing any unknown function of  $\frac{X}{p}$ . The absence of any indication of the existence of an intermediate stage between the electron and ion renders nugatory all attempts to determine an average velocity for the negative carrier.

The mobility of the negative ion was found to be practically independent of the frequency of alternation employed, in other words, the applied field has little or no effect on the mobility or the nature of the ion (cf. curve G, fig. 7 and curve, fig. 5). Of course, it is highly probable that excessively large values of the field would produce a marked effect on the mobility of the ion but this statement in no way invalidates the general conclusion.

In this connection it is easy to account in general terms for the results obtained by previous observers who found (as Kovarik)\* that the mobility depended upon the rate of alternation of the field or (as Lattey)† that the velocity was an unknown function of the field. When these observers speeded up their commutating device they brought the electrons into greater relative prominence; and as a larger speed implied of

\* Kovarik, loc. cit.

+ Lattey, Proc. Roy. Soc., lxxxiv, p. 173, 1910-11.

597

necessity a larger field the velocity appeared to increase faster than the field.

The proportion of electrons increases as the pressure is diminished; but in this respect again, the field appears to be without effective influence. The statement that the carriers are practically all electrons when  $\frac{X}{p}$  exceeds '2 is readily seen to be erroneous from a casual inspection of the curves, e. g., in curve B (fig. 7) we have  $p = .87 \text{ X} = \frac{60}{2} = 30$ ;  $\frac{X}{p} = 34.5$  and at the same time a large percentage of ions.

The fact that electrons can travel considerable distances in dry air without attaching themselves to neutral molecules is remarkable and appears to indicate that the distribution of carriers between ions and electrons must be determined immediately after the act of ionization. We may look upon the act of ionization as resulting in the expulsion of an electron with a certain velocity: this velocity decreases as the electron recedes from the parent molecule owing to the positive charge acquired by the latter. If in addition we regard attachment between an electron and an uncharged molecule as possible only when their relative velocity at impact is above a critical value, it is easy to see that at low pressures when the free path of the electron is relatively large the number of such attachments (i. e. the proportion of negative ions) would be smaller than at the higher pressures.\* Expressed in general terms, there appear to be definite forces of repulsion at small distances between an electron and an uncharged molecule; when however, the electron has sufficient velocity to penetrate into the sphere of action of the molecule the forces are now no longer repulsive but attractive. The phenomenon is in many respects similar to the impact of a bullet upon a target.

Moreover, the fact that electrons can traverse several cms. of a gas at pressures as high as  $10^{\text{cms}}$  without attaching themselves to neutral molecules would seem to imply à fortiori that the system (i. e. ion) resulting from the initial attachment of an electron and a molecule would in a similar manner retain its identity and pass through the gas unencumbered. Such a deduction might, however, be open to objection, but what can be stated with the highest degree of certainty is that both the positive and the negative ions in dry air remain unchanged through a variation in pressure from 1 atmosphere down to

\*In accordance with this view the applied field will begin to affect the distribution when the energy acquired by the electron between collisions is sufficient to cause attachment to a neutral molecule. With the moderate field strengths used in these experiments such an effect would be likely to occur only at the lowest pressures.

the lowest pressures employed in these experiments; for the positive ion this pressure was  $\frac{1}{20}$ <sup>mm</sup> and for the negative  $\cdot 15^{mm}$ . The experimental result of Todd that at pressures below

The experimental result of Todd that at pressures below  $1^{mm}$  there is a simplification in the nature of the positive ion is not confirmed.

The difference in the mobilities of the negative and positive ion is in all probability the result of a difference in the potential energy of inductive attraction between the ion and the uncharged molecule. Such a difference of course requires explanation.

Finally, the actual mobilities obtained for the negative and positive ions, viz., 1.93 and 1.23 in thoroughly dried air, are worthy of notice; it would appear that the effect of thoroughly drying the air is to increase slightly the value of the negative mobility and decrease that of the positive.

#### SUMMARY.

1. An investigation has been made of the velocities of the positive and negative carriers in thoroughly dried air under a variety of experimental conditions.

2. From 1 atmosphere down to the lowest pressure employed (viz.  $\frac{1}{20}$  m<sup>m</sup>) it was found that the mobility of the positive ion varied inversely as the pressure, indicating that the nature of the positive ion remains unchanged over this wide range of pressures.

3. The negative carriers were found in general to consist of two kinds, electrons and ions, the former increasing in number relatively to the latter with diminishing pressure. Each kind possesses its characteristic velocity in an electric field and there was no evidence of any intermediate stage in the nature of the negative carrier. The electrons appeared in measurable amount in the present experiments at pressures below 8<sup>cms</sup>.

4. The negative *ion* remains unaltered in character over a range of pressures from one atmosphere down to the lowest pressure employed (viz.  $\cdot 15^{mm}$ ).

5. A brief discussion of the results is given in which the view is expressed that all previous experiments on the velocity of the negative ion at relatively low pressures are based on the untenable assumption of the presence of an "average" ion and are thereby invalidated.

Sloane Laboratory, Yale University, New Haven, Conn., April 14, 1915.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIX, No. 233.—May, 1915. 39

## SCIENTIFIC INTELLIGINCE.

## I. CHEMISTRY AND PHYSICS.

1. The Production and Uses of Hydrogen.—A. ]. SEEKER has given an account of the technical employment of this gas. Formerly it was used occasionally for the filling of balloons and in the oxyhydrogen flame of the so-called "calcium light." It has become essential for the filling of dirigible balloons, but these have now perhaps become of secondary importance in comparison with heavier than air machines. The oxyhydrogen flame is now commonly used in working refractory metals. Liquid oils and soft greases are now "hydrogenated" to produce acceptable lard and butter substitutes and also fats suitable for the manufacture of hard soaps. Finally the use which promises to consume enormous quantities is the synthetical production of ammonia from hydrogen and atmospheric nitrogen. All these uses make the production of cheap hydrogen a problem of considerable importance. In view of the impending exhaustion of the Chili saltpeter beds, the problem of the fixation of atmospheric nitrogen has received increased attention. The production of cyanamide from calcium carbide and nitrogen, and the flaming arc process for making nitric acid directly from the air have been successfully established, but these methods require cheap water power for the electrical energy. In countries lacking cheap power the synthetic ammonia process appears to be promising and it is in successful operation in Germany. It consists in passing a mixture of pure nitrogen and hydrogen under a pressure of 150 to 250 atmospheres through a tube filled with a catalyzer and heated to 650 to 700° C. The hot gases then pass through a heat regenerator and thence through an ammonia absorber, after which they are replenished with fresh gas mixture and forced by a pump back over the outer walls of the contact tube and then through the contact mass to repeat the circulatory course already described. Only a part of the mixture is converted into ammonia by a single passage through the converter, but the circulation is continuous. The contact mass consists of pure iron containing many other substances called promoters. The studies of Wegener and others lead to the opinion that at a height of about 75 miles the atmosphere consists of pure hydrogen and nitrogen that would be ideal for the synthetic ammonia process, but even if this is so no means of piping these gases down to our sphere of action are known.

Large amounts of hydrogen are obtained as a by-product in the electrolysis of salt solutions in the manufacture of chlorine and caustic soda. The reaction, which is as follows :  $\circ NaCl + 2H_2O = 2NaOH + Cl_2 + H_2$ , produces 245 million cubic  $\pi_{c}$  of gen per year at Griesheim, Germany. In another method,

clay-lined retort is filled seven-eighths full of coke, ignited and raised to a white heat by an air blast. The retort is then closed and a cheap hydrocarbon like crude petroleum or coal tar is injected into it for about twenty minutes, or until the temperature has fallen below the proper "cracking" point, the gas thus generated passing through a sprinkling tower and a filter into a gasometer. The air blast is again turned on and the process is repeated indefinitely with periodical renewal of the coke and removal of the ashes. The product contains about 96 per cent of hydrogen, and by passing it through suitable absorbents it can be further purified to about 98.4 per cent. The total cost is 3 or 4 cents per cubic meter. The method of passing superheated steam over red-hot iron is little used now, as is also the method of conducting water-gas through suitable absorbents so that the hydrocarbons and the carbon monoxide are removed. However, another process employing water gas is increasing in application. In this the water gas, consisting mainly of carbon monoxide and hydrogen, is compressed and cooled to the liquefying point of carbon monoxide. Upon relieving the pressure the expansion cools the mixture still further, so that most of the impurities separate in the liquid form, while hydrogen 97 or 98 per cent pure passes off. The mixture consisting largely of liquefied carbon monoxide is afterwards vaporized and used in gas engines for power.

At European army posts hydrogen for military balloons is commonly made from scrap iron and sulphuric acid. For field operations zinc is used in place of iron with sulphuric acid, but there are three other more modern means of generating hydrogen for field purposes, called the "Hydrolith," "Silicol," and "Hydrogenite" processes. Hydrolith is calcium hydride, which reacts directly with water as follows :  $CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$ . It is a convenient but expensive method. The silicol process consists in treating powdered ferro-silicon or mangano-silicon with water and caustic soda. It does not appear to have gained extensive use on account of the troublesome manipulations and the difficulty of controlling the evolution of gas. Hydrogenite is composed of ferro-silicon (containing 90 to 95 per cent of metallic silicon) 25 parts, caustic soda 60 parts and dry slaked lime 20 parts. This mixture of finely powdered dry materials, compressed in blocks, decomposes when a hot wire is thrust into it, according to the equation,  $Si + Ca(OH) + 2NaOH = NaSiO + CaO + 2H_{a}$ . Chem. Engr., xx, No. 6. H. L. W.

2. The Density of Lead from Ceylon Thorite.—Having previously found, as the result of an examination of less than 1 g. of lead from Ceylon thorite, that this lead gave an atomic weight rather more than a unit higher than ordinary lead; FREDERICK SODDY has extracted about 80 g. of this metal from 20 kg. of the finest grade of the same thorite. This product and a similar weight of ordinary test lead were carefully purified by identical processes and finally melted in a vacuum and carefully cast in graphite moulds in such a manner that the metal solidified from the bottom upward. Kahlbaum, Roth and Siedler had found the density  $\left( D \frac{20^{\circ}}{4^{\circ}} \right)$  of lead distilled in a vacuum to be 11.3415, and after subjecting it to a pressure of 10,000 atmospheres, 11.3470. Soddy's ordinary lead gave 11.3465 as the average of 3 determinations agreeing within 8 units in the last place, while his thorite lead gave 11.376. If the atomic volumes of isotropic elements are identical so that the densities are proportional to the atomic weights, then taking ordinary lead as 207.10, the thorite lead would have the atomic weight 207.64. During the purification of this lead bismuth was specially looked for, but if any at all was present its quantity was less than one part in 10 millions of the mineral, so that it would appear that bismuth is not one of the products of the thorium disintegration. It is an interesting fact that a little iodine was present, and between 1 and 2 grams of this element were extracted from the sample of thorite. A trace of thallium was probably also present.—Nature, xciv, 615.

H. L. W.

3. The Analysis of Alloys containing Tin, Antimony and Arsenic.-F. A. STIEF has devised for this analysis a rapid method which, although not new in general principles, is original in some of its important details and may be carried out upon a single sample without filtration. Only an outline of the process can be given here, and the original article should be consulted by anyone using the method. The alloy is dissolved in hot concentrated sulphuric acid, a proper amount of hydrochloric acid is added and arsenious chloride is distilled off and determined volumetrically by iodine in bicarbonate solution. In the residue, after proper dilution with water, antimony is titrated with permanganate. The liquid then receives a suitable treatment with more acid and iron wire, and the tin is finally determined by means of iodine solution.-Jour. Indust. and Engr. Chem., vii, 211. H. L. W.

4. Density and Dispersion of Liquid Hydrogen and Nitrogen.-It has been shown theoretically by O. Wiener that the Lorenz-Lorentz formula,  $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d} = \text{const.}$ , may be written

 $\frac{\epsilon-1}{\epsilon+u} \cdot \frac{1}{d} = \frac{\epsilon'-1}{\epsilon'+u} \cdot \frac{1}{d'} = \text{constant, where } \epsilon \text{ and } \epsilon' \text{ denote respec-}$ 

tively the dielectric constants of the same substance in the gaseous and liquid states. The corresponding densities are symbolized by d and d'. u is called the "form-number" by Wiener. When u=2 the molecules of the substance in question are strictly spherical in form, and when u is greater than 2 the excess affords a measure of the departure of the molecules from the spherical shape. The special conditions hypothecated in Wiener's theoretical considerations are best fulfilled at low temperatures, hence liquid hydrogen and nitrogen afford good tests of the theory.

Since certain necessary data were lacking in the literature of the subject, H. Augustin has recently undertaken the experimental determination of the quantities needed. The first problem was to find the value of the density of liquid hydrogen at a known temperature. The experimental method consisted in ascertaining the loss of weight of a quartz sinker immersed in the liquefied gas. The volume of the quartz cylinder and the apparent loss of weight in liquid hydrogen were about 23.3cm3 and 1.6342 g. respectively. These numbers may give some idea of the dimensions of the apparatus employed and of the degree of accuracy attainable. Because of the low temperature of the liquid a number of experimental difficulties had to be overcome. The final form of apparatus used was too complicated to admit of detailed explanation in this place. Suffice it to say that the apparatus was ingeniously designed and that the data obtained by its aid seem to be very reliable. The final value for the density of liquid hydrogen is given as 0.07105 gram per cm<sup>3</sup>, with a mean error of six units in the last decimal place. (The corresponding pressure and temperature were  $745.52^{\text{mm}}$  and  $-252.83^{\circ}$  C.)

The next problem was the determination of the indices of refraction of hydrogen and of nitrogen in the liquid state. These data were found by E. Wiedemann's method of total reflection. By using monochromatic light and a Gauss eye-piece, Augustin was able to make accurate settings of the cross-hairs on the welldefined boundary between the light and dark regions of the field of view. Earlier investigators who employed the same general method did not isolate the colors and hence they obtained only mean values of the indices of refraction. The radiations used by Augustin had the following wave-lengths: 404.7, 435.9, 546.1, 579.0, and 656.3 $\mu\mu$ . The first four lines are emitted by mercury and the last by hydrogen. The corresponding indices of refraction of liquid hydrogen relative to hydrogen vapor were found to be 1.11262, 1.11179, 1.11003, 1.10974, and 1.10924 in the order named. The relative indices for liquid nitrogen are given as 1.20125, 1.20010, 1.19788, 1.19746, and 1.19715 respectively. When the refractive indices are laid off as ordinates with the wave-lengths as abscissæ the points fall almost exactly on smooth curves, thus indicating a high degree of relative accuracy of the data.

In order to calculate the form-number, u, mentioned in the first paragraph, it was necessary to use the questionable process of extrapolation to obtain the indices of refraction of the vapors of hydrogen and nitrogen at the respective boiling points, since the formula involves the absolute indices of the liquids. For hydrogen the values of u corresponding to all the colors except the violet were found to be 2.02, 2.02, 2.04, and 1.90, giving a mean value  $2.00 \pm 0.02$ . It thus appears that the molecules of hydrogen behave dielectrically as if they were true spheres. The author remarks that this result (u = 2) is especially noteworthy because the values found heretofore for most liquids differed markedly from 2. A similar computation for nitrogen led to the numerical result  $u = 2\cdot12 \pm 0\cdot02$ , and to the conclusion that the molecules of this element act as if they were approximately spherical in shape. Further experimental work to remove any doubt about the legitimacy of the extrapolated data is said to be in progress. —Ann. d. Physik, vol. xlvi, p. 419, Feb. 1915. H. S. U.

5. The Absorption Spectrum of Chlorophyll.—Since the results obtained by earlier investigators have not been fully concordant and since the wave-lengths used have not exceeded  $2\mu$  the problem has been taken up anew by D. VAN GULIK. Furthermore, Willstätter and Stoll have succeeded in separating the two components, "a" and "b," of chlorophyll and in making pure preparations of each constituent. The former furnished van Gulik with the material studied. In order to transmit the heat waves very pure carbon bisulphide was used as solvent. The radiations were emitted by a Nernst glower and spectrally dispersed by a quartz prism. The values of the absorption coefficient a, as defined by the equation  $I' = I.10^{-ad}$ , were determined for wavelengths lying between the limits  $576\mu\mu$  and  $3.6\mu$ .

The a component has an intense absorption band in the red with its maximum at  $0.65\mu$ . Weak absorption continues into the infra-red and a relatively weak secondary maximum falls between  $0.8\mu$  and  $0.9\mu$ . The b component has a strong maximum at  $0.63\mu$  with a weaker companion band on the more refrangible side. This constituent of chlorophyll, however, exerts practically no absorption from  $0.8\mu$  to  $0.9\mu$ . From  $1\mu$  to  $3\mu$  neither component shows appreciable absorption. At  $3.3\mu$  a double band of absorption sets in, for both the a and b preparations, and extends to about  $3.55\mu$ . The principal maximum has the wave-length  $3.4\mu$ and the secondary,  $3.5\mu$ . In this region the absorption curves of the two components are very similar in shape and intensity. The bands in the visible spectrum have been investigated very often in the past, but the doublet at  $3.4\mu$  is new. The author of the original paper is in doubt concerning the physiological significance to plant life of the infra-red bands. Although the solar radiation, as transmitted by the earth's atmosphere, may be sufficiently intense to influence vegetation, the water in the plant cells may prevent the radiation from penetrating as far as the region occupied by the chlorophyll particles.-Ann. d. Physik, vol. xlvi, p. 147, Dec. 1914. H. S. U.

6. A New Type of Band Series.—In the year 1913 two accounts of the same band spectrum were published almost simultaneously by W. E. Curtis and E. Goldstein, working independently and in different countries. The former found that the spectrum was best developed, in the wider parts of the tubes, when an electric discharge, with small capacity and a short airgap, was passed through helium at a pressure somewhat higher than that which is usual in sealed tubes of the gas. It is not certain, however, that the spectrum is due to helium because slight traces of hydrogen have always made their presence known. The negatives taken by Curtis (removed by enlistment) have been recently studied by A. FOWLER with the result that some remarkable facts have been revealed. The spectrum comprises, among other things, bands with single heads and bands with double heads, all of which are degraded towards the red. The present paper relates only to the bands having two heads.

The important facts brought out by the preliminary study of the plates may be summarized as follows: (1) The doublets do not follow the ordinary law of band spectra, but can be arranged in two series of the type hitherto exclusively associated with line spectra, and can be approximately represented by the usual formulæ involving the Rydberg constant. Nine bands of the main series and four of the fainter second series have been identified. (2) The two series may be likened to the Principal and Diffuse series in the case of line spectra, but the usual relation between such series is not certainly indicated, and no equivalent of the Sharp series has yet been traced. (3) The doublet separations are not in accordance with those associated with line spectra; they diminish in passing along the series, but do not vanish at the limit. - Proc. Roy. Soc., vol. xci (A), p. 216, March 1915. H. S. U.

## II. GEOLOGY.

1. Problems of American Geology, by WILLIAM NORTH RICE, FRANK D. ADAMS, ARTHUR P. COLEMAN, CHARLES D. WALCOTT, WALDEMAR LINDGREN, FREDERICK L. RANSOME, WILLIAM D. MATTHEW. A series of Lectures Dealing with Some of the Problems of the Canadian Shield and of the Cordilleras, Delivered at Yale University on the Silliman Foundation in December, 1913. Pp. xvii+505, pls. 7, figs. 63, maps and diagrams 4. Yale University Press, 1915.-This volume of lectures was planned to commemorate the centennial of the birth, in 1813, of James Dwight Dana, and the semi-centennial of the publication in 1863 of the first edition of his most important work, the Manual of Geology. As Dana was so eminent a geologist, the Geological Department of Yale University desired that the lectures should be of high scientific attainment. It was furthermore held that the best form of commemoration was to contribute the results of new researches on subjects of present vital interest; subjects which are an outgrowth of the interests of the previous generation, rather than to plan a review of past accomplishments. The completed volume shows the value of this point of view.

Professor Rice presents an introductory chapter on "The Geology of James Dwight Dana." He shows the great advances in philosophic concepts in geologic science which were made by Dana and also the corrections in certain points of view which

later years have brought forth. Professor Rice, as a student of Dana's and one who grew up in that period of profoundly changing thought, the third quarter of the nineteenth century, is qualified from personal experience to give this historic introduction and show the relations of present geologic research to that of the previous generation.

Chapter II deals with the Problems of the Canadian Shield the Archeozoic. The author is Frank Dawson Adams. Within the Canadian Shield are displayed the oldest known rocks of the continent; rocks which have been reinterpreted within the present generation and give knowledge of what may be called the heroic period in the history of the earth. The author begins by considering the present limits and physiography of this shield and the older of the rocks which constitute it. The granite gneisses are found to be intrusives of widely different ages. The studies of the nature of these igneous rocks and of their mode of intrusion are of the highest interest.

Dr. A. P. Coleman, in Chapter III, takes up the study of the Proterozoic of the Canadian Shield. The striking features of the deposition and metamorphism of the Sudbury Series are described and an interpretation is given of the physiographic and climatic conditions of Sudburian time. The Sudburian was followed by a great interval of igneous intrusion, of mountain uplift and erosion which separated it from the true Huronian. In the renewal of the sedimentary record which took place then, the Huronian tillites, as evidence of glacial climates, easily hold first place in present interest. The closing parts of the chapter deal with the deposits of the Animikie and Keweenawan periods.

The opening of the Paleozoic is dealt with by C. D. Walcott in Chapter IV, under the title of "The Cambrian and its Problems in the Cordilleran Region." The progress of the Cambrian seas across the peneplained surface of older rocks is described and numerous sections of the sediments are given. In the interpretative portion : in lower Cambrian time the evidence is regarded as indicating a warm climate becoming colder toward its close. In Middle Cambrian time the climate was temperate and equable. In the Upper Cambrian it became more varied. Finally there is given a review of the remarkable life record which Walcott has recovered from these Cambrian formations.

Chapter V, The Igneous Geology of the Cordilleras and its Problems is by Waldemar Lindgren. He concludes that the character of the igneous rocks from the earliest to the latest times, changing in successive eras, calls for at least three magma basins of primary importance; the first, acidic; the second, basic; the third, intermediate in composition. The original relations of these in the earth, their causes and modes of irruption and eruption form the problems which are discussed in the latter part of the chapter.

Chapter VI is by F. L. Ransome, of the United States Geological Survey, on the Tertiary Orogeny of the North American Cordillera and its Problems. Descriptions of the orogenic lines extending throughout North America, their dates of origin, and their character are first given. Then comes a brief consideration of the different theories of orogeny in their relation to the significant features of the Cordillera.

Chapter VII, the concluding essay of the volume, is by W. D. Matthew and is on the Tertiary Sedimentary Record and its Problems. The opening part of the chapter deals with the modes of sedimentation which are involved. This is followed by a discussion of the succession and correlation of the Cordilleran Tertiary formations. The life record of the Tertiary, its interpretation and its problems, are then taken up. This section includes the place of evolution and lines of dispersal for each order of mammals and the relations in time and place which are held by the Cordilleran fossil Tertiary representatives.

From this brief survey of contents it is seen that the volume holds an important place in the progress of geology, elucidating and evaluating the principles and relations which coordinate the ever-accumulating mass of detail, and directing the further progress of research which in turn makes more accurate our knowledge of the past. J. B.

2. West Virginia Geological Survey; I. C. WHITE, State Geologist. Logan and Mingo Counties, by RAY V. HENNEN and DAVID B. REGER, Assistant Geologists. Part IV, Paleontology, by W. ARMSTRONG PRICE, Paleontologist. Pp. 776, figures 23, plates I-XV; maps I-III bound separately. Morgantown, 1914.— The series of unusually complete County Reports issued by the West Virginia Geological Survey has been enlarged by the publication of a volume devoted to Logan and Mingo counties. Like its predecessors, this report contains a detailed description and revision of the geologic formations (Pennsylvanian in age) exposed, as well as a discussion of the topography, structure, and paleontology. In the chapters on Economic Geology particular attention is given to the outcrops and structure contours of the Campbell Creek Coal bed—the celebrated "No. 2 Gass Coal" of the mining engineer. H. E. G.

3. Illinois Geological Survey; FRANK W. DEWOLF, Director Bulletin No. 21, Lead and Zinc Deposits of Northwestern Illinois, by G. H. Cox. Pp. 120, 13 figures, plates I-XXII. Urbana, 1914.— The portion of Professor Cox's detailed description of the Illinois lead and zinc deposits which is of most general interest is the discussion of ore genesis. The theory proposed, which is believed to account for a variety of puzzling features, is outlined as follows: The ultimate source of the ores is the pre-Cambrian crystallines of the Lake Superior region; the immediate source is the Maquoketa shales on which the disseminated particles of ore were originally deposited from the waters of the Ordovician sea. Organic matter in the shales permitted precipitation of ore and, as the shales were eroded, descending waters carried the ore particles downward until they came to rest in cavities of the Galena limestone. H. E. G. 4. South Dakota Geological Survey; ELLWOOD C. PERISHO, State Geologist. Bulletin Number Six, 1914. Report on the Biology of Harding County, Northwestern South Dakota, by S. S. VISHER; and Report of the State Geologist for 1913–1914. Pp. 127; pls. VI. Pierre, S. D., 1914.—With the very inadequate funds at his disposal, the Director of the South Dakota Survey has been able to accomplish little along the lines of geological research. Biological surveys have, however, prospered, and a large collection of plants and animals from the state has been installed in the State Museum, and described in a series of preliminary reports. Bulletin No. 6 is devoted to an ecologic study of the interesting steppe country of Harding County. H. E. G.

5. Report of the State Geologist on the Mineral Industries and Geology of Vermont, 1913-1914, GEORGE H. PERKINS. Pp. 448; pls. I-LXXVIII, 41 figures. Burlington, 1914. The 1913-14 Report of the State Geologist of Vermont contains the results of an exhaustive study of the marbles and marble industry of the state, including a paper by Dr. Dale, also published as Bulletin 521 of the United States Geological Survey. Areal studies under the direction of Professor Richardson were continued in the towns of Greenboro, Hardwick, Woodbury, and Bennington. Professor Jacobs contributes a carefully prepared article on talc and the talc deposits of Vermont. H. E. G.

6. Les Variations Périodiques des Glaciers, XIX<sup>me</sup> Rapport, 1913; rédigé par Axel Hamberg et Paul-L. MERCANTON. From the Annales de Glaciologie, vol. ix, December, 1914, pp. 42-65. Leipzig.—Of 61 glaciers in the Swiss Alps measured during the year 1913, 26 certainly, 10 probably, have decreased in length; 10 glaciers have probably grown longer, and the Grindelwald Glaciers have maintained the advance begun in 1907, interrupted only during the dry year of 1911. For the eastern Alps 8 out of 37 glaciers studied in 1913 have advanced; 4 remained stationary; and 25 continued to retreat. Professor Brückner states that the increase in the number of advancing glaciers is unquestioned. In the Italian Alps the retreat of the larger glaciers has been maintained, while the smaller ones show considerable fluctuation in response to varying snowfall. The list of 39 Norwegian glaciers furnished by Professor Oven includes 9 ice tongues which have increased in length during The 1913. The glaciers in the Caucasus are in general retreat. Alaskan glaciers during 1912 and 1913 exhibited considerable activity. At Yakutat Bay, Hidden, Nunatak, Hubbard, and Turner glaciers retreated; the cascading glaciers adjacent to Nunatak advanced 328 feet between 1910 and 1913. The glaciers of Mount St. Elias and those of Copper River Canyon are in retreat; a glacier at the head of Snug Harbor seems to have advanced between 1904 and 1911. The glaciers entering the fiord of Glacier Bay were studied by Lawrence Martin in 1913. The Grand Pacific, which had retreated 7545 feet between June 1 and August 1, 1912, had advanced 3937 feet by September 9, 1913.

De Margerie, Reid, Lamplugh, and the southwest tributary of Rendu glacier advanced during 1913. The great Muir glacier continues to retreat. A comparison of the map of 1892 with that of 1913 shows a recession between those dates of 7.76 miles. This glacier is now well displayed for measurement and it is found to have been 2378 feet thick at a point 5.6 miles from the terminus of 1892. The thickness of ice in the Grand Pacific glacier 12.1 miles from the terminus 1914 was at least 2493 feet.

H. E. G.

7. Additional Facts in Regard to the Discovery of the Meteorites of Brenham, Kiowa County, Kansas .- The remarkable group of pallasites of Brenham, Kiowa county, Kansas, were described by Dr. George F. Kunz in this Journal for October, 1890 (vol. xl, p. 312). Recently Mr. JOHN W. DAVIS of Greensburg, Kansas, who first called attention to this occurrence, has given to the editor the following facts in regard to the discovery, which fix the exact date of the find : "I first saw this meteorite on the 20th of September, 1885, and at once identified its meteoric nature. Cowboys riding over the prairie, and cattlemen occupying the country between the Medicine River and the Arkansas River, had known of the strange heavy stones at least four years before that time. It was one of them who took me to the place and showed them to me. After I identified them as meteorites, people living in that immediate vicinity took an interest in them and collected eight or ten large pieces and had them in their door yards and gardens. One piece weighing 202 pounds was discovered 12 miles southwest of the place I have just described about a year later. Over a bushel of small fragments were found lying together and very much oxidized. Some of these little ones were almost round and showed no signs of broken surfaces. Outside the 202-pound specimen mentioned, the others have all been found within an area three miles long and one mile wide, lying a little southeasterly. Most of them were a little above the surface of the ground, just showing at the grass roots, and none of them have been found with their top surface more than eight or ten inches deep; these last were completely covered by soil, and were discovered by plowing. There is some broken country within the area described, which has never been disturbed, and doubtless other specimens will be found there. Benjamin McFadden, the cowboy who told me about these meteorites and showed them to me, said he buried one of them several years before in a badger hole, and pointed toward the locality; he died two months later of typhoid fever, and of course no one now knows the exact spot. The soil where these meteorites were found is a heavy loam, black or rather dark brown in color, with a small proportion of sand, and was covered with a heavy coat of buffalo grass; such a surface could hardly have been penetrated very far even if the force of impact had been very great."

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The National Academy of Sciences.-The annual spring meeting of the National Academy was held in Washington on April 19 to 21; a large number of members were in attendance. The following gentlemen were elected to membership: Henry Seely White, of Vassar College; Charles Greeley Abbot, of the Astrophysical Observatory, Smithsonian Institution; Robert Andrews Millikan, of the University of Chicago; Alexander Smith, of Columbia University; Samuel Wendell Williston, of the University of Chicago; William Ernest Castle, of Harvard University; Frank Rattray Lillie, of the University of Chicago; Graham Lusk, of Cornell University Medical College, New York City; Victor Clarence Vaughan, of the University of Michigan; Granville Stanley Hall, of Clark University.

The list of papers presented is as follows:

THOMAS H. MORGAN: Localization of the hereditary material in germ cells. JACQUES LOEB: Stimulation of growth.

L. B. MENDEL: Specific chemical aspects of growth.

EUGENE F. DU BOIS: Basal metabolism during the period of growth.

I. S. KLEINER and S. J. MELTZER: Retention in the circulation of injected dextrose in depenceratized animals and the effect of an intravenous injection of an emulsion of pancreas upon this retention. JOEL STEBBINS: The electrical photometry of stars. GEORGE E. HALE: A vortex hypothesis of sun spots. EDWIN B. FROST: The spectroscopic binary,  $\mu$  Orionis.

ROBERT W. WOOD: One-dimensional gases and the experimental determi-nation of the law of reflection for gas molecules. The relations between resonance and absorption spectra.

EDWARD L. NICHOLS and H. L. HOWES: On the polarized fluorescence of ammonio-uranyl chloride.

ROBERT A. MILLIKAN: Atomism in modern physics.

WILLIAM MORRIS DAVIS: Problems associated with the origin of coral reefs; suggested by a Shaler Memorial Study of the reefs of Fiji, New Caledonia, Loyalty Islands, New Hebrides, Queensland and the Society Islands, in 1914.

F. W. CLARKE: Inorganic constituents of marine invertebrates.

ROY L. MOODIE: Amphibia and Reptilia of the American Carboniferous.

H. F. OSBORN and J. H. MCGREGOR: Human races of the Old Stone Age of Europe, the geologic time of their appearance, their racial and anatomical characters.

CHARLES A. DAVIS: On the fossil Algæ of the petroleum-yielding shales of the Green River Formation.

NATHANIEL L. BRITTON: The Forests of Porto Rico.

J. WALTER FEWKES: Pictures on prehistoric pottery from the Mimbres valley in New Mexico and their relation to those of Casa Grande.

CHARLES B. DAVENPORT: Inheritance of temperament. Inheritance of Huntington's chorea.

The second of the series of lectures, two in number, on the William Ellery Hale foundation, were delivered by Professor T. C. Chamberlin of the University of Chicago upon the subject: "The Evolution of the Earth." A lecture was also given by George W. Parker, official representative of the Academy, upon the Board appointed by the President of the United States to study and report upon the Alaskan Fur Seals during the summer of 1914. The subject of this lecture was "The Fur Seal Herd of the Pribilof Islands."

2. The Common Law and the Case Method in American University Law Schools. A Report to the Carnegie Foundation for the Advancement of Teaching ; by JOSEF REDLICH. Bulletin No. 8. Pp. xi, 84. New York City, 1914 .--- Under the department of the Carnegie Foundation devoted to Education Enquiry, several important investigations have already been carried on, notably that pertaining to American Medical Schools. This latest bulletin presents the conclusions reached by Professor Redlich of the University of Vienna, who came to this country to study the American method of the teaching of law. It is gratifying that he should speak in the highest terms of American schools, finding legal education here more highly developed than in England. The case method, here in use, he concludes has proved itself eminently successful in the training of practitioners, in part from the fact that Anglo-American law is still almost entirely a law of adjudicated cases, and hence the principal task of the practitioner is to discover from scattered sources what the law actually is. This method, by training the student's reasoning power, renders a service that will be of great practical assistance to him in his future profession. While fully recognizing the value of the case method, Professor Redlich suggests that an exaggerated importance may be attached to it. In particular he takes issue with those who would banish from the curriculum any form of lecture or other dogmatic instruction; both at the beginning and at the end of the curriculum he recommends lecture courses, covering phases of legal instruction which can be satisfactorily imparted in no other way. He thinks also that the effectiveness of the case method is endangered by the increasing size of classes, and he recommends the lengthening of the law course to four years, with a corresponding diminution of the time required to be spent in college.

3. Publications of the Allegheny Observatory of the University of Pittsburgh.—The following have recently been issued: Vol. III, No. 11. A Description of the large screw-measuring Engine of the Allegheny Observatory; by FRANK SCHLESINGER. Pp. 83-97; 1 plate, 1 fig.

No. 12. The Orbit of 88 d Tauri; by ZACCHEUS DANIEL. Pp. 93-97; 1 fig.

No. 13. A Description of the Porter Spectrograph, and a determination of the Solar Rotation; by FRANK SCHLESINGER. Pp. 99-118; 3 plates, 1 fig.

No. 14. The Orbit of  $\delta^i$  Lyræ; by FRANK C. JORDAN. Pp. 119-124; 1 fig.

No. 15. The Spectrum and Orbit of  $\delta$  Orionis; by FRANK C. JORDAN. Pp. 125-136; 2 figs.

No. 16. The Orbit of R.Z. Cassiopeiæ; by FRANK C. JORDAN. Pp. 137-145; 2 figs. No. 17. The Orbit of 108 Hercules; by ZACCHEUS DANIEL and LOUISE F. JENKINS. Pp. 147-152; 1 fig.

No. 18. The Orbit of 25 Serpentis; by FRANK C. JORDAN. Pp. 153-159; 1 fig.

4. Laboratory Manual for the Detection of Poisons and Powerful Drugs; by WILHELM AUTENRIETH. Translation of the 4th German edition by WILLIAM H. WARREN. Pp. xv, 320. Philadelphia, 1915 (P. Blakiston's Sons & Co.).-Despite the already enormous and steadily increasing number of books dealing with appropriate topics in almost every field into which the science of chemistry extends, it is difficult to find a dependable manual of chemical toxicology. The volume by Professor Autenrieth, which has now reached its fourth edition, has become one of the really valuable works of reference on the subject of the detection of poisons. Its usefulness is determined in good measure by the fact that the analytical procedures selected by the author represent as a rule the methods which experience in a highly specialized department of chemistry has sanctioned. The directions are sufficiently explicit to serve as a reliable guide to any careful worker. Now we find the new American translation including a consideration of several drugs which have grown in prominence in recent years; and the addition of details in respect to the physiological aspect of some of the poisons enhances the usefulness of the book. Autenrieth's "Poisons" really "supplies a want" and deserves a favorable notice. L. B. M.

5. What is Adaptation? by R. E. LLOYD. Pp. xi, 110. London, 1914 (Longmans, Green & Co.).—The author shows by rather abstruse reasoning that adaptation is a primary attribute of all living things, that it is entirely independent of natural selection, and that the species of organisms are as perfectly adapted at the time of their origin as at any later period. The theory of natural selection is entirely rejected in favor of the more recent theory of the origin of species by mutation. W. R. C.

#### OBITUARY.

DR. RICHARD LYDEKKER, the English naturalist, geologist, and traveler, died on April 19 at the age of sixty-five years. From 1874 to 1882 he was on the staff of the Geological Survey in India. His publications include "Indian Tertiary Vertebrata," "Geology of Kashmir," "Catalogues of Fossil Mammals, Reptiles, and Birds in the British Museum," ten volumes; "Phases of Animal Life," "The Great and Small Game of India, Burma, and Tibet," and many other books chiefly in natural history.

PROFESSOR A. A. W. HUBRECHT, the eminent Dutch zoologist, died at Utrecht on March 21 in his sixty-fifth year.

DR. ARTHUR SHERIDAN LEA, the English physiologist, died on March 23 at the age of sixty-one years.
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# CONTENTS.

	1 460
ART. XXX.—Formation and Distribution of Fluviatile and	
Marine Gravels; by H. E. GREGORY	487
XXXI.—Coal Measures Amphibian with an Osseous Tarsus:	
by R. L. MOODIE	509
XXXIIContributions to Sardinian Petrography: I. The	
Rocks of Monte Ferru; by H. S. WASHINGTON	513
XXXIIIEstimation of Pentavalent Vanadium by Means	
of Sodium Thiosulphate; by G. O. OBERHELMAN	530
XXXIVDevelopment of the Mesenteries in the Zooids	
of Anthozoa and its Bearing upon the Systematic Posi-	
tion of the Rugosa; by T. C. BROWN	535
XXXVUse of the Roentgen Ray in Paleontology: Ski-	
agraphy of Fossils; by R. M. FIELD. (With Plate VIII)	543
XXXVINew Ordovician Eurypterid; by E. W. SHULER	551
XXXVII.—New Mosasaur from the Ft. Pierre: by F. B.	
LOOMIS	555
XXXVIII.—Growing Crystals for Measurement: by J. M.	
BLAKE	5.1
XXXIX.—Primary Analcite of the Crowsnest Volcanics: by	
J. D. MACKENZIE	571
XLNew Genera of Permian Reptiles; by S. W. WILLISTON	575
XLIRadium Content of Water from the Gulf of Mexico:	
by S. J. LLOYD	580
XLIIMobilities of Ions in Air; by E. M. WELLISCH	583

### SCIENTIFIC INTELLIGENCE.

- Chemistry and Physics—Production and Uses of Hydrogen, A. F. SEEKER, 600.—Density of Lead from Ceylon Thorite, F. SODDY, 601.—Analysis of Alloys containing Tin, Antimony and Arsenic, F. A. STIEF: Density and Dispersion of Liquid Hydrogen and Nitrogen, H. AUGUSTIN, 602.—Absorption Spectrum of Chlorophyll, D. VAN GULIK: New Type of Band Series, A. FOWLER, 604.
- Geology—Problems of American Geology, W. N. RICE, etc., 605.—West Virginia Geological Survey: Illinois Geological Survey, 607.—South Dakota Geological Survey: Report of State Geologist on Mineral Industries and Geology of Vermont, 1913-1914: Les Variations Périodiques des Glaciers, XIX<sup>mo</sup> Rapport, 1913, A. HAMBERG et P. L. MERCANTON, 608.— Additional Facts in Regard to the Discovery of the Meteorites of Brenham, Kiowa County, Kansas, J. W. DAVIS, 609.
- Miscellaneous Scientific Intelligence-National Academy of Sciences, 610.— The Common Law and the Case Method in American University Law Schools: Publications of the Allegheny Observatory of the University of Pittsburgh, 611.—Laboratory Manual for the Detection of Poisons and Powerful Drugs (W. Autenrieth), W. H. WARREN: What is Adaptation? R. E. LLOYD, 612.

Obituary-R. Lydekker: A. A. W. HUBRECHT: A. S. LEA, 612.

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# FOURTH SERIES

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WITH PLATE IX.

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Plate IX.



Equus scotti, mounted specimen, Yale Collection.

### тне

# AMERICAN JOURNAL OF SCIENCE

# [FOURTH SERIES.]

ART. XLIII.—The Vertebrate Fossils of Rock Creek, Texas; by Edward L. TROXELL.\* With Plate IX.

[Contributions from the Marsh Publication Fund, Peabody Museum, Yale University.]

OUTLINE.

Introduction The use of ratios List of species Equidæ Camelidæ Extinction Canidæ Suidæ Testudinidæ Megalonychidæ Elephantidæ Summary Bibliogrephy List of illustrations



### Introduction.

In the field season of 1912 Peabody Museum of Yale University sent out an expedition to the Panhandle region of Texas under the charge of Professor R. S. Lull. The party spent about six weeks at the head of Rock Creek (see map, fig. 1) in Briscoe County searching for vertebrate fossils, and from this locality were secured the specimens described in this paper.

About thirteen species were found, consisting of seven different families represented to-day by the living forms of camel, dog, horse, elephant, sloth, peccary, and turtle.

Besides the two principal deposits, various fragments and isolated bones were found along Rock Creek and Tule Canyon.

\*Abstract of a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Yale University, 1914.

Am. Jour. Sci.—Fourth Series, Vol. XXXIX, No. 234.—June, 1915. 40



FIG. 1.

FIG. 1. Outline map of Rock Creek.

From the Equus scotti quarry of J. W. Gidley additional specimens of the horse were found, one of which is now mounted in Peabody Museum, making in all about eight skeletons taken from this one hill during a period of thirteen years. The Mylodon-camel quarry yielded all the other material listed, but the skeletons were never so perfectly preserved as those of Equus scotti.

<sup>1</sup>The use of ratios.—The results of this paper are derived mostly from the use of "ratios." Apparently nowhere in the literature has such an application been made of "ratios," comparing one type to another. Osborn in his "Craniometry of the Equidæ," and other writers, have used ratios of one dimension to another, on the same skull, calling such a "ratio" an "index." The "index of slenderness" or of "elongation" had already been devised to meet the needs in describing the long slim cannon-bones of Equus calobatus, n. sp. (fig. 4), when in conversation Professor Osborn suggested the value of the "speed index." He also said that the ratios between homologous parts were useful in showing specific differences, and it is probable that this principle has been applied in his study of the Tita notheres soon to be published.

Professor Lull has frequently suggested the great constancy of the relation between the teeth and limb bones. This idea was utilized, not by a direct comparison of the teeth to the skeleton, thus getting an *index*, but by comparing the teeth and skeleton of the fossil to be studied to the teeth and skeleton, respectively, of a known recent animal, thus getting a *ratio*. This not only serves to separate out the individuals, but also indicates specific and generic characters.

The use of "ratios" and "indices" will be more fully illustrated in the description of the various forms.

I take pleasure in expressing my gratitude to Professors Schuchert and Lull for their generous assistance in the preparation of this paper. Professor Schuchert made it possible for me to go with the Yale Expedition in 1912, and has done me many other favors. To Professor Lull, through whose inspiring personality and interesting courses I was led to take up the study of vertebrate paleontology, I am indebted for criticisms which were of great aid in my work on the material treated in this paper.

### LIST OF SPECIES.

# Class Mammalia.

### Equidæ.

- 1. Equus scotti (separate quarry)
- 2. E. (Asinus) calobatus, n. sp.

# Camelidæ.

- 3. Auchenia hesterna
- 4. Eschatius conidens
- 5. ? E. macrocephalus

# Canidæ.

- 6. Canis dirus
- 7. C. texanus, n. sp., cf. mississippiensis
- 8. C. ? scevus
- 9. C. temerarius

# Elephantidæ.

- 10. Elephas columbi (or a young imperator) Megalonychidæ.
- 11. Mylodon harlani

# Suidæ.

12. Platygonus compressus

# Class Reptilia.

### Testudinidæ.

13. Testudo campester

F1G. 2.



FIG. 2. Restoration of Equus scotti, by R. S. Lull.

### Equidae.

*E. scotti* Gidley.—The type specimen of this species was found in 1899 by J. W. Gidley (6.111) at the head of Rock Creek; the more mature specimen (Plate IX and fig. 2) found by the Yale Expedition furnishes a few points of added interest. The skeleton is that of a female five or six years of age and as now mounted stands about fifteen hands high.

The limbs of the Yale specimen are heavy; the hoofs are about a sixth broader than those of the Arabian horse of to-day. The skull is heavy. *E. scotti* was a ponderous animal, a form not suited to rapid movements but one probably living in a region surrounded by luxuriant vegetation with plenty of food and water and close in its habits to the mammoth and groundsloth with which it may have been associated. Gidley has ascribed to the type specimen certain characters which would link it with *Equus asinus* or *E. quagga*, especially in the longer body, much larger head, shorter back and steeply sloping



FIG. 3. Posterior and ventral anterior views of atlases. 1, Equus caballus; 2, E. calobatus, n. sp.; 3, E. scotti. About one-sixth nat. size.

sides. The type was a young animal and therefore may show characters and proportions differing from the more mature Yale specimen, thus more closely resembling the ass and quagga.

There are, however, a number of characters shown by the Yale specimen which indicate a very close relation to Equus caballus and a distinct separation from Equus asinus. The ratios between Equus scotti and the smaller Arabian horse run with unusual constancy and give the average of 88.8 per cent. The characters of the sacrum, especially in the manner in which the dorsal and ventral foramina enter the neural canal (fig. 5), the general form of the atlas (fig. 3) and the ratios of the skeletal parts, all show a great similarity of E. scotti to E. caballus. The width of the muzzle measured across the alveoli of incisors number three is greater than the width across the premaxilla over the canines. This is a horse character, distinguishing it from the ass.

Applying the principles of Craniometry, the skull is shown to be exceedingly like that of the recent horse, *E. caballus*, sometimes surpassing the average horse in the extreme of horse eccentricities, and again showing a slight tendency to some of the characters of the mule. The cephalic index is:

E. scotti	38.4 per cent
Horse	40* to 44 per cent
Ass	46* to 49 per cent

An average of the palatocranial angle for nine horses was  $*22.5^{\circ}$ , for two asses it was  $*20.9^{\circ}$ , and for five zebras  $*21.75^{\circ}$ . This angle as found in *E. scotti* is 20°, considerably less than that of the average zebra or ass and even less than that of the average horse. Due to a slight crushing of the horizontal part of the palate the angle is made even greater than it should be.

FIG. 4.

FIG. 4. Limb bones. 1, Equus calobatus, n. sp., hind limb; 2, E. calobatus, n. sp., fore limb; 3, E. scotti, hind limb; 4, E. scotti. fore limb. One-sixteenth nat. size.

This angle in *E. scotti* seems to contradict the statement by Professor Osborn (*loc. cit.*) that: "In *Neohipparion* of the Miocene, *Hipparion* of the Pliocene and *E. scotti* of the Pleistocene the face is strongly bent down on the cranium," for *E. scotti* shows less tendency than *E. caballus* toward cytocephaly.

In the form of the orbits, *E. scotti* departs widely from the ass and even goes beyond the horse in the horizontal elongation. The orbital indices are:

E. scotti	69.7	per	$\operatorname{cent}$		
Horse	*84.2	to	93.5	per	cent
Ass	*96.0	to	104.2	per	cent

The horizontal diameter is slightly increased in *E. scotti* because of fracture.

NOTE: All measurements indicated thus \* are taken from Osborn (15.85).

 $Equus \ calobatus$ , n. sp.—In the quarry which produced the greater variety of specimens, limb bones of Equus (fig. 4) were found which were unusually long and slender. Associated with these were various parts of the skeleton which correspond closely in size. This specimen, so unique in the form of the limbs, and so distinct from *E. scotti* and *E. caballus*, may well constitute a new species. Because of the close similarity to the recent ass, fossil specimens of which are almost unknown, this type will be designated Equus (Asinus) calobatus, n. sp., the specific name meaning "he who walks on stilts."

The limbs of the new type offer a most interesting study, and it is upon these that the species is founded. The cannonbones in particular are most unusual in the development of their great length. The tibia is not so long, but in general it is more slender than that of E. caballus, although the latter, as represented by the Arabian horse, has a higher speed index.

The cannon-bone of the fore limb is 19.4 per cent longer than that of the Arab horse, and it is over a half longer than that of *Equus asinus*. The length of this cannon-bone in *E. calobatus*, whose diameters give an average ratio of 85.4 per cent of that of *E. scotti*, is actually greater in length by more than  $4^{\text{cm}}$ .

Of all the species studied, the speed index is highest in the cannon-bone of the ass (8.68); next to it is that of the new species, in which the index is 8.57. It is very high in either, but considering the greater size of the fossil (a half taller, and therefore probably over three and a third times as heavy), its index is exceedingly high. Compared to the Arabian horse, a good cursorial type, the slim fossil shows an index 18 per cent higher, and compared to the ponderous E. scotti, it is 44 per cent higher.

The speed index is found by dividing the length by the transverse dimensions of the shaft. The shaft measure in E. asinus is particularly small; this makes the speed index correspondingly high. If the average of all the diameters (see table, page 620) be taken and divided by the length, the ratio may be called the "index of slenderness." This index shows that E. calobatus has the slenderest cannon-bone of all, the order of slenderness being:

Ε.	calobatus	14.3	per cent
$E_{\cdot}$	asinus	15.7	
E.	caballus	17.0	66
Ε.	scotti	19.0	66

The reciprocal of the "index of slenderness" may be taken as the "index of elongation."

	$\mathbf{sn}$	я							
Metacarpal	tedole) .qa .n	ullad <b>a</b> O	ittooZ	suniaA	Cal C	$\frac{Cal}{S}$	s o	$\frac{A}{Cal}$	A N
Width of distal end	4.56	4.91	24.9	3.58	92.9	0.64	85.2	78.5	62.0
Diameter of keel	3.54	3.59	4.27	2.78	9.86	83.0	84.0	78.5	65.1
Shaft, transverse diam.	3-35	3.32	4.10	2.20	101.0	4.18	81.0	65.7	53.6
Proximal end transverse diam.	5.39	5.27	5.73	3.85	102.4	94•0	91.8	11.4	67.2
Proximal end antpost. diam.	3.70	3.42	4.15	2.53	108-2	89.1	82.4	68.4	61.0
Averages of cross dimensions	4.11	4.10	4.80	2.99					
Length	28.70	$24 \cdot 10$	24.4	19.1	119-4	117.7	98.86	ç.99	78.3
Average ratios					103.8	90.8	87.2	2.1.4	64.5
Speed index $\frac{No. 7}{No. 3}$	8.57	7.26	5.95	89.8	118.0	144.0	122.0	101.3	146.0
Index of slenderness $\frac{No. 6}{No. 7}$	14.8	17.0	19.7	15.7					

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Equus

Ratios

620 Troxell-- Vertebrate Fossils of Rock Creek, Texas.

In spite of the fact that the "speed index" generally indicates a cursorial adaptation, it is quite probable that the slenderness and elongation have gone too far in this fossil type for the best speed development.

The ungual phalanx of E. calobatus, compared to that of E. scotti, is very narrow, as shown by the low ratio of 71.8 per cent. Compared to E. caballus africanus, it shows low ratios in the transverse dimensions, but a higher ratio in the altitude, corresponding to the greater height of the animal. This hoof

FIG. 5.



FIG. 5. Cross sections of sacra. A, Equus calobatus, n. sp.; B, E. scotti and E. caballus. One-fourth nat. size.

bone of the new species is very much like the narrow hoof of the modern ass.

An additional similarity between *E. calobatus* and *E. asinus* is shown in the atlas, which in its general form, the shape of its wings, the internal sulcus, the ventral tubercle, the foramen transversarium, and the anterior ventral groove, shows a great resemblance between the two.

*E. calobatus*, n. sp., shows a marked contrast to *E. scotti* and *E. caballus* in the form of the sacrum. In the last two species, the dorsal (d, fig. 5) and ventral (v) sacral foramina enter the neural canal (n) quite independently, their confluence being in a wide space or vestibule on the wall of the canal. This is due to the fact that the centra and thus the canal are wider than the space between the dorsal foramina; the latter therefore enter the roof of the canal. On the other hand, because of the narrowness of the neural cavity in *E. calobatus*, the dorsal foramen as well as the ventral lies outside the border of the neural canal. They therefore join to form the true intervertebral foramen (i) which in turn opens into the sacral canal.

Certain similarities between the sacrum of *E. calobatus* and that of *E. asinus* are notable, most of which are due to the coössification of the spines. In *E. calobatus* they form a solid plate with but a single foramen, representing all of the interarcuate spaces. Such a solid fusion of the neural spines is an adaptation of nature to meet the needs of a great stress in the direction of the median plane, or else is simply an old age character.

Very little is known of the fossil ancestors of E. asinus. According to Flower and Lydekker (5.383), teeth and bones from the Pleistocene deposits in Madras are considered to be of that species. Specimens related to the ass and quagga have been reported from America, but the resemblance is based on seemingly meager evidence. Nearly every part of the skeleton of E. calobatus which is known, however, shows a closer relation to E. asinus than to either E. caballus or E. scotti.

# Camelidæ.

From quarry number one camel material was found, consisting of fragments and small bones. By the method of ratios,

FIG. 6.

FIG. 6. Auchenia hesterna, third upper molar. 1, crown, and 2, side views. One-third nat. size. comparison was made with a recent form, and from the relative size it was found that there were three different individuals, probably representing as many species.

Auchenia hesterna. — The parts which were larger than the standard *Camelus bactrianus* No. 1551 of Peabody Museum showed very definite characters which undoubtedly correlate the specimen with the South American llama. The morphology of the larger bones as well as the constancy of ratio to the llama emphasizes this close relation, although the fossil is two or two and one-half times as large as the recent South American form.

The large third upper molar (fig. 6) when compared to the standard gave a ratio considerably over 100 per cent, identifying it as belonging to the largest animal. This large tooth, with its broad grinding surface, cement-filled lakes, and hypsodont crown, indicates the grazing habit of its owner. Because of this and because of the good cursorial adaptation, as shown by the high speed index of the limb bones (fig. 7), the animal is judged to have been a plains dweller in a semi-arid climate, traveling far for food and water.

*Eschatius conidens.*—There were found parts of the skeleton of a camel of moderate size, giving an average ratio less than 90 per cent that of the standard. With this group was a fragment of the maxillary (fig. 8) containing two molar teeth, whose average ratio is 84 per cent. Especial interest is attached to this portion of skull because it shows, in front of the first molar, a small round alveolus representing a conical tooth, the

only remnant of the premolar dentition. The only specimens similar to it are those of *Eschatius conidens* (2.16) from the valley of Mexico and another much broken specimen from Oregon.

The teeth of the Yale specimen, by their setting at an angle trending backward, their lack of cement filling, narrow short crowns, and sharp cusps, indicate the browsing character of the animal.





FIG. 7. Auchenia hesterna, first phalanx. 1, front, and 2, side views. One-third nat. size.

A moderate-sized scapula (ratio 84 per cent) (fig. 10) probably belongs with the teeth just mentioned. The bone is light, it has a good coracoid for leverage, a broad articulation not easily dislocated, and is, undoubtedly, possessed of universal



FIG. 8. Eschatius conidens, maxillary with alveolus of  $P^4$ , the sole remnant of the premolar dentition, and  $M^1$  and  $M^2$ . One-third nat. size.

movement, so far as such is to be found in ungulates. Such an animal should be fleet and agile, capable of scrambling about over a wooded, hilly country.

With the fragment of maxillary and its teeth and the scapula just mentioned, there were other parts such as a cervical vertebra, the proximal end of a cannon-bone (fig. 12) and a



FIG. 9. Auchenia hesterna. glenoid aspect of scapula. One-third nat. size. FIG. 10. Eschatius conidens, glenoid aspect of scapula. One-third nat. size.

small phalanx (fig. 13), which seemed further to indicate a rather slender agile animal with the browsing adaptation.

The small phalanx is specifically distinct from the larger phalanges. It may belong to *Eschatius conidens*, since its ratio is but 6 per cent lower than that of the *Eschatius* teeth.



FIG. 11. Auchenia hesterna, head of cannon-bone. One-third nat. size. FIG. 12. Eschatius conidens, head of cannon-bone. One-third nat. size.

Measurements and Ratios of Phalanx No. 200.

	Fossil No. 200
Ratio	
108	9.7
66	2.5
88	2.8
60	2.1
77	2.0
67	1•4
88	1.4
	6.96
	Ratio 108 66 88 60 77 67 88

79

The bone is long and slender, the ratio of its length to that of the recent camel is 108 per cent, while the next highest ratio is only 88 per cent. The phalanx is exceedingly narrow, giving a ratio of 42 to 48 per cent less than that of the length. The speed index is very high. The lateral roughenings found in the other bones are absent in this phalanx, but the posterior tuberosity is very prominent; it has a peculiar V-shaped notch in the lower half.

The narrowness of the bone, the lack of symmetry, the flat inner surface, all indicate a close proximity to its fellow. The

Fig. 13.

FIG. 13. *?Eschatius conidens*, first phalanx of camel, showing unusual slenderness and dissymmetry. 1, anterior; 2, external; 3, posterior; 4, proximal aspects. One-third nat. size.

toes did not have a great spread. The bone stood quite erect and probably belonged to an animal not semi-digitigrade as the camel generally is, but more truly unguligrade and a good cursorial type.

Certain rather inconspicuous characters of the bones correlated with *E. conidens* show a closer relation to the Old World type of *Camelus* than they do to *Auchenia*. The dental formula, however, shows the genus *Eschatius* to be much more specialized than any other of the group.

*Extinction of Camels.*—The camels, though indigenous to North America, became entirely extinct in this country. As early as the Lower Pliocene we find fossils in the Old World, showing that one branch had migrated, probably across "Bering Land," giving rise to the genus *Camelus*.

In South America the earliest cameloids are found in the Pliocene. These were ancestral to the South American genus Auchenia represented by the llama, alpaca, guanaco, etc. It seems probable that in the late Tertiary some forms allied to Auchenia became adapted to mountain life, and either as a cause or result were smaller. The smaller animal could cross the barriers impassable to the larger Auchenia and early

moved southward across the newly formed isthmus and was probably already established at the beginning of the Glacial Period. The larger *Auchenia*, not fitted for other than plains habitation, continued within the barriers which were passable to its smaller cousin and hence became extinct. Its extermination resulted, in a more or less direct way, from the advance of the great ice sheet, though the cold itself would not necessarily have accomplished the destruction. It is estimated that a drop of 7° in yearly average temperature would be sufficient to restore Glacial conditions in Europe (16.134). With the ice there came a change of vegetation; incident to its approach there would be greater precipitation, then swollen



FIG. 14. Pathologic camel phalanx. Anterior view. One-third nat. size. FIG. 15. Normal camel phalanx, front and rear views. One-third nat. size.

streams, floods and swampy lands. The region thus became uninhabitable to the animals of arid land adaptation and their extinction followed. So to-day the North American Auchenia is known only by its very abundant fossil remains.

Much has been said about the effect of diseases in causing the extermination of races. The interesting pathologic phalanx (fig. 14) is probably a result of exostosis or uncontrolled deposition of bony material. The bone was not broken, because it shows the same length as the normal one (fig. 15) of the same size. Possibly the disease which caused the death of the individual also contributed to the destruction of the species.

## Canidæ.

There were found with the Rock Creek material parts of dog-like animals belonging apparently to four individuals.

The study of these specimens offers an interesting test of the use of "ratios," by which the parts are separated into well defined groups. Each bone is compared in as many dimensions as possible with the corresponding part of Canis familiaris No. 1077 of the Peabody Museum Östeological Collection and its average is tabulated in the index list.



FIG. 17.



### FIG. 18.





FIG. 16. Canis dirus, proximal phalanx. Anterior, lateral, and posterior views. One-half nat. size.

FIG. 17. Canis dirus, tibia, posterior view. One-third nat. size. FIG. 18. Canis texanus, n. sp., holotype, ramus and dentition. Onethird nat. size.

The largest animal, of which there are four parts (group 1), gives an average ratio of 151 per cent; the second, group II', which includes the type of *C. texanus*, n. sp., and seven parts constituting the paratype, gives an average of 114 per cent.

The third group, a single tooth, M', gives a ratio of 86 per cent. This tooth, in addition to its small size, is duplicated in group II, thus eliminating the possibility of its belonging with the type of *C. texanus*.



FIG. 19. Canis ? priscolatrans, first upper molar. One-third nat. size. FIG. 20. Canis texanus, n. sp., paratype, first upper molar. One-third nat. size.

The last group consists of but two bones which belonged to a small animal 65 per cent of the size of the recent dog.



FIG. 21. Canis temerarius, first phalanx. One-half nat. size.FIG. 22. Canis temerarius, tibia. One-half nat. size.

Index list.

Group I	No. 10079 Field number	Ratio	Figure
Phalanx	145	163	16
Tibia	41	148	17
Rib	354	143	
Premolar P <sup>3</sup>	12	150	
Average		151	

Group II	No. 10058		
	Field number	Ratio	Figure
Molar M <sup>1</sup>	83	119	20
Humerus	246	117	23
Ramus	69	117	18
Magnum	432	113	
Scapula	325	112	
Cuboid	308	110	
Metatarsal	319	109	
Average		114	
Canis familiaris	No. 1077	100	Used for com- parison
Group III	No. 10080		1
Molar M <sup>1</sup>		86	19
Group IV	No. 10077		
Phalanx	12	67	21
Tibia distal	244	62	22
Average		65	

FIG. 23.



FIG. 23. Canis texanus, n. sp., paratype, humerus. 1, side, and 2, rear views. One-third nat. size.

The detailed measurements of the bones and the ratios of each dimension to that of the recent dog, *Canis familiaris* No. 1077, are given in the following tables. Sometimes the

AM. JOUR. Sci.—Fourth Series, Vol. XXXIX, No. 234.—June, 1915. 41

ratios are quite constant and again there is a great variation, significant of the specific differences in the two types compared.

GROU	PI.		
Description	Fossil No. 10079	Ratio	Recent No. 1077
Phalanx	No. 145		
Length	4.3	143	3.0
Prox. diam. trans.	1.6	160	1.0
Prox. diam. antpost.	1.3	144	0.9
Distal diam. trans.	1.4	175	0.8
Distal diam. antpost.	1.0	167	0.6
Shaft, diam. trans.	1.2	171	0.7
Shaft, diam. antpost.	0.9	180	0.2
Ŧ		163	
Speed index $\frac{L}{W}$	3.28		4.29
Tibia	No. 41		
Length	26.2	119	22.0
Width, prox. trans.	5.6	137	4.1
Distal antpost. diam.	3.6	171	2.1
Shaft, trans. diam.	$2 \cdot 2$	137	1.6
Shaft, antpost. diam.	2.6	173	1.5
Shaft, distal trans. diam.	4.2	150	2.8
т		148	
Speed index W	11.9		15.0
Rib	No. 354		
Across tubercle	1.4	127	1.1
Radius of curvature	9.5	158	6.0
		143	
P <sup>3</sup>	No. 12		
Antero-posterior diameter	1.8	150	1.2

## GROUP II.

Description	Fossil No. 10058	Ratio	Recent No. 1077
M <sup>1</sup> (Large)	No. 83		
Antpost. diam. over middle	1.3	118	1.1
Grinding surface, transverse diam.	1.2	133	0.9
		125	

Description	Fossil No. 10058	Ratio	Recent No. 1077
Humerus	No. 246		
Length	21.1	111	19.0
Shaft, diam. antpost.	2.1	123	1.7
Shaft., diam. trans.	1.7	106	1.6
Diam. prox. end antpost.	5.8	121	<b>4</b> ·8
Diam. prox. end trans.	4.2	114	3.7
Diam. distal end antpost.	3.6	124	2.9
Diam. of trochlea	1.9	127	1.5
Distal end trans. diam.	4.4	107	4.1
т		117	
Speed index $\frac{1}{W}$	12.4		11.9
Jaw	No. 69		
Length, M <sub>3</sub> over C <sub>1</sub>	11.6	125	9.3
M <sub>1</sub> , diam. ant. post.	2.8	117	2.4
M <sub>1</sub> , diam. trans.	1.1	110	1.0
		117	
Magnum	No. 423		
Length	2.4	114	2.1
Breadth	1.4	108	1.3
Thickness	0.2	117	0.6
		113	
Scapula head	No. 325		
Width over coracoid	4.2	111	3.8
Glenoid cavity, width	2.6	118	$2 \cdot 2$
Neck, diam. antpost.	3.3	103	3.2
Glenoid cavity, length	3.2	116	3.0
		112	
Cuboid (L.)	No. 308		
Length	2.3	128	1.8
Diam. of shaft	1.1	110	1.0
Diam. of shaft, small	0.6	75	0.8
Diam. prox.	1.5	115	1.3
Diam. prox., small	1.2	120	1.0
		110	
Speed index	3.03		2.25
Metatarsal	No. 319		
Length	9.3	107	8.7
Diam. prox. antpost.	1.7	121	1.4
Shaft, diam.	1.8	106	1.7
Dist. antpost. keel	1.1	100	1.1
т		109	
Speed index $\frac{L}{W}$	5.17		5.12

632 Troxed	ll—Verte	brate Fossi	ls of	Rock	Creek.	Texas.
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GROUP	III.		
Description	Fossil No. 10080	Ratio	Recent No. 1077
$M^{1}$ (small)			
Greatest trans. diam.	1.7	94	1.8
Across metacone trans. diam.	1.5	88	1.7
Antpost. diam. parametacone	1.2	80	1.5
Antpost. diam. over middle	0.8	82	1.1
-			
~ · ·		86	
GROUP .	IV		_
Description	Fossil No. 10077	Ratio	Recent No. 1077
Phalanx _	No. 12		Small toe
Length	2.0	77	2.6
Prox. diam. trans.	0.2	70	1.0
Prox. diam. antpost.	0.6	66	0.9
Dist. diam: trans.	0.2	63	0.8
Dist. diam. antpost.	0.4	66	0.6
Shaft, diam. trans.	0.4	66	0.6
Shaft, diam. antpost.	0.3	60	0.2
Ŧ		67	
Speed index $\frac{L}{W}$	5.00		4.33
Small tibia	No. 244		
Thickness, dist, ant,-post.	1.2	57	2.1
Shaft, diam. trans.	1.0	63	1.6
Shaft, diam. antpost.	1.0	67	1.5
Width, dist. trans.	1.7	61	2.8
		60	

The foregoing tables furnish the basis for classifying the bones into groups representing the separate individuals, and further serve, as already suggested, to point out specific characters. A still further use of ratios in an attempt to identify the different animals with known types results in the following tables. The dimensions of the different specimens were taken from the descriptions in the literature, and the ratios to the recent *C. familiaris* No. 1077 were computed. From the ratios of all the available dimensions of each type, only the average ratio is given in the table below.

## Ratios of Specimens in the Literature.

Per cent

Canis haydeni Leidy (9.21)	159
Canis dirus Leidy (8.167)	152
Group I. Peabody specimens	151
Canis indianensis (dirus) (3.458). Cope's Texas specimen,	
about	150

Per	cent
anis dirus (13.244). Rancho La Brea specimen of Merriam	14.1
anis indianensis (12.288). Rancho La Brea specimen of	
Merriam	138
anis indianensis Leidy (11.230). California	137
Canis (Ælurodon) sævus Leidy (9.21)	115
anis mississippiensis Allen (1.49)	114
roup II. Canis texanus, n. sp. Peabody specimens	114
anis priscolatrans Cope (4.227)	106
tandard Canis familiaris No. 1077	100
roup III. M <sup>1</sup> . Peabody specimens	86
anis temerarius Leidy (9.21)	69
roup IV. Peabody specimens	65
anis vafer Leidy (9.21)	49

The general tendency is to put the larger specimens of *Canis* with the species *C. dirus* Leidy.<sup>\*</sup> Prof. W. B. Scott in his new book (16.204) mentions *C. dirus* and *C. indianensis*, which he considers synonymous. It seems quite fitting, therefore, that the first seven specimens, including group I of the Peabody Museum fossils, be placed under *C. dirus* Leidy.

### Measurements of C. texanus n. sp.

	Fossil No. 69	Ratio	Eskimo dog in Amherst College Museum
Depth of jaw at P	<b>-</b> 3·0	78	2.35
Depth of jaw ant. to M,	. 3.25	75	2.45
Depth of jaw post. to M,	- 3.8	68	2.6
Depth of jaw post. to M	- 4.25	78	3.33

		Canis texanus n. sp	Rai	<i>C. dirus</i> ncho La Brea
Description Inferior dentition		No. 10058	Ratio	(13.232)
C <sub>1</sub> antpost. edge of enamel		1.4	80	1.75
P <sub>1</sub> antpost. diam. greatest		0.6	78	0.77
P <sub>2</sub> antpost. diam. greatest		1.12	75	1.54
P <sub>3</sub> antpost. diam. greatest	1.	1.4	84	1.67
P <sub>4</sub> antpost. diam. greatest		1.6	80	2.00
M, antpost. diam. greatest		2.75	77	3.57
M, trans. diam. of heel		1.0	74	1.35
M <sub>1</sub> trans. diam. of trigonid		1.12	80	1.43
M <sub>2</sub> ant. post. diam. greatest		1.1	86	1.28
M <sub>2</sub> trans. diam. greatest		0.8	80	1.0
M <sub>3</sub> antpost. diam. greatest		0.62	100	0.62
Average			81.3	

\*J. A. Allen (1.49) was probably the first to point out the precedence of the name C. dirus over C. indianensis (10.368), which was a later name applied to the type to which the preoccupied name of C. primævus (7.200) was first given by Leidy.

Canis savus Leidy has recently (13.219) been classed under  $\pounds lurodon$  savus.

Canis mississippiensis Allen is based on a tibia and humerus; only the latter is capable of comparison with the paratype humerus (fig. 23) of *C. texanus*. Group II, which includes the type of *C. texanus*, is very near *C. mississippiensis* in size, but the character of the dentition cannot be compared.

Canis texanus as a new species is distinguished from the wolf in the greater curve and twist of the ramus and in its greater depth; in the prominent cusps of  $P_4$ , which slope inward and backward; in the talonid of  $M_1$ , which has a single large cusp; and in the weak metaconid of  $M_2$ .

C. priscolatrans, giving a ratio of 106, is 22 per cent larger than the molar (fig. 19) of group III, but the written description conforms well with this tooth. C. priscolatrans may not be distinct from C. mississippiensis nor C. texanus, n. sp.

The group IV, which is composed of two bones (figs. 21, 22), shows an average ratio of 65 per cent; this is nearest *C. teme-rarius* Leidy, which gives a ratio of 69 per cent to the recent dog.

C. vafer Leidy, with a ratio of 49 per cent, seems too small to be referred even to the small bones of group IV.

The phylogeny of the Canidæ is not well known, even though this group is native to North America. The ancestry is traced back through *Tephrocyon* to *Cynodesmus* and then lost in primordial obscurity. The descendants of these early forms are represented to-day by our dogs, wolves, and foxes, and the recent animals are almost indistinguishable from the fossils.

Carnivores are much more difficult of preservation than other animals, and it is quite unusual for fossil remains of this order to be found. They usually roam about singly or in small groups. They are wary animals, with a keen sense of danger, and are necessarily much fewer in number than the herbivores on which they feed.

The fossil dogs give us little knowledge of their environment. The large heavy beast referred to *C. dirus* may be the analogue of our timber wolf; the smallest, identified as *C. temerarius*, may represent the fox. Either would be best adapted to a timbered country. *C. texanus*, n. sp., and *C. priscolatrans*, represented by the single molar, may be analogous to the prairie wolf or coyote, a swifter type preying upon the cursorial plains dwellers. It is not strange that we should find the species commingled, since even to-day, in the Panhandle of Texas, we find the great Lobo or timber wolf and also the coyote.

## Suidæ.

In the Mylodon-camel quarry at Rock Creek there were two parts (fig. 24) of an animal allied to the modern peccary. In some of the characters, especially the form of the cusps, there is a resemblance to *Dicotyles torquatus*. Most of the fossil Suidæ of the Pleistocene have been referred to the genus *Platygonus*, especially to *P. compressus*, but Flower and Lydekker (5.291) state that: "Large peccaries also occur in the Pleistocene of the United States, which, although they have been referred to a distinct genus, *Platygonus*, on account of

Fig. 24.



FIG. 24. *Platygonus compressus*, fragment of ramus. 1, crown, 2, side view; 3, tusk. Two-thirds nat. size.

their relatively smaller incisors and somewhat simpler premolars, may well be included in *Dicotyles*."

The range of the ratios between the Rock Creek specimen and one of *P. compressus* is very small, 125 to 136 per cent, while there is a greater variation with the recent specimen of *Dicotyles torquatus*.

*Platygonus*, indigenous to North America, appears first in the Middle Pliocene and disappears with the Equus zone of the early Pleistocene.

# Testudinidæ.

*Testudo*, sp. ind.—The presence of a turtle in the quarry, though giving no definite clue to the age of the beds, yet tells us of undoubted river conditions.

# Megalonychidæ.

Mylodon harlani.—The duplication of parts indicates the presence of at least three individuals of the edentate  $Mylodon^*$  in quarry number one. Only broken parts of the skulls were found and a few isolated teeth, but there seems to be almost a complete specimen represented by the vertebræ and the limbs. The huge pelvis, measuring about three and one-half feet across, was, strangely enough, preserved in a sand bed, where other bones were considerably worn by water action.

Though a leaf-feeder, *Mylodon* is native to a semi-arid climate. A late South American immigrant, its presence in the quarry cannot be later than the earliest Pleistocene.

## Elephantidæ.

*Elephas ?columbi.*—A tooth, the proximal end of a femur, and the middle portion of a tusk were found. These parts are small, probably not more than two-thirds the size of a fullgrown elephant. The lamellæ of the molar as well as the smaller size indicate the Columbian or a young Imperial mammoth.

*Elephas columbi* does not appear until the early Pleistocene; if the identification of the species be correct, and it be taken in connection with *Platygonus* and *Mylodon*, it indicates that the layers of quarry number one are no earlier nor later than the Equus beds.

## Summary.

The material collected by the Yale Expedition of 1912 at Rock Creek, Texas, included thirteen different species, representing seven families. The living types to which they are most nearly allied are the camel, dog, horse, elephant, sloth, peccary, and turtle.

Very satisfactory results were obtainable, especially in the study of fragmentary material, by the use of "ratios." This device, little used heretofore, not only served to associate the parts of an individual according to size, but also pointed out differences in proportion which were indicative of the variations between the species.

An additional specimen of *Equus scotti* Gidley was found, which is now mounted in the Peabody Museum. It seems quite probable that *E. scotti* is a true horse and is not allied to the ass or quagga, as was formerly supposed.

Equus (Asinus) calobatus, n. sp., the holotype of which is among the Rock Creek material, is distinguished by the unusually long and slender limb bones. Of the modern types, it is nearest to the ass, which it resembles very much.

\* Described by Professor Lull in this Journal for April, 1915.

Two distinct types of camel were found. The large Auchenia hesterna, showing characters closely relating it to the South American species, is a plains or desert form, as indicated by its grazing and cursorial adaptations. Eschatius conidens is of moderate size. This genus is characterized by the loss of all the premolars but one, which is a simple cone. The teeth indicate the browsing habit of this animal, while the associated limb bones are probably those of an agile form, adapted to hilly country.

By "ratios" the canid material was easily separated into four distinct groups, which were judged to represent as many different species. The largest is *Canis dirus*, which Professor Cope had already found at Rock Creek. The second animal is designated C. texanus, n. sp., cf. mississippiensis. Of the latter only two limb bones are known, while the new species is based on the left ramus with all its teeth, and on five parts of the skeleton. The third group consists of but a single upper The fourth group comprises two bones which by molar. reason of their small size were identified as C. temerarius.

A tusk and a fragment of the ramus of *Platygonus com*pressus was discovered. Parts of three or more individuals of the tribe of giant sloths were found. These, with P. compressus, indicate the early Pleistocene age of the fauna.

The identification of the elephant material is doubtful, but because of its association and small size, it is judged to be a young imperial mammoth.

The extinction of this entire fauna, except the dogs and turtles, was probably brought about in a more or less direct way by the advance of the early Pleistocene glaciers, causing a change in the environment and rendering it uninhabitable.

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### LIST OF ILLUSTRATIONS.

### PLATE IX. Equus scotti, mounted specimen, Yale Collection.

- FIG. 1. Outline map of Rock Creek. 2 in.  $= 1\frac{1}{2}$  miles. 2. Restoration of Equus scotti, by R. S. Lull.

  - 3. Posterior and ventral anterior views of atlases of
    - 1. Equus caballus.
    - 2. Equus calobatus, n. sp.
    - 3. Equus scotti.
      - About one-sixth natural size.
  - 4. Limb bones.
    - 1. Equus calobatus, n. sp., hind limb.
    - 2. Equus calobatus, n. sp., fore limb.
    - Equus scotti, hind limb.
       Equus scotti, fore limb.
    - - One-sixteenth natural size.
  - 5. Cross sections of sacra.
    - A. Equus calobatus.
      - B. Equus scotti and E. caballus.
        - One-fourth natural size.
  - Auchenia hesterna, third upper molar, crown and side view.
     Auchenia hesterna, 1st phalanx, front and side view.

  - 8. Eschatius conidens, maxillary with alveolus of P<sup>4</sup>, the sole rem-nant of the premolar dentition, and M<sup>1</sup> and M<sup>2</sup>.
  - 9. Auchenia hesterna, scapula head.

  - Eschatius conidens, scapula head.
     Auchenia hesterna, head of cannon-bone.
  - 12. Eschatius conidens, head of cannon-bone.
  - 13. ? Eschatius conidens, 1st phalanx of camel, showing unusual slenderness and dissymmetry.
  - 14. Pathologic camel phalanx.
  - 15. Normal camel phalanx. front and rear views.
  - 16. Canis dirus, 1st phalanx. One-half natural size.
  - 17. Canis dirus, tibia, posterior view.
  - 18. Canis texanus, n. sp., holotype, ramus and dentition.
  - 19. C. ? priscolatrans, 1st upper molar.

  - C. teranus, n. sp., paratype, 1st upper molar.
     C. temerarius, 1st phalanx. One-half natural size.
  - 22. C. temerarius, tibia. One-half natural size.
  - 23. C. texanus, n. sp., paratype, humerus, side and rear views.
  - 24. Platygonus compressus, fragment of ramus and tusk. Two-thirds natural size.

All figures one-third natural size, unless otherwise indicated.

# ART. XLIV.—The Volumetric Determination of Polythionic Acids by Potassium Iodate; by George S. JAMIESON.

In a recent paper\* from this laboratory it was shown that sulphurous acid could be titrated with a solution of potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid and a small volume of an immiscible solvent, such as chloroform, according to the general method of L. W. Andrews.<sup>+</sup> It has been found that thiosulphuric and tetrathionic acids can be titrated in the same manner, while dithionic acid on account of its stability cannot be determined by this method.

In order to test the method for the titration of thiosulphates, a solution containing 3.567 g. of normal potassium iodate in  $1000^{\circ\circ}$  was used.<sup>‡</sup> According to the equation of the reaction  $2\text{KIO}_{3} + \text{Na}_{2}\text{S}_{Q}_{3.5}\text{H}_{2}\text{O} + 2\text{HCl} = \text{Na}_{2}\text{SO}_{4} + \text{K}_{2}\text{SO}_{4} + 2\text{ICl} + 6\text{H}_{2}\text{O}$  1<sup>cc</sup> =  $\cdot002068$  g. of  $\text{Na}_{2}\text{S}_{2}\text{O}_{3.5}\text{H}_{2}\text{O}$ . The titrations were made in glass stoppered bottles in exactly the same manner as in the determination of sulphurous acid. It is important to titrate as soon as possible after the thiosulphate is brought in contact with the hydrochloric acid, which should not be warmer than 18° C. Also it is best to dissolve the thiosulphate in a little water previous to adding the hydrochloric acid. For convenience several solutions of sodium thiosulphate of various strengths were prepared and standardized by titration with known amounts of pure iodine in the usual manner, observing all precautions.

The following results were obtained :

No.	$rac{\mathrm{Na}_{2}\mathrm{S}_{2}\mathrm{O}_{3}.5\mathrm{H}_{2}\mathrm{O}}{\mathrm{taken}}$	ccKIO₃ used	$\mathrm{Na_2S_2O_3.5H_2O}\ \mathrm{found}$	Error
1	.0506	24.4	.0505	0001
2	.0758	36.6	.0757	0001
3	$\cdot 1210$	58.5	.1208	0002
4	·1011	48.7	.1007	0004
$\overline{5}$	.0603	29.4	.0607	+ .0004
6	.0253	12.3	·0253	.0000
7	·0506	24.5	.0507	+.0001
8	.0253	12.2	0252	0001

The titrations given in the table below were made with a potassium iodate solution which had the value  $1^{cc} = 005300$  g. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.5H<sub>2</sub>O.

\* This Journal, xxxviii, 166. 1914.

+ Jour. Amer. Chem. Soc., 25, 756, 1903.

<sup>‡</sup>This solution was previously used for the determination of sulphurous acid mentioned above.

No.	$rac{\mathrm{Na}_{2}\mathrm{S}_{2}\mathrm{O}_{3}.5\mathrm{H}_{2}\mathrm{O}}{\mathrm{taken}}$	ccKIO <sub>3</sub> used	${ m Na_2S_2O_3.5H_2O}\ { m found}$	Error.
1	·0847	16.0	·0848	+ .0001
2	·1008	19.0	.1007	— ·0001
3	.0613	11.6	.0614	+ .0001
4	.0413	7.8	.0413	•0000
5	·1145	21.6	$\cdot 1145$	•0000
6	$\cdot 1329$	25.1	.1330	+ .0001
7	·1554	29.35	·1555	+.0001
8	.1716	32.4	·1717	+ .0001
9	·2051	38.7	·2051	•0000
10	·2430	45.95	$\cdot 2435$	+.0005
11	.1923	36.3	.1924	+ .0001
12	·1936	36.6	·1939	+.0003

The results in both tables show a satisfactory agreement among themselves and with the actual amounts present.

A volumetric method for the determination of tetrathionic acid has been described by E. Abel\* which is based upon adding an excess of standard iodine solution to the solution of the tetrathionate which has been made strongly alkaline. Then the solution is acidified with hydrochloric acid and the liberated iodine is titrated with a standard solution of sodium thiosulphate in the usual manner. The iodate method has the advantage in requiring only a single standard solution. In order to test the method, sodium tetrathionate was prepared according to the method of F. Kessler<sup>+</sup> by grinding sodium thiosulphate with a slight excess of iodine in the presence of a few cubic centimeters of water. When the sodium thiosulphate was entirely dissolved, two volumes of absolute alcohol were added. After the solution had stood for two hours, the sodium tetrathionate crystals were filtered by suction and washed with 98 per cent alcohol until all the iodine and sodium iodide were The sodium tetrathionate was found to contain removed. some sulphate which was determined by the following method. Weighed portions of the salt were dissolved in water and acidified with one gram of tartaric acid. Barium chloride was added to the solution, and when the precipitate had settled, it was filtered and determined in the usual manner. The following results were obtained:

I. 3225 g. Sub. gave 0181% BaSO<sub>4</sub> = 331% of Na<sub>2</sub>SO<sub>4</sub>

II. 3333 g. Sub. gave 0186% BaSO<sub>4</sub> = 3.39% of Na<sub>2</sub>SO<sub>4</sub>

Average - 3.35% of Na<sub>2</sub>SO<sub>4</sub>

Two water determinations were made at about 112° C.

I. II.	1.0000 g. 0.5000 g.	Sub.	gave	11.27% 11.37%	of ''	water ''	Calc. water for $Na_2S_4O_6.2H_2O$ after correction for 3.35% of $Na_2SO_4$ . 11.35%
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\* Z. anorg. Ch. lxxiv, 395.

† Pogg. Ann. 1xxiv, 255, 1848.

## Jamieson—Polythionic Acids.

In the table of analyses given below, the actual amount of  $Na_2S_2O_5$  present for each titration is stated. The first six titrations were made with the potassium iodate solution mentioned above, which contained 3.567 g. of KIO<sub>3</sub> in 1000<sup>cc</sup>, and according to the equation of the reaction

$$2\mathrm{Na}_{2}\mathrm{S}_{4}\mathrm{O}_{6} + 7\mathrm{KIO}_{3} + 10\mathrm{HCl} = 4\mathrm{H}_{3}\mathrm{SO}_{4} + 2\mathrm{Na}_{2}\mathrm{SO}_{4} + 2\mathrm{K}_{2}\mathrm{SO}_{4} + 7\mathrm{ICl} + 3\mathrm{KCl}$$

the equivalent of the solution is  $1^{cc} = 001287$  g. of Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>. The sodium tetrathionate was titrated in the same manner as the thiosulphate except that it was not necessary to take precautions about cooling the hydrochloric acid before adding the tetrathionate.

The following results were obtained :

	Wt. of Na <sub>2</sub> S <sub>4</sub> O <sub>6</sub>	ccKIO <sub>3</sub>	Wt. of Na <sub>2</sub> S <sub>4</sub> O <sub>6</sub>	
No.	taken	used	found	Error
1	.0452	35.1	$\cdot 0452$	•0000
$^{2}$	.0340	26.35	·0339	— ·0001
3	.0429	32.2	.0427	0002
4	.0612	47.5	.0611	0001
<b>5</b>	·0400	30.7	·0395	0005
6	.0672	52.0	·0669	0003
71	$\cdot 0454$	13.85	·0457	+ .0003
8	.0507	15.3	.0505	<b>- ·</b> 0002
· 9	·0640	19.35	·063S	<b>- ·</b> 0002
10	•0766	$23 \cdot 2$	.0765	
11	.1373	41.7	$\cdot 1375$	+ .0005
12	.0872	26.43	.0871	0001
13	.1065	32.3	.1065	.0000
14	.0890	26.8	·0884	0006

+ Titrations 7–14 were made with an iodate solution which had the value -  $1^{ce}=$  :003297 g, of Na\_2S\_4O\_6.

These results show a satisfactory agreement with the actual amounts of sodium tetrathionate taken.

Dithionates were found to react so slowly with potassium iodate in the presence of strong hydrochloric acid that it was possible to titrate and determine the amount of sodium thiosulphate in the presence of large quantities of potassium dithionate. Likewise, tetrathionates could be estimated in the presence of dithionates. The stability of dithionates has been observed previously by R. H. Ashley.\* It was found that barium and sodium dithionate were only partially decomposed by potassium iodate after reacting for a day and no iodine was

\* This Journal, xxii, 259.

liberated for some time after bringing the constituents together.

The following experiments were made:

No.	${f Na_2S_2O_3.5H_2O}\taken$	${f K_2 S_2 O_6} \ {f taken}$	$\mathrm{Na_2S_2O_3.5H_2O}$ found	Error
1	·0616		·0615	— ·0001
2	·0616	0.20	.0615	0001
3	$\cdot 1233$	1.00	.1230	0003
4	$\cdot 1849$	1.00	·1851	+ .0005

These results show that the dithionate does not interfere with the titration of the thiosulphate.

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# ART. XLV.—Datolite from Great Notch, New Jersey; by C. W. COOK and E. H. KRAUS.

DURING the past summer the Mineralogical Laboratory of the University of Michigan obtained from the Ward's Natural Science Establishment of Rochester, N. Y., a number of crystal specimens of datolite, from Great Notch, N. J. Although these crystals show no new forms, they seem worthy of description on account of their very interesting and unusual type of development and the fact that they show a selective coating. The specimens consist of both isolated crystals and crystal aggregates, the individual crystals ranging from 3<sup>mm</sup> to 35<sup>mm</sup> in their major diameter.

Crystallography.—On account of the coating which covers most of the faces of the crystals accurate measurements were difficult and in some instances impossible. A number of the forms shown in fig. 1 have therefore been determined by their zonal relationships. However a sufficient number of the faces were identified by goniometric measurements to insure the proper orientation of the crystals. On account of the imperfection of the faces in general, no attempt was made to establish an axial ratio. Maintaining the stand taken in an earlier paper on datolite,\* the authors have assumed the position adopted by Levy<sup>+</sup> and Dana,<sup>±</sup> and which has recently been championed very strongly by Ungemach.§

\* Datolite from Westfield, Mass., this Journal (4), vol. xxii, pp. 21-28, 1906; Zs. Kryst., xlii, pp. 327-333, 1906. † Description d'une collection de mineraux, etc., pp. 179 and 182, 1838.

<sup>+</sup> System of Mineralogy. 6th edition, 1892, pp. 504-505. SZs. Kryst., xlix, pp. 459-476, 1911.
#### Cook and Kraus—Datolite from Great Notch. 643

The crystals uniformly show a very pronounced tabular development parallel to the hemi-orthodome  $x\{102\}$  (see fig. 1). Among the various types already described, the one under discussion approaches most closely to that described by Dana<sup>\*</sup> from Bergen Hill, N. J., which he characterizes as rhombohedral and states is 'a rare and quite unique form.' The tabularity of the Great Notch crystals is however their most striking characteristic. The pronounced similarity to crystals



from Guanajuato, Mexico, described by Farrington<sup>+</sup> is also to be noted.

 $\begin{array}{l} \text{In all the following twenty-two forms were observed:} \\ \text{Pinacoids} &- a\{100\}, b\{010\}. \\ \text{Prisms} &- \Delta\{210\}, m\{110\}, o\{120\}. \\ \text{Clinodomes} &- m_x\{011\}, g\{012\}. \\ \text{Orthodomes} &- x\{102\}, \phi\{101\}, j\{502\}. \\ \text{Pyramids} &- n\{111\}, \delta\{221\}, 9\{212\}, o\{213\}, v\{\bar{1}11\}, \epsilon\{\bar{1}12\}, \lambda\{\bar{1}13\} \\ & B\{\bar{1}21\}, q\{\bar{1}22\}, \alpha\{\bar{1}24\}, Y_1\{\bar{1}34\}, \iota\{\bar{2}12\}. \end{array}$ 

Of the above forms the orthodome  $x\{102\}$  is always the predominating one. It is always heavily coated, and when the coating has been removed, as indicated later, shows the effect of natural etching so that a series of images is obtained, making very accurate readings impossible. The prism  $m\{110\}$ occurs as a rhomboidal face with a coating making definite readings difficult. The prisms  $\Delta \{210\}$  and  $o \{120\}$  occur as thin edges. Of the pyramids,  $n \{111\}$  and  $\epsilon \{\bar{1}12\}$  are always comparatively large,  $\epsilon \{\bar{1}12\}$  ranking next in size to  $x \{102\}$ , and

\* Edward S. Dana, this Journal (3), vol. iv. pp. 16-22, 1872.

† O. C. Farrington, this Journal (4), vol. v, pp. 285-288, 1898.

## 644 Cook and Kraus—Datolite from Great Notch.

are free from coatings. On account of the waviness of the faces of  $\epsilon$  {112}, the pyramid n {111} exhibits a comparative brilliance which makes it, next to the peculiar type of development, the most striking feature of the crystals. The other pyramids, with the exception of  $\lambda$  {113},  $\alpha$  {124}, and Y, {134}, appear as bevelings between the more prominent faces.  $\lambda$  {113} when present show small triangular faces, and  $\alpha$  }124} and Y, {134} form with the clinodome g {012} a rounded surface. Of the clinodomes, only  $m_x$  {011} is always present. It has present is always coated. g {012}, when it occurs, appears as small triangular faces. The pina-



coid a {100} is always present with small triangular faces, while b {010} appears occasionally beveling the edge between the faces of the clinodome  $m_x$  {011}.

The goniometric measurements upon which the orientation of the crystals is based are as follows:

						Obser	ved.	Cal	culate	d.*
m	: m''	′ =	(110)	: (110)	=	$64^{\circ}$	46'	.64°	49'	
$\dot{m}_x$	: m'.	, =	(011)	: (011)	=	103	26	103	22	30''
m	: x	=	(110)	: (102)	=	52	56	53	15	
m'	: γ	=	$(\bar{1}10)$	: (111)	=	22	44	22	57	
a	: at	=	(100)	: (102)	=	44	56	45	00	
g	:g'	=	(012)	$(0\bar{1}2)$	=	64	42	64	38	30
n	: n'''	=	(111)	: (111)	=	59	39	59	4	30
a'	: €	=	(100)	: (112)	=	49	48	49	57	
ε	<b>:</b> ε′	=	$(\bar{1}\bar{1}2)$	$(\bar{1}\bar{1}2)$	=	48	46	48	19	
λ	: λ'	=	$(\bar{1}13)$ :	$(\bar{1}\bar{1}3)$	=	39	10	38	45	30
a	:j	=	(100)	(502)	=	10	42	11	20	

\* These are the values variously calculated by Dana, Ungemach, and Kraus and Cook.

#### Cook and Kraus—Datolite from Great Notch.

645

Selective Coating.—The examination of a large number of the crystals shows that certain faces are always dull. This dullness was at first believed to be due to natural etching. However, it was found that when the crystals were boiled in dilute hydrochloric acid and then suddenly cooled, dull appearing material separated off in the form of flakes leaving a shiny surface, which generally showed some signs of natural etching. As shown in fig. 2, the pinacoid  $\alpha$  {100} and the pyramid n {111} are always free from this coating, while the same is generally true for  $\epsilon$  {112}. The other prominent faces at least are coated. (The crystal is represented in fig. 1 without the coatings.) Generally the coating is much heavier on the orthodome  $x \{102\}$  than on the other forms. The prism  $m \{110\}$ has the next heaviest coating and the clinodomes have the lightest. Another interesting feature of this coating is the occurrence of a beveling on the lower edge of the coating of the orthodome  $x \{102\}$  upon which appear striations that are apparently parallel to the plane of symmetry of the crystal. An examination of the distribution of the coatings shows that they are symmetrical to the plane of the a and c axes, to an axis of binary symmetry parallel to the b axis, and to the center, thereby placing the crystals in the prismatic class of the monoclinic system to which they have been assigned upon morphological grounds.

With regard to the composition of the coating it may be pointed out that some of the specimens show stilbite in association with the datolite in such a relationship as to leave no doubt that the stilbite is younger. This leads to the conclusion that the coating on the datolite is stilbite. This hypothesis is also supported by the fact that in some instances the coating presents a sheaf-like appearance.

University of Michigan, Ann Arbor, Mich., November 9, 1914.

AM. JOUR. Sci.—Fourth Series, Vol. XXXIX, No. 234.—June, 1915. 42

# ART. XLVI.—A Fully Exposed Reef of Calcareous Algæ (?) in the Middle Cambrian of the Teton Mountains;\* by ELIOT BLACKWELDER.

Most field geologists have seen in Paleozoic limestones the large hemispherical masses of concentric laminæ to which the name *Cryptozoon* has generally been applied. Usually, however, the structures are exposed only in plane section in the sides of quarries or on flat glaciated surfaces. It seems to be rare to find them so preserved and exhumed as to stand out much as they may be supposed to have appeared when originally formed. This fact is justification for describing an instance in which those conditions are realized.

On the west slope of the Teton Range in western Wyoming an interstream ridget has been carved from a sequence of Paleozoic formations. The Cambrian there consists of alternating hard limestones and more or less calcareous gray and greenish shales with sandy strata near the bottom. Many of the beds are sparingly fossiliferous,-the faunas indicating Middle and Upper Cambrian horizons. About 400 feet below the base of the Bighorn dolomite, and about 40 feet above the massive bed of limestone which is the chief cliff-making member of the unnamed formation, between the Flathead quartzite and the Gallatin limestone, masses of limestone having the form of an old-fashioned beehive lie imbedded in a matrix of calcareous green shale, although resting upon massive limestone. At the point where the outcrop of the bed crosses the sharp crest of the ridge, which at that place is slightly above timber-line, the shale has been largely removed from the limestone bodies. Much of it has been washed away by water from the melting snows in early summer; and, in addition, the exposed position of the outcrop has given the wind an opportunity to blow away all loose small particles. Although the bed is but 7 feet thick, the gentle dip gives it a relatively broad outcrop and hence the denuding agencies have stripped the shaly matrix from an area of an acre or more. The accompanying photograph (fig. 1) shows a portion of the ancient reef (?) thus exposed. Farther back on the right, one may see the clean dip slope of the Middle Cambrian limestone referred to above. As shown by the photograph, the limestone masses are of various sizes, averaging 2 to 4 feet in diameter. They are nearly hemispherical in form and all are characterized by numerous tumid projections (see fig. 2). The bodies stand iso-

\* Published by permission of the Director of the U. S. Geological Survey. † The exact point is 1'9 miles N. 64° W. of bench mark 10,685 on the Grand Teton Quadrangle of the U. S. Geological Survey. It is on the divide between the two forks of Leigh Creek, which are, however, incorrectly named Leigh and Badger Creeks on the maps mentioned.

FIG. 1.



FIG. 1. A portion of the exposed reef showing dome-shaped limestone masses with mammillated surfaces. The slight dip of the strata is indicated by the general slope.

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FIG. 2. Close view of a single limestone dome, showing the cabbage-shaped bodies cemented by a small amount of mortar-like material.

# 648 E. Blackwelder-Reef of Calcareous Alga (?).

lated although closely spaced. Since the shale is not in the least cemented to the limestone it can be removed completely, leaving a clean limestone surface. This fact also suggests that the limestone domes were already solid and stony when the mud (now shale) began to be sifted over them in the water of the Cambrian sea. The fortunate removal of the friable shale matrix permits a satisfactory examination of the masses in three dimensions. Furthermore, many of them have been split open by the frost, and hence the internal structure can now be seen. All that is left to be desired is that these inner sections might be polished so that their minute structures would become visible.

On examining a single mass or colony, it is found to consist of a thick outer shell made of globular masses about the size and shape of a cabbage, closely packed together and cemented by small quantities of dense blue-gray limestone which has precisely the appearance of mortar in a stone wall (see fig. 2). The resemblance of the tumor-like bodies to cabbages is further enhanced by the fact that they show a distinct concentric structure, or at least a hemispherical banding parallel to the outer surface. An attempt has been made to show this in fig. 3, since photographs in the field were unsuccessful in recording the rather obscure internal structure. Inside of the mammillated shell, but intergrading with it, there is a vaguely distinguished central portion consisting of dense limestone of slightly mottled gray color, in which several concentric shells are tinged with ocher yellow,-doubtless because of the presence of ferrous carbonate in the limestone. This central banding, although roughly concentric, is slightly wavy in sympathy with the mammillary structure of the outer part.

A closer study of specimens taken from different parts of the mass, carried on with the aid of the microscope and chemical tests, shows that all but certain portions of the interior now consist of dolomite rather than limestone. As anticipated from the very common association of iron oxides with dolomite, the ocherous portions are exclusively dolomitic, but they enclose more or less continuous layers of dense grav limestone. The dolomitic part has either a uniform or a finely-brecciated structure, each little rhomb being coated with limonite. On the other hand, the limestone bodies which seem to represent the original portions of the rock show vague layers and also many circular and elliptical sections which may have been originally canals or tubes. They are not brecciated. Inside of these limestone portions there are also obscure, more or less branching bodies, colored a dark sepia brown, apparently by bituminous matter. The cabbage-shaped bodies of the outer shell consist entirely of dolomite of a dark smoky gray color,

E. Blackwelder—Reef of Calcareous Alga (?). 649

somewhat mottled in a very indefinite fashion with paler gray. The texture is fine and relatively uniform, and there is no distinct trace of original structure. The mortar-like matrix, seen on the outside, is of a much lighter gray tint, and likewise consists of dense, fine-grained dolomite without mottling.

The occurrence of these hemispherical bodies at a definite horizon, bottomed on limestone, suggests a reef of colonial

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FIG. 3. Drawing, made in the field, to show the internal structure of one of the domes that had been split open by frost action.

organisms, such as corals, hydroids, bryozoans or algæ. The concentric internal structure of each mass supports the hypothesis that it originated by a process of growth upward and outward from a center. From the fact that the only parts of the mass now consisting of lime carbonate are disconnected bodies and layers near the center, it is inferred that although originally a lime-carbonate structure, it has been dolomitized from the outside inward, by a magnesia-bearing solution. The probability that this pseudomorphic alteration has affected many limestones,\* either reef-rock or of other origin, renders it unnecessary to argue the question at length in this case. To this process may be ascribed the lack of recognizable coarser organic structure throughout the dolomitic part of the mass.

\* See the following:

Skeats, E. W.: Chemical and Mineralogical Evidence as to the Origin of the Dolomites of southern Tyrol, Quart. Jour. Geol. Soc., vol. 1xi, pp. 97-139, 1905.

Steidtmann, E. : The Evolution of Limestone and Dolomite, Jour. of Geol., vol. xix, pp. 323-345, 392-428, 1911. Blackwelder : Origin of the Bighorn Dolomite, Bull. G. S. A., vol. xxiv,

pp. 607-624, 1913. Wallace, R. C. : Pseudobrecciation in Ordovician Limestones in Manitoba, Jour. of Geol., vol. xxi, No. 5, pp. 402-421, 1913, and many others.

The minute cellular texture that may have been possessed by the organisms could not be expected to survive the crystallization which inevitably affects lime-carbonate masses with the march of time.

Since corals and bryozoans are often found well preserved in rocks no more altered than these, their absence here creates a strong presumption that the domes are not of coralline or bryozoan origin. They are best referred to some organism of extremely delicate internal structure such as many of the modern calcareous algæ. In view of the fact that algæ even to-day are known to construct large and stony masses of lime carbonate which constitute important or even predominant parts of many so-called coral reefs, the writer believes that the bee-hive shaped masses here described were built by colonies of algæ. The internal structure suggests that during the growth of a given colony, it was first enlarged by the addition of concentric crusts, but that after reaching a diameter of two to three feet, a process of budding set in all over the periphery, and thereby produced a multitude of miniature colonies which are now represented by the mammillary outer layer. The life of the reef may well have been terminated by the increasing muddiness of the water under the influence of some physiographic change that ensued.

Madison, Wis., Feb. 8, 1915.

# ART. XLVII.—Limestone Solution on the Bottom of Lake Ontario\*; by E. M. KINDLE.

THE fishermen who set their nets in the deeper waters of Lake Ontario very frequently bring to the surface in them, slabs of limestone to which they apply the name "honeycomb rock." This term of the fishermen has been suggested by the extraordinary appearance of the surfaces of these specimens which are deeply pitted by irregular cell-like cavities. This peculiar pitted appearance is shared by every specimen of limestone which has come under the writer's notice from the deep waters of both Lake Ontario and Lake Huron. It is clearly the result of aqueous solution in waters generally 100 feet or more in depth. All of the specimens seen appear to indicate a much more powerful solvent action of the water at the depths represented, than that which prevails at and near the surface. A series of specimens secured during the last field season from a depth of 150', 16 miles southwest of Presque Isle, Lake Ontario, have suggested some of the factors in the great effectiveness of fresh water in dissolving limestone at considerable depths which it is proposed to consider in this paper.

It has been shown in an earlier paper by the author<sup>+</sup> that strong currents scour the bottom of Lake Ontario at irregular intervals. It appears probable, that, while such currents are in some deep-water zones depositing more material than they remove, in others scour predominates over deposition. This inequality results in considerable areas of limestone bottom in Lake Ontario where little or no sediment has been permitted by the currents to accumulate since the basin has been occupied by the lake. One of these rock bottom areas lies southwest of Brighton, Ontario, about 20 miles, under 150 to 200 feet of water. This is an important fishing ground for Brighton fishermen.

Mr. E. J. Whittaker, my assistant, secured, during one visit in a fishing boat to this area, more than a dozen slabs of the "honeycomb rock" which came up entangled in the nets. These vary from a few inches to nearly a foot in diameter and represent remnants of detached strata of thin-bedded, nonmagnesian limestone. Every specimen is deeply and irregularly etched. The cavities show every conceivable variety of outline and shape. The individual pits will, perhaps, average three fourths of an inch in depth, the walls of adjacent cells being frequently broken by cavities connecting them. The deeper

\*Published with the permission of the Director of the Geological Survey of Canada.

+ This Journal (4), vol. xxxix, pp. 192-196, Feb., 1915.

#### E. M. Kindle—Limestone Solution.

cavities frequently pass entirely through the slab. The closely placed, rounded and thin-walled cavities give to some specimens a vesicular appearance. Frequently the advanced stage of solution and thin walls of the cavities give the specimen a very fragile character, the outer surface being composed of cell walls of paper-like thinness and delicate points of limestone left at the junction line of such walls after their solution.

Fig. 1.



FIG. 1. Limestone showing solution cavities from a depth of 150 feet, Lake Ontario.

The general appearance of these limestones which have been corroded in deep water is shown in figure 1. A specimen of dolomite from Lake Huron is shown in figure 2. This specimen was obtained by Dr. M. Y. Williams from fishermen who took it from their nets in water of considerable, but not precisely determined depth. This figure is introduced because of the marked contrast which it shows with the Lake Ontario specimens. The well-developed cavities of corrosion in the Georgian Bay specimen have a depth of about three inches, as

652

# E. M. Kindle-Limestone Solution.

F1G. 2.



F1G. 3.



FIGS. 2 and 3. Dolomite from deep water in Georgian Bay, showing solution cavities. Two views of the same specimen.

# E. M. Kindle-Limestone Solution.

compared with one inch in the others, and in some cases a width of two and a half inches. This difference in the type of cavities resulting from solution, appears to be due to the difference in the composition of the rock. The Lake Ontario specimens are composed of fairly pure limestone, while the Lake Huron specimen is a hard, fine-grained magnesian limestone which does not effervesce on a weathered surface in acid, although a fresh surface shows a feeble reaction. Another specimen of the Georgian Bay "honeycomb limestone" has been figured, but not described, by Brock and Young.\* The very extensive corrosion shown by these specimens of dolomite from the bottom of Georgian Bay affords conclusive evidence of the high efficiency of the solvent power of water at considerable depths, even on a rock so refractory as dolomite.

While some of the limestone specimens show clear, fresh surfaces, others are entirely covered by green algæ growing on These specimens of algæ are of special interest owing to them. the depth—150′—from which they were obtained.† They were sent to Mr. Frank S. Collins, a specialist on this class of plants, for determination. Mr Collins writes concerning these as followst:-- "I have received the specimens of a Cladophora that you collected in deep water in Lake Ontario; it is an interesting collection, being from a greater depth than recorded for any Cladophora and the plant is certainly a species not hitherto recorded for America. I think it is C. profunda Brand, found in the lakes of the Bavarian highlands, at a depth of fifteen meters, but it differs somewhat from that species, so I have sent some to Prof. Brand for him to decide whether it is distinct." A second letter from Mr. Collins, after hearing from Prof. Brand, follows§:-

"I have heard from Dr. Brand in regard to your Cladophora, and the following is a translation of his letter :--

'Thanks for your interesting sending. The Cladophora is indeed C. profunda, a slender and irregularly branched form, which may be characterized as "forma ima" of variety Nordstedtiana. Irregularites are very common in C. profunda, and arise from the most different causes; among others from (always accessory!) attachment. Moreover the depth have some influence with your plant, for the quantity of attached diatoms indicates a weak state of growth.

The epiphytic, occasionally somewhat violet alga, very

\*A descriptive sketch of the geology and economic minerals of Canada, pl. xlvii, Can. Geol. Summary, 1909. †This figure was furnished by the fishermen, but is corroborated by the navigation charts, which indicate water 150 to 200 feet deep in this part of the lake.

<sup>‡</sup>Letter to the author, Dec. 22, 1914. § Letter to the author Feb. 15, 1915.

sparingly branched, is a *Chantransia* or *Pseudochantransia*; probably imperfectly developed *P. pygmæa* (Kuetz.) nob.

Ihr ganz ergebener

F. Brand.'

I think fifteen meters is the greatest depth recorded for this species in Europe and no other *Cladophora* is known to go as low as that; so if 150 feet is correct for your plant, it is three times as great a depth as before known. It probably occurs in loose masses of considerable extent wherever it occurs at all."

While the solution erosion to which these specimens have been subjected is of the same general kind as that sometimes observed on the face of limestone ledges near the surface of the water, it is wholly different in degree. The writer has never observed any examples of limestone solution in shallow water which approached even remotely the deeply corroded cavities shown by all specimens from the deep waters of Lake Ontario. Ordinarily limestone slabs in shallow water show no direct evidence of solution. The efficiency of wave action in removing such evidence by attrition might be offered as an explanation of the different results which follow limestone solution in deep and shallow waters. But this explanation fails because examples of such etching are wanting in small protected inlets where wave action is absent just as they are on exposed coasts.

The explanation of the very markedly different results of water acting as a solvent on limestone at considerable and at slight depths rests upon certain chemical and biological facts which will be briefly set forth. The importance of carbon dioxide as the active factor in the solution of limestone is too familiar to require more than mention. It is a familiar and generally recognized fact that the solvent power of water on limestone varies with the amount of carbonic acid in the water. The effectiveness of water as a solvent of limestone will therefore depend on the factors which tend to increase or decrease the amount of this substance in it. These factors include the varying degrees of solubility of the gas in water at different temperatures and pressures together with the source of supply of the gas. The first named factors represent well known data of chemistry which may be stated thus: Water at 14° under a pressure of one atmosphere dissolves its own volume of the gas; at the same temperature under two atmospheres two volumes, and at three atmospheres three volumes, etc., of carbon dioxide.\* The amount which can be absorbed increases also rapidly with the decrease of the temperature. The etched limestone specimens under consideration came from a depth at

\* Richter's Textbook of Inorganic Chemistry, p. 230.

# E. M. Kindle-Limestone Solution.

which the water pressure is equivalent to about six atmospheres. The temperature at this level is also always low; both pressure and temperature factors thus combine to give the water at that depth a potential capacity for holding at least six times its volume of carbon dioxide or about six times the amount which it is capable of holding at the surface. The amount of the gas actually dissolved in the water at that depth would be also conditioned by the nature of the source of supply. If any large or important source of carbon dioxide supply exists at the bottom at 150' and greater depths, it is very evident that the water there, owing to its multiplied capacity for absorbing the gas, will hold much greater quantities of it than near the surface and act as a solvent of limestone with correspondingly greater effectiveness. Living animals and plants are the great sources of carbon dioxide in lakes as well as in the sea. "Where life is abundant, there carbon dioxide is abundant also and its activity as a solvent of calcium carbonate is greatest."\* The discovery which has been described on a preceding page of an abundance of green algæ in these deep waters demonstrates the presence of a very important source of this gas in the algal flora of the lake bottom. Another though less important source of the carbon dioxide is represented by the fresh water sponges and molluscan fauna found in the same habitat. The abundance of fish which makes the area under consideration a favorite fishing ground of the Brighton deep water fishermen affords collateral evidence of a wealth of bottom life which makes it a good feeding ground for fish. The evident abundance of animal and algal life must afford a rich and constant supply of carbon dioxide to these bottom waters of the lake. The metabolism of the algae which grow directly on and often completely cover the limestone slabs which have been brought up must furnish a continuous supply of carbon dioxide to the lowest zone of the lake. Water at this depth would seldom be disturbed by wave action and except when affected by occasional bottom currents would generally remain motionless. It would thus appear that under ordinary conditions the metabolism of the plant life and molluscan life on the bottom would result in a bottom zone of lake water becoming very highly charged with carbon dioxide. The lake water would therefore act as a much more effective solvent at the bottom than near the surface and to this fact chiefly is due, the writer believes, the deep and rapid corrosion of the limestone.

Victoria Memorial Museum

Geological Survey, Ottawa, Canada.

 $^{\ast}$  W. L. Carpenter and C. Wyville Thompson, Depths of the Sea, 1874, pp. 502–511.

# ART. XLVIII.—On certain Points in Petrographic Classification; by WHITMAN CROSS.

THE Quantitative Classification of Igneous Rocks, proposed by Cross, Iddings, Pirsson and Washington,\* is based on principles and conceptions which, at the time the system was first published, in 1902, had been given but little prominence in petrography. Both principles and essential features have been discussed in a scientific spirit by petrographers of various countries. This discussion and the criticism or suggestion based on it have been helpful to the backward science of systematic petrography and are, of course, welcomed by the authors of the Quantitative system.

The name "Quantitative System" was used because it was desired to emphasize the fact that definite quantitative factors were used in it throughout, making it contrast with earlier systems. But manifestly there may be many other quantitative systems and I shall here refer to this first one as the C. I. P. W. classification or system, following a precedent established by several writers.

Some of the criticisms and comments which have been freely, and in certain cases casually, made concerning the C. I. P. W. system, have seemed to its authors too evidently fallacious to need reply. But when such critical comments are repeated by petrographers with the reputation enjoyed by R. A. Daly and Waldemar Lindgren we must take a different attitude, for their remarks should certainly be free from the suspicion of prejudice or flippancy.

Dr. Daly has severely assailed the C. I. P. W. classification in his interesting work "Igneous rocks and their origin"<sup>+</sup> and while the criticism appears to me clearly fallacious, I must assume that it was carefully considered and deliberately made. The classification is said to be fatally defective in that "even its minor subdivisions individually include rock types which are strongly contrasted chemically and separate others which are almost alike chemically, mineralogically and genetically." The system is then stigmatized, on account of this "defect," as one which "disregards vital principles of scientific classification." These principles are not formulated.

The main conception, quite erroneously called a "principle," which is involved in Daly's criticism, may, I hope, be fairly expressed thus: A division of a classification of rocks should not include types that differvery markedly in character

<sup>\*</sup>Whitman Cross, Joseph P. Iddings, Louis V. Pirsson and Henry S. Washington, "Quantitative Classification of Igneous Rocks," Jour. Geol., vol. x, 1902, pp. 555-690 and in book form, Univ. of Chicago Press, 1903. † R. A. Daly, "Igneous Rocks and their Origin," New York, pp. 10, 11, 1914.

nor separate types that are very much alike. I suspect that this idea is entertained by many petrographers, with whom "the wish is father to the thought."

A principle is defined as "a truth which is evident and general." I should state the real principle involved in this matter as follows: Since igneous rocks form a continuous series or field, as to chemical, mineral, and textural characters, the divisions of their systematic classification by these factors necessarily separate types that are nearly alike and include types that are relatively very unlike. Petrographic system is in this respect analogous to any regular division of mass, space or time. The conception I attribute to Daly is antithetical to this principle. The C. I. P. W. system operates as Daly has pointed out, but this result is in harmony with the nature of things.

The criticism by Daly is strongly inconsistent as well as untenable, for the same "defect" he abhors in the C. I. P. W. system is clearly present even in the one he himself uses and advocates. For example, certain monzonites are very closely related to certain syenites but are relatively very different from those monzonites which are near relatives of essexite or gabbro.

Perhaps the prevailing vagueness of the current modal or mineralogical system of rock classification, whose partitions are elastic like rubber and permit some dilation or complementary contraction of its subdivisions according to the desires of the individual petrographer regarding certain rocks, may blind Daly to the existence in it of the same "defect" found by him in the C. I. P. W. classification.

An inconsistency in Daly's criticism, suggesting the control of prejudice, is further strikingly shown on the page following his denunciation of the C. I. P. W. system. He there states his adoption of the modal or Rosenbusch scheme, which he thinks will be improved in the course of time. To this Daly adds that "To become an ideal Mode classification it should be made quantitative." \* But the divisions of this "ideal" modal, quantitative system would have sharpedly defined boundaries and necessarily include contrasting and separate similar rock types, under the general principle enunciated above.

Another fallacious comment on the C. I. P. W. system has been recently repeated by Lindgren + in a note on Iddings' review of Daly's book, above referred to. Lindgren says that Daly "does not stand quite alone" in his criticisms of

658

the Quantitative classification, and adds: "There are many of us who fail to see in this elaborate system anything but an admirable card classification of analyses." The same idea has been expressed before in the remark that the system classifies analyses, not rocks.

Now the authors of the C. I. P. W. system attempted a chemical classification of igneous rocks and spent long study on it. I must personally express my surprise and regret that a petrographer of Lindgren's standing should feel warranted in making a belittling and by no means lucid criticism of this work without a word of justification. His comment fails to explain (1) what he finds admirable in the system as a card classification of analyses, (2) how a classification of analyses, using the data presented by them, can be admirable if it does not classify the rocks analyzed, (3) why the system does not classify the rocks, (4) how chemical data should be used to classify rocks so that his objection may not apply.

Like Daly's criticism this comment touches abstract principles, in this case of chemical classification, but it rests partly, I\_think, on a misconception of the C. I. P. W. system.

The main interest a petrographer, as such, can have in classifying rock analyses is as to their usefulness to him, as complete or incomplete, good, bad, or indifferent, as Washington has done. He is interested in a good analysis only when it represents the composition of a known rock.

The fundamental importance of chemical composition of an igneous rock, bearing, together with variable and in part extraneous physical factors, primarily on its magmatic and genetic relations and later on its mineral composition, is beyond any need of discussion. To be sure, an Irish petrographer makes the claim that the chemical composition represented by analysis is not fundamental because the chemical composition of a specimen depends entirely on its mineral composition, while the latter depends partly on physical conditions. The classificatory value of chemical composition is stated by Daly, after an admirable review of the difficulties of accurate mineralogical classification, in these words—" the basis for an ultimate classification is now universally found in the chemical analysis (total analysis) of the rocks" (op. cit. p. 9).

In discussing rock classification by chemical composition it is desirable to first consider what a complete analysis of an igneous rock represents. 1. It represents as nearly as we can ever determine it the composition of the magma the consolidation of which has produced the hyaline, hypohyaline or crystalline rock. 2. It is a concise report, exhaustive in its way, made by an expert, on the fundamental material property of a rock. But this report is far from satisfactory in form when

# W. Cross—Petrographic Classification.

the power of chemical composition to influence the mineral composition of the rock is considered. It is apparently this power which is the natural factor in chemical composition which should be used in systematic classification of rocks.

The customary statement of an analysis follows an old conventional form, giving simply the sum total of certain acid or basic radicals found in the material analyzed. The petrographer, in his attempts to interpret the significance of the proportions of a single analysis or of the differences in a series of analyses, as bearing on mineral development, has restated the analyses in various ways. They have been translated into a percentage statement of the elements. The molecular proportions of substances stated by analysis have been calculated and expressed in percentages. It is clearly possible, moreover, to transform all rock analyses into terms of a certain set of mineral molecules, selected for the purpose, and following some invariable rule for the calculation, as is necessary to secure comparable results. Such a set of molecules is the norm on which the C. I. P. W. system is based.

This primary character of the norm was not pointed out with sufficient clearness by the authors of the C. I. P. W. system in their original publication. They were too intent on explaining the reasons for the norm chosen, its practicability, and relation to the mode of the rock. Nevertheless the abstract character of a norm is evident from the discussion of the question as to the particular norm best suited to the purpose of the C. I. P. W. system.

The interpretation of analyses has also been attempted by means of various ratios between single constituents or groups of constituents and these factors have been used to characterize rock types established on mineral composition. In fact the use of chemical composition in a systematic way most frequently attempted by petrographers has been not a true chemical classification but rather a chemical characterization of primary mineral types, themselves established on a very faulty basis.

The chemical classification of igneous rocks may be effected by the use of the data presented in the analyses as stated by the chemist, as by percentage of silica, or of any consistent restatement or interpretation of those analyses, as in Rosenbusch's use of Atomzahlen. If chemical composition be chosen as the first and mineral constitution as the second factor in a system, it seems natural to apply the first factor in some way which expresses as nearly as possible some definite relation to the second. The C. I. P. W. system is an attempt to do this, recognizing that variable physical conditions attending the formation of the rock from the magma modify in different degrees and in different ways the specific mineral constitution but not the chemical character of the whole.

If this view of chemical classification is correct the criticism by Lindgren and others that the C. I. P. W. system classifies analyses and not rocks is not true. It appears to be an incorrect generalization based on the fact that the system leading to the new nomenclature is founded on proportions of normative molecules named after minerals of the same composition, while the crystalline rock analyzed usually does not have exactly that composition. But the C. I. P. W. system recognizes this fact most explicitly. It makes no assumption that the mode of a rock is, or, deploring the vagaries of Nature, that it ought to be, like the norm. The norm is merely a restatement of the chemical analysis in terms of mineral molecules, by which the major significance of complex variations in analyses may be expressed and more clearly comprehended.

The authors of the C. I. P. W. system call it "chemico-mineralogical,"\* referring to the statement of the analysis in mineral molecules, and call the systematic terms "magmatic names" since they may be considered as applying to the magma before the rock has formed from it. The C. I. P. W. system is extended to the actual rock by modifying terms expressing its motex<sup>‡</sup> (mode and texture), but if one has in mind simply the chemical classification the magmatic name clearly applies also to the rock.

The criticisms of the C. I. P. W. system here considered really go back of that system to fundamental questions, in one case to petrographic system in general and in the other to methods of chemical classification. It is not the object of this discussion to consider the particular norm adopted by the authors of the C. I. P. W. system or the classification founded on it. I wish to say, however, that there are reasons for that norm, and that it is made up mainly of mineral molecules used by Michel-Lévy, Rosenbusch, Brögger, Harker and many other petrographers, in studies of the relation between the chemical and mineral constitution of igneous rocks. But the C. I. P. W. system is not assumed by its authors to be the "ultimate" classification of igneous rocks, although they believe it to be a step toward that end. Discussion of its merits and demerits and the test of use will determine its future, but criticisms in which fundamental principles or conditions of petrographic system are disregarded can not affect the issue.

\* Op. cit., p. 111. ‡ Op. cit., pp. 168-172. † Op. cit., p. 163.

AM. JOUR. Sci.—Fourth Series, Vol. XXXIX, No. 234.—June, 1915. 43 -

# ART. XLIX.—The Separation of Magnesium from Lithium by Means of Ammonium Carbonate in Alcoholic Solution; by J. GRAY DINWIDDIE.

(Contributions from the Kent Chemical Laboratory of Yale Univ.-cclxvii.)

THE following work was undertaken to determine the conditions under which lithium may be separated quantitatively from magnesium by means of ammonium carbonate in alcoholic solution. It has been shown\* that by the agency of such a solution magnesium may be separated quantitatively from sodium and potassium and that very small amounts of magnesium may be detected qualitatively in presence of limited amounts (100 mgm.) of lithium. In the quantitative procedure, the solution containing the salts of magnesium, sodium, and potassium is brought to a volume of about 50<sup>cm<sup>3</sup></sup>, an equal amount of absolute alcohol is added, precipitation is made by addition of 50<sup>cm<sup>3</sup></sup> of a saturated ammoniacal solution of ammonium carbonate in 50 per cent alcohol, and the mixture is allowed to stand half an hour after stirring vigorously for five minutes. If the amount of alkali salt present is small, the precipitate may be collected without further treatment upon asbestos in the perforated crucible, washed with the precipitant, dried, ignited, and weighed as magnesium oxide. When the amount of alkali salt is large the precipitate may be freed from included alkali salt by decanting the supernatant liquid through the prepared asbestos filter, dissolving the precipitate in hydrochloric acid and reprecipitating by ammonium magnesium carbonate as at first. This second precipitate, collected upon the filter used in the decantation, leaves upon ignition a practically pure magnesium oxide. The essential condition of this process is that precipitation shall be brought about by a considerable excess of ammonium carbonate in a 50 per cent alcoholic solution.

In the work to be described, it was convenient to make use of 93 per cent alcohol instead of absolute alcohol in making up the solution to be treated and the precipitant, but the proportions of solution and precipitant were so adjusted that the liquid at the time of precipitation should be 50 per cent alcohol.

The alcoholic solution of ammonium carbonate was made by mixing 1500<sup>cm<sup>3</sup></sup> of the saturated aqueous solution of that reagent with 360<sup>cm<sup>3</sup></sup> of concentrated ammonium hydroxide and 1900<sup>cm<sup>3</sup></sup> of 93 per cent alcohol, settling out the precipitated ammonium carbonate, and filtering off the clear solution. In carrying out

+ A System of Qualitative Analysis for the Common Elements, Noyes and Bray : reprint from The Technology Quarterly, xxii, p. 472.

<sup>\*</sup>Gooch and Eddy, this Journal (4), xxv, 444, 1908.

the determinations, portions of the magnesium chloride solution (15<sup>cm<sup>3</sup></sup>-20<sup>cm<sup>3</sup></sup>) were measured out and carefully weighed, lithium chloride was introduced in the amounts stated. 25<sup>cm<sup>3</sup></sup> of 93 per cent alcohol and 50<sup>cm<sup>3</sup></sup> of the precipitating mixture were added. the mixture was stirred vigorously (for perhaps a minute) and set aside for five hours or more. The supernatant liquid was decanted upon asbestos in the perforated crucible (weighed). the precipitate was stirred up with more of the precipitating mixture and allowed to settle, and the liquid was again decanted upon the same asbestos filter. In the cases in which a single precipitation was employed, the precipitate was simply transferred to the filter and washed with the precipitating mixture, and ignited to constant weight. When two precipitations were made, in order to remove possible inclusions of lithium salt from the precipitated ammonium magnesium carbonate, the precipitate was dissolved in the least necessary amount of hydrochloric acid, the solution was diluted to a volume of 10<sup>cm<sup>3</sup></sup>, 13<sup>cm<sup>3</sup></sup>-15<sup>cm<sup>3</sup></sup> of 93 per cent alcohol and 50<sup>cm<sup>3</sup></sup> of the precipitant were added, and the precipitate was transferred, washed, and ignited as described.

The following tables show the results obtained with solutions of magnesium chloride with and without the addition of lithium chloride in varying amount. The mean of the three determinations in which the solution contained no lithium salt was taken to fix the value of the magnesium solution and by comparison with this standard the errors of the single determinations were computed.

#### TABLE I.

${f Solution}\ {f MgCl}_2$	MgO found grm	MgO found per grm. of solution grm	Average MgO per grm. of solution
20·4071 20·3956	0·2788 0·2779	$\left.\begin{array}{c}0.013662^{*}\\0.013626^{*}\end{array}\right\rangle$	0·013651
15.4271	0.2108	$0.013664^{+})$	

#### Standardization of the Magnesium Solution.

\* One precipitation.

+Two precipitations: washings made with precipitant saturated with precipitate.

It will be seen that while the separation of 0.2 grm. of magnesium oxide from lithium amounting to 0.5 grm. of the chloride or 0.083 grm. of the element may be reasonably good in a single precipitation, the ammonium magnesium carbonate only once precipitated is largely contaminated, presumably

# Dinwiddie-Separation of Magnesium.

#### TABLE II.

Solution of MgCl <sub>2</sub>	LiCl ta	=⊂=Li ken	MgO taken	MgO found	Error	Number of precipi- tations
grm.	grm.	grm.	grm.	grm.	grm.	
14.8191	0.2	0.083	0.2023	0.2028	+0.0005	1
15.1409	1.0	0.166	0.2067	0.3191	+0.1124	1
20.7421	0.•5	0.083	0.2831	0.2834	+0.0003	2
20.1706	0.2	0.083	0.2753	0.2761	+0.0008	2
19.9744	1.25	0.207	0.2727	0.2730	+0.0003	2
20.3998	1.25	0.302	0.2785	0.2783	-0.0001	2
19.9291	2.10	0.347	0.2718	0.2730	+0.0012	2

Separation of Magnesium from Lithium.

with lithium carbonate, when the amounts of lithium are considerably greater. Two precipitations made in the manner described will yield, however, a very fair separation of the magnesium (about 0.3 grm. of the oxide) from lithium chloride equivalent to 0.2 grm.-0.3 grm of the element.

The author wishes to thank Prof. Gooch for advice and assistance in carrying out the above work.

ART. L.-Extrusive Basalt of Cambrian Age in the Blue Ridge of Virginia; by THOMAS L. WATSON and JUSTUS H. CLINE, University of Virginia.

THE James River Gap section of the Blue Ridge of Virginia early attracted the attention of geologists, because of the splendid exposures of the rocks and the excellent opportunities offered for their study. As early as 1835 Professor William Barton Rogers, State Geologist of Virginia, was attracted to this section and frequent references are made to it in his annual reports on the Geology of the Virginias. In later years important contributions to our knowledge of the geology of this section were published by Professors Fontaine, J. L. and H. D. Campbell, and others, and our present general conceptions of the geology of the Blue Ridge in middle Virginia are based largely on the results obtained by these investigators in the James River Gap.

These investigators have shown that the Blue Ridge in this section is composed of a central core of pre-Cambrian granitoid igneous rocks, chiefly syenitic in character, flanked on both the southeast and northwest sides by siliceous sediments. On the northwestern slope the sediments were designated by Rogers as Formation No. 1 (Lower Cambrian), but the corresponding sediments on the southeastern slope were considered as probable pre-Cambrian (Huronian) in age, because chiefly of their more highly metamorphosed condition and the great difference in thickness of the beds as compared with those on the northwestern slope. All doubt, however, as to the age of the sediments on the southeastern slope was dispelled in 1884 when Professor J. L. Campbell reported that borings of scolithus linearis had been discovered by H. D. Campbell in the quartzites which underlie the slates of the Snowden slate belt.\* This discovery correlated the sediments on the two sides of the Blue Ridge in this section and at the same time definitely established its anticlinal structure. In 1892 Walcott+ discovered, on the south side of James River opposite Gilmore, the Olenellus fauna in a calcareous sandstone above the Scolithus quartzite of the Balcony Falls section, which established the Lower Cambrian age of these sediments.

During the progress of recent investigations by the Virginia Geological Survey in the vicinity of James River Gap in the Blue Ridge, well-defined occurrences of extrusive basalt were

\* Campbell, J. L. : Geology of the Blue Ridge near Balcony Falls, Virginia,

a Modified View, this Journal (3), vol. xxviii, pp. 221–223, 1884. † Walcott, C. D : Notes on the Cambrian Rocks of Virginia and the South-ern Appalachians, this Journal (3), vol. lxiv, pp. 52–57, 1892.

noted which, from their relations to the associated sediments, must be assigned to Lower Cambrian age. In this part of the Blue Ridge proper the well-known pre-Cambrian basaltic rock (Catoctin schist) which makes up a considerable part of the mountain farther north does not occur, but instead the central core of the main ridge is formed entirely of a quartz-bearing hypersthene-syenite and related granitoid rocks not later than Algonkian in age.

The earliest sediments deposited on the eroded surface of the pre-Cambrian igneous rocks, which form the central core of the Blue Ridge in the James River section, are of Lower Cambrian (Loudoun) age, and are made up of conglomerate and arkose and finer material such as slate and shaly sandstone. The Loudoun is succeeded conformably by a series of siliceous and argillaceous sediments, the age of which has been determined on fossil grounds to be Lower Cambrian. They include the Weverton sandstone, Harper's shale, and Antietam sandstone, which extend more or less continuously along the northwest slope of the Blue Ridge in northern Virginia.

At several points in the vicinity of James River Gap Cambrian sediments are arched in anticlinal fashion entirely over the Blue Ridge and for short distances completely conceal the pre-Cambrian igneous rocks. Remnants of this Cambrian series of siliceous sediments are preserved in relatively small synclinal basins in places on the southeastern slope of the Blue Ridge. As a rule only the Loudoun member is found in these positions, since in most places the later beds have been removed by erosion.

In the vicinity of James River Gap, however, the conditions are somewhat unusual. Here we find in a complexly folded synclinal basin near the southeastern base of the main ridge the three lowest members of the series, including the Loudoun, Weverton, and Harpers, with the Weverton abounding in borings of *scolithus linearis*.

Well-defined occurrences of extrusive basalts are found within the Loudoun near its contact with the granitoid rocks in the James River Gap and vicinity. The one first observed by the writers, and which shows most clearly the relations of the lava both to the overlying and underlying sediments, is located along the road slightly less than half a mile northwest of Snowden Station. The geologic relations at this point are shown in the accompanying section (fig. 1), which shows the entire Loudoun conformably overlain by two massive beds of Weverton quartzite, one of which contains numerous borings of *scolithus*. The basement on which the Loudoun rests is the usual granitoid rock forming the central core of the Blue Ridge in this section, which at this point is pink in color after the predominant feldspar.

## Watson and Cline-Extrusive Basalt.

The basal bed of the Loudoun is an arkosic conglomerate containing numerous well-rounded fragments of the underlying pink granitoid rock up to 2 inches or more in diameter, imbedded in a finer-grained matrix of highly feldspathic sandy material. The lower bed is  $80\pm$  feet in thickness, and is succeeded by a sheet of fine-grained basaltic lava of  $75\pm$  feet in thickness which is well exposed along the road and in a small ravine near by. The bottom portion of the lava sheet contains numerous fragments of the underlying arkosic conglomerate, while the upper surface is amygdaloidal in texture, the amygdules being composed of epidote and quartz, chiefly the latter. The lava sheet is succeeded by a second bed of arkosic con-



glomerate  $65\pm$  feet thick, similar to the one on which it rests. The basal part of the upper conglomerate contains numerous fragments of the basalt, which passes upward into finer-grained arkose and sandy shales that are ultimately succeeded conformably by the fossiliferous Weverton quartzite.

In addition to the occurrence of Cambrian basalt shown in accompanying section (fig. 1), two others were noted near the southeastern part of the Blue Ridge in the same vicinity and in the same stratigraphic position. On the Grant tract about two miles north of Snowden, slaty basaltic material was observed associated with the Lower Cambrian sediments near their contact with the pre-Cambrian granitoid rocks. About one-and-ahalf miles northwest of Snowden in a small syncline at the southeastern foot of Rocky Row Mountain a small area of Cambrian sediments occurs, a very good cross section of which is exposed along the wagon road leading from Snowden to Balcony Falls. In the southeastern limb of this syncline extrusive basalt, similar to that near Snowden, is interbedded with the Loudoun sediments and separated from the pre-Cambrian rocks by a slight thickness of arkosic conglomerate. The lava at this point is in part highly amygdaloidal, but in the outcrop the amygdules have been largely removed, giving the rock a

vesicular appearance. Intimately associated with the basalt is a dark-colored fine-grained slate showing distinct evidence of bedding which is considered by the writers and described below as a probable tuff partly composed of terrigenous material. On the northwest slope of the Blue Ridge darkcolored slates occur in James River Gap near the Rockbridge-Amherst counties line a short distance east of Balcony Rock. The slates show the same color and occupy the same stratigraphic position as the basalts along the southeastern foot of the mountain and although they contain much clastic material which is certainly terrigenous in origin, the writers consider that probably they are in part igneous and are to be correlated, on this account, with the basalt on the southeast slope of the mountain. Basaltic rocks also occur in the James River Gap section at points east and south of Snowden. About two miles south of east from Snowden and a short distance northwest of the Jordan furnace, basaltic material occurs near the contact of the granitoid rocks and Cambrian sediments; and about 2 miles south of James River near Peters Creek. there is an abundant occurrence of basalt in a spur of Piney Mountain, with outcrops of both Cambrian sediments and syenite nearby. These two latter occurrences of basalt are probably to be correlated with those of unmistakable Cambrian age in the vicinity of Snowden, although their exact age relations could not be determined in the field.

These basalts are dark-colored aphanitic rocks, usually showing pronounced slaty cleavage. In part they are amygdaloidal with the cavities either partially or completely filled with epidote and quartz. In some of the more highly weathered portions of the rock the amygdules have been largely removed, leaving the walls of the cavities stained with limonite. In some specimens the amygdules are abundant, but they are usually small, only a few attaining a size as great as a quarter of an inch in diameter.

Microscopic study of thin sections of the basalt shows that the rock has pronounced ophitic texture. While the lathshaped feldspars have largely altered to an aggregate of secondary minerals, including chiefly quartz, sericite, kaolin, and finely divided calcite, their original outlines are perfectly preserved. With the exception of magnetite which is abundant in small octahedra and shapeless grains, whatever dark constituents the rock originally may have contained have entirely altered. The partial alteration of the magnetite has resulted in much leucoxene, which is an abundant constituent in all sections studied. The rock also contains considerable chlorite, some epidote, and a small amount of secondary rutile.

The dark-colored slates associated with amygdaloidal basalt at the foot of Rocky Row Mountain about one and a half miles northwest of Snowden strongly resemble the basalts in color. They possess, however, a distinct thin-bedded structure (lamination) and a perfect cleavage parallel to the bedding planes, giving very smooth surfaces. The rock in thin section is composed of considerable terrigenous material, chiefly quartz grains along with some feldspar fragments. The quartz grains are in part rounded and in part angular, with the former in greatest abundance. Feldspar fragments are altered largely to an aggregate of secondary minerals, chiefly sericite, and in some cases epidote. Magnetite mostly in small octahedra is very abundant. Most of the thin section is composed of very finegrained material, much of which is sericite and quartz and some of which appears to be microscopic needles of feldspar. Some chlorite is also present.

Specimens of the dark slates found on the northwest slope of the Blue Ridge near the Rockbridge-Amherst counties line and a short distance east of Balcony Rock are fine-grained rocks, showing distinct bedding and a well-developed secondary cleavage which cuts the bedding planes at an angle of about 45 degrees. The only mineral recognizable in the hand specimen is pyrite which occurs as disseminated glistening grains along the bedding planes.

Microscopic examination shows that the rock contains a large amount of feldspar in rounded and angular grains almost entirely altered to an aggregate of secondary minerals, chiefly sericite. Quartz occurs abundantly, but less so than feldspar, usually in well-rounded grains. Zircon is fairly common. In addition to these the coarser grained constituents of the rock include magnetite much altered to leucoxene and fairly abundant crystals of pyrite. This material, most of which is certainly of terrigenous origin, is imbedded in a fine-grained matrix very similar in character to the principal material composing the slates associated with the amygdaloidal basalt one and a half miles northwest of Snowden. Although microscopic examination does not establish a tuffaceous origin for this rock, its stratigraphic position, which is identical with that of the basalts along the southeastern slope of the Blue Ridge and its resemblance otherwise to the basalts, suggests a probable pyroclastic origin.

The strong resemblance of some of the Cambrian basalt to the Catoctin schist renders the distinction between the two difficult on lithologic grounds alone. It is only where the exact relations of the basalt to the Cambrian sediments can be determined that the two basalts may be distinguished. They are of similar origin and it is quite probable that the later basalt represents the product of waning volcanic activity extending upward into the Lower Cambrian from the Algonkian, which was noted for widespread igneous activity in the Blue Ridge region.

University of Virginia, March 22, 1915.

# ART. LI. — On the Identity of Footeite with Connellite together with the Description of two new Occurrences of the Mineral; by W. E. FORD and W. M. BRADLEY.

Some time ago a suite of specimens from the Bisbee District was sent to this Laboratory by the Foote Mineral Co. of Philadelphia. These specimens were of cuprite upon which occurred small radiating groups of slender prismatic crystals having a beautiful blue color. Tests upon the latter showed that it was a hydrous copper chloride and at first it was considered to be the rare mineral, footeite. This conclusion was strengthened when, through the courtesy of Mr. L. P. Gratacap of the American Museum ef Natural History in New York City and of Dr. W. T. Wherry of the National Museum in Washington, it became possible to compare the Bisbee mineral with specimens of the original footeite. Optical tests showed that the two were identical.

A little later specimens from the Tintic District, Utah, were sent to us by Mr. Lazard Cahn which showed a mineral almost identical in appearance and association with the blue mineral from Bisbee. This mineral was labeled connellite and upon testing gave the expected reactions for a small amount of the sulphate radical. This naturally led to a more detailed examination of the mineral from Bisbee and it was found that the original tests had been incomplete and that it also contained sulphuric acid and was therefore connellite. Further, a test made upon a small crystalline fragment from one of the specimens of the original footeite preserved in the American Museum of Natural History gave the same reaction. As the optical and crystallographic characters of these three occurrences also agreed perfectly with those given for the original connellite from Cornwall, there was no question but that they all belonged to the same species. As the name, connellite, has priority over that of footeite, the latter must therefore be discarded. The detailed description of the investigation follows.

Footeite. — A hydrous copper chloride from the Copper Queen mine, Bisbee, Arizona, was described in 1891 by G. A. Koenig<sup>\*</sup> and named footeite in honor of Mr. A. E. Foote of Philadelphia. The footeite was associated in its occurrence with another new species which was named paramelaconite and both minerals were found with malachite upon limonite. The footeite, of which only a small amount was observed, occurred in minute needle-like prismatic crystals. The crystal habit was described as apparently hexagonal, but because of the ob-

\* Proc. Acad. Phil., 291, 1891, and Zs. Kr., xix, 601, 1891.

servance of inclined extinction with an angle of  $7\frac{1}{2}^{\circ}$  on a face in the prism zone, and because of the arrangement of the terminal faces, it was decided that the mineral had a monoclinic symmetry. No goniometer measurements were made, but a few angles which were obtained under the microscope were recorded. Twins were observed which were said to be like those of harmotone in habit.

The pyrognostic properties were given as follows: When heated in a closed tube the crystals became black without change in form, and water was deposited in the upper part of the tube with first a gray and then a green sublimate below it. In the flame it gave the characteristic color of copper chloride. By reduction on charcoal it gave a copper globule. It was easily and quietly soluble in acids.

A partial analysis was made upon a sample weighing only 0.0165 g., only chlorine and copper oxide being determined. The water present was not determined directly but was estimated by difference. Under the circumstances of the analysis it is not surprising that the small amount of sulphuric acid present should have been overlooked. The analysis by Koenig is quoted later.

It was found on a new study of the original footeite material that there was an error in the determination of its crystallographic symmetry as made by Koenig. A section cut perpendicular to the prism zone showed under the microscope in convergent light a normal uniaxial interference figure with optically positive character. Also the prismatic sections were always found to show parallel extinction. The crystal system is therefore hexagonal, since Koenig in his description notes the apparent hexagonal symmetry. This agrees with the description of the better crystals of connellite from Cornwall.

New occurrence of Connellite from the Bisbee district. The connellite, to be described, was found at the Czar mine at Bisbee, Arizona. It occurs as small radiating masses of very slender to capillary prismatic crystals which lie in cavities of massive cuprite. In some cases the crystals are separated from each other, and in other cases they lie close together forming a radiating prismatic mass. The cuprite is of exceptionally fine quality, the grains being in places quite transparent. Occasionally in the cavities of the massive mineral small brilliant cubic crystals were observed. Malachite with a delicate radiating fibrous structure, massive azurite and chrysocolla occur in smaller amounts. On two specimens minute grains of spangolite were observed. This rare mineral was identified by its color, cleavage, and optical characters. Intimately associated with the connellite and usually as a thin laver between it and the cuprite occurred a bluish white clay-like mineral which proved to be a decomposable copper silicate, presumably a form of chrysocolla.

Optical and crystallographic characters.—The color of the mineral is a fine deep azure-blue. When examined under the microscope the slender crystals showed no dichroism and always gave an extinction parallel to the prismatic edges. From faces in the prism zone only indistinct interference figures could be obtained, but sections cut perpendicular to that zone gave very distinct normal uniaxial figures. The mineral is optically positive. By immersion in high refracting liquids the refractive indices were determined as:  $\omega = 1.730$ ,  $\epsilon = 1.754$ ,  $\epsilon - \omega = .024$ .

The crystallization is hexagonal. It was possible to mount several crystals under the microscope so that the prism angles might be measured. These gave angles close to the required  $60^{\circ}$ . One crystal was measured on the reflecting goniometer and, although the minute character of the faces together with their vertical striations made accurate measurements impossible, the average of a series of the prism angles obtained was  $60^{\circ}$  44'. These measurements show clearly that the mineral must be hexagonal and not tetragonal. Only a few instances were observed where terminal faces could be distinguished. They were so small, however, and so distorted and irregular in their development, that it was impossible to determine their character.

Blowpipe reactions, etc.—The mineral has a fusibility of 2.0, being readily fusible in the bunsen burner flame, giving at the same time a bluish green flame color. It gives the flame color when heated in the candle flame but does not fuse. In the closed tube it yields water which reacts strongly acid. It is insoluble in water but readily dissolves in acids and gives the customary reactions for chlorine, sulphuric acid and copper in the solutions. It is also readily soluble in ammonium hydroxide.

Connellite from the Tintic district.—Through the courtesy of Mr. Lazard Cahn and of Mr. George L. English of the Ward's Natural Science Establishment in Rochester, the authors have been enabled to examine quite a series of specimens from this district. They come from the Grand Central mine, Eureka, Utah. The character of the mineral and its occurrence is strikingly similar to that of the connellite from Bisbee. In fact, if the specimens from the two localities had not been authentically labeled, they would most probably have been ascribed to the same district.

The connellite from the Tintic district occurs usually as small masses with a columnar structure. The prisms do not often become separate and detached from each other as is the

case with some of the specimens from the Bisbee occurrence. It is found with cuprite which has a massive to granular structure with frequently small brilliant crystals projecting into the cavities. On two specimens the connellite needles were observed embedded in a pale bluish white material which was very soft and had a felt-like appearance. It was very evidently an alter-ation product of the connellite. This material was easily soluble in hydrochloric and nitric acids and in ammonium hydroxide. It was impossible to separate it completely from the associated connellite and not enough was available for an analysis. It gave distinct tests only for copper, chlorine and water, and in general behaved like nantokite. Other specimens showed a light blue compact material closely associated with the connellite which gave the tests for chrysocolla. Atacamite was observed, in one case being intimately associated with the connellite. On another specimen, small cleavable masses of spangolite were noted. The optical characters and chemical reactions of the Tintic mineral were identical with those of the material from Bisbee.

Analyses.—Connellite from both of the new localities was analyzed by Bradley. The methods used were as follows: The mineral was dissolved in dilute nitric acid from which solution the chlorine was precipitated and weighed as silver chloride. The excess of silver in the filtrate was precipitated by hydrochloric acid and removed. The nitric and hydrochloric acids were then removed by evaporation with sulphuric acid and the copper was precipitated from the resulting solu-tion as cupric sulphide and ignited in a current of hydrogen gas and weighed as cuprous sulphide. The sulphuric acid was precipitated from a hydrochloric acid solution by the addition of barium chloride and weighed as usual. On attempting to determine directly the amount of water present by heating in closed tubes, it was found difficult to obtain neutral water although the various methods ordinarily used to retain hydrochloric and sulphuric acids were employed. In attempting to explain this peculiarity, tests were made for the presence of various other acids and surprisingly enough the mineral was found to contain a small amount of nitric acid. Positive tests for N<sub>2</sub>O<sub>5</sub> were obtained upon the connellite from both localities in four different ways, namely by the ferrous sulphate, the diphenylamine, the brucine and phenol disulphonic acid methods. Similar tests were made upon a portion of the small crystal group obtained from the specimen of the original occurrence of the so-called footeite belonging to the American Museum of Natural History with the result that it was also shown to contain nitric acid. Because of the very restricted amount of the mineral available for analysis it was possible to

## 674 Ford and Bradley—Footeite and Connellite.

determine the amount of N<sub>a</sub>O<sub>5</sub> present only by the phenol disulphonic acid or Sprengel's method. This is a delicate and accurate colorimetric method used commonly in water analyses and there is no doubt as to the substantial accuracy of the determinations made by it. The authors' thanks are due to Prof. G. S. Jamieson of the chemical department of the Sheffield Scientific School for assistance in making these determinations. The water determinations quoted were made by heating the mineral mixed with lead chromate in closed glass tubes and passing the vapors given off through layers of hot copper filings and lead chromate. The water collected in the upper portion of the tube was then weighed directly. It was found difficult to control this operation so as to insure the absolutely neutral character of the water collected. In the case of the determination given in the analysis of the connellite from the Tintic district the water was perfectly neutral, but in the case of the analysis of the Bisbee material it still showed a slight acid reaction. It is thought probable, however, that any increase of weight due to the presence of the small amount of an acid radical would be fully compensated by other errors of the method and that the values given represent fairly accurately the amount of water present. It is to be regretted that the amount of material available for analysis was so small as to preclude the use of other methods.

Below are given the following analyses: I, The original footeite by Koenig;\* II, Connellite from Cornwall by Penfield; † III, Connellite from the Czar mine, Bisbee, Arizona, by Bradley; IV, Connellite from the Grand Central mine, Tintic District, Utah, by Bradley; V, Theoretical composition according to the proposed new formula:

	I	II	III	IV	v
CuO	71.6	72.3	73.38	73.41	73.98
Cl	5.6	7.4	6.82	7.05	6.93
SO <sub>3</sub>		4.9	3.12	3.84	3.92
N <sub>2</sub> Ŏ,			0.72	0.30	
H <sub>2</sub> O		16.8	17.13	16.81	16.73
Total		101.8	101.20	101.41	101.56
O = Cl		1.7	1.23	1.28	1.56
		100.1	99.67	$99 \cdot 82$	100.00

Discussion of Analyses.—The above analyses show a substantial agreement in the percentages of the different radicals. They present, however, some difficulties when the attempt is made to interpret them and to derive from them a satisfactory

\* Loc. cit.

† This Journal, xl, 82, 1890.

formula. The mineral not only contains two or three different acid radicals, but is unusually basic in character. It is especially difficult to decide what part the small amount of nitric oxide plays in the formula. The ratios derived from Analyses II, III and IV are given below.

	II		III		IV	
CuO	·911	or 18.6	·921	or 18.8	·922	or 18.8
Cl	·208	$4 \cdot 2$	.192	3.9	$\cdot 198$	4.0
SO <sub>3</sub>	.061	1.2	·039 )	0.0	·047 )	1.0
N,Ŏ,			•006 ∫	0 5	·002 ∫	10
H <sub>4</sub> O <sup>-</sup>	.931	19.0	·951	19.4	•933	19.0

In deriving the above ratios the small amount of nitric oxide was considered as isomorphous with the sulphuric oxide. The only reasons justifying this view is that there does seem to be a mutual variation in the percentages of the two radicals and because of the small amount present it is obviously necessary to consider the nitric oxide as playing some isomorphous rôle in the formula. The effect upon the ratios, however, would be slight, no matter how the nitric oxide was regarded. The ratios derived from the three analyses point fairly clearly to the following formula as expressing the composition of the mineral, namely,  $16CuO.2CuCl_2.1Cu(SO_4, (NO_3)_2).19H_2O$ . Or, disregarding the nitric oxide, the formula might also be written,  $16Cu(OH)_2.2CuCl_2.1CuSO_4.3H_2O$ .

Penfield's analysis agrees less perfectly with this formula than do the newer analyses. In interpreting his analysis he considered that a small amount of the water in the mineral occurred as hydroxyl isomorphous with the chlorine and from this viewpoint he derived the formula, Cu<sub>15</sub>(Cl.OH)<sub>4</sub>SO<sub>16</sub>.15H<sub>2</sub>O<sub>5</sub> which written similar to the one given above would become 12CuO.2Cu(Cl.OH), 1CuSO, 15H, O. While, at first glance, this formula would seem to be considerably different from the new one proposed above, it will be seen, by comparing Penfield's analysis with the theoretical composition as given in column V on p. 674, that the variation is not so very great. It is to be remembered that Penfield had only 0.0740 g. of material available for his analysis. Further, his assumption that a part of the water existed as hydroxyl replacing some of the chlorine was made in order to simplify his formula and could not in the nature of the case be subjected to proof. In view of these facts it is felt that the proposed new formula has stronger evidence in its favor and better expresses the composition of the mineral than that assigned to it by Penfield.

With the hope of obtaining more definite data as to the chemical structure of connellite, repeated attempts were made

675

#### 676 Ford and Bradley—Footeite and Connellite.

to obtain it by artificial means but with only negative results. The authors gratefully acknowledge the advice of Prof. H. W. Foote in regard to this portion of the investigation.

A large number of tests were made upon specimens of atacamite, brochantite and other similar minerals in order to ascertain if they might not also contain small amounts of nitric oxide which had previously been overlooked. In only one case, however, was any evidence of its presence discovered. A solution of an atacamite from the United Verde mine, Jerome, Arizona, gave a faint color reaction with diphenylamine, indicating the presence of a trace of nitric acid.

Mineralogical Laboratory of the Sheffield Scientific School of Yale University, New Haven, Conn., April 12, 1915.

# SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. The Fixation of Atmospheric Nitrogen.-In an address delivered recently before two sections of the American Chemical Society, W. S. LANDIS has discussed this important topic, giving special attention to the calcium cyanamide industry at Niagara Falls. It is well known that the first step of this process is the production of calcium carbide, CaC<sub>2</sub>, from lime and coke in an electric furnace. This product is then finely ground and heated with atmospheric nitrogen in order to form a mixture of calcium cyanamide, CaCN<sub>2</sub>, and free carbon. The magnitude of the operation may be perceived from the statement that 2,000,000 cubic feet of practically pure nitrogen (or about 75 tons) are used daily for this purpose at Niagara Falls. The crude cyanamide contains about 22 per cent of nitrogen, and it is used as a fertilizer, after being ground, treated with a little water to decompose any unaltered calcium carbide, and oiled to prevent the formation of dust. At present this appears to be the chief use of the cyanamide, but it may be used for several other purposes. For instance, when mixed with water and heated under pressure its nitrogen is all converted into ammonia according to the equation CaCN, +  $3H_0O=2NH_s+CaCO_s$ . Another transformation is effected by melting down a special grade of cyanamide with a flux, such as common salt, when the free carbon present combines with the cyanamide forming cyanide. The resulting product is equivalent to about 25 per cent of its weight of potassium cyanide, and it is stated that this crude form of cyanide is perfectly serviceable in the metallurgical operation of extracting gold and silver from ores, and is very much cheaper than the higher grade

cyanide that is now extensively used.—Jour. Indust. and Eng. Chem., vii, 433. H. L. W.

2. Electroplating with Cobalt.—Commercial plating with nickel is an industry of very great magnitude, but although it has been known for a long time that the closely related metal cobalt is capable of yielding similar results, there has been heretofore no practical application of this metal in this way, doubtless on account of its greater value due to its use in producing the blue color of glazes used in the ceramic industry, etc. On account of an increased production of cobalt in recent years in the Province of Ontario, there is probably a need of a more extensive utilization of this metal. H. T. KALMUS, C. H. HARPER, and W. L. SAVELL, of the Canadian Department of Mines, have made extensive experiments with cobalt plating, and have found that this metal has some advantages over nickel which in practice may overcome its higher cost. One of the best cobalt plating solutions, used with metallic cobalt anodes, is made as follows :

Cobalt sulphate (anhydrous),	312 grams
Sodium chloride,	19.6 "
Borie acid,	nearly to saturation
Water,	1000°°

The cobalt may be deposited on various metals and alloys, and the platings are firm, hard and uniform. They may be buffed to a satisfactorily finished surface having a beautiful luster, which, although brilliantly white, has a slightly bluish cast. An advantage of the solution that has been mentioned is that it is capable of plating at least 15 times as fast as the fastest satisfactory nickel solution. It appears that the cobalt plating rapidly deposited is harder than nickel plate, so that less cobalt is required to give the same protection. As the present price of cobalt is about four times that of nickel, it may seem doubtful that the former can replace the latter in practice. The authors, however, claim this to be probable.—Jour. Indust. and Eng. Chem., vii, 370.

H. L. W.

3. The Use of Mercuric Oxide for Standardizing Volumetric Solutions.—M. A. ABELMANN finds mercuric oxide a good basis for standardizing, since it can be obtained perfectly pure, and it is stable and not hygroscopic. For purposes of acidimetry it can be dissolved in an excess of  $\frac{1}{10}$  normal hydrochloric acid when a sufficient amount of sodium chloride is present and heat is applied. For iodometric standardization the oxide is dissolved with hydrochloric acid in a closed glass stoppered flask, then an excess of potassium iodide and some potassium hydroxide are added, and then the mercury is precipitated as metal by the use of formaldehyde. Now, after acidifying with acetic acid, the mercury is dissolved by volumetric iodine solution in excess, and the excess is found by means of sodium thiosulphate solution, using starch as an indicator.—Bulletin, xvii, 9. II. L. W.

4. A Manual of Practical Physical Chemistry; by FRANCIS W. GRAY. 12mo, pp. 211. London, 1914 (Macmillan and Co.,

AM. JOUR. Sci. – FOURTH SERIES, VOL. XXXIX, No. 234.–JUNE, 1915. 44 Limited).—In preparing this text-book for the use of students in laboratory work, the author has taken into consideration the fact that periods of laboratory work are usually limited to two or three hours, and he has prepared a series of 39 "time-limit exercises" to be used in such laboratory periods. He has also incorporated introductions to several sections of the subject, and in these parts of the book and elsewhere are to be found several important experiments which are suitable when unlimited time is available. Special attention is paid to the subject of accuracy, to the discussion of which an introduction of no less than 35 pages is devoted. The experiments appear to be well chosen and to be clearly and concisely described. H. L. W.

5. Practical Physical Chemistry; by ALEXANDER FINDLAY. 12mo, pp. 327. London, 1914 (Longmans, Green and Co. Price \$1.30 net).-This excellent text-book for the use of students in connection with laboratory experiments has now reached its third edition, after a period of eight years since its first appearance. Several important additions have been made in the present issue, so as to make it more serviceable to the increasingly large number of students who now make a special study of this branch of chemical science. An appendix has also been added, giving tables of some of the more important physical data required in the course that is given. The first chapter deals with the calculation of results and errors, and includes a particularly clear and practical discussion of the use of approximate numbers. The experiments given in the practical part of the book appear to be very well chosen and clearly described. H. L. W.

6. Molecular Association; by W. E. S. TURNER. 8vo, pp. 170. London, 1915 (Longmans, Green and Co. Price \$1.40 net).— This is one of the series of monographs on inorganic and physical chemistry, edited by Professor Alexander Findlay. They are of much importance for the use of advanced students and teachers of chemistry. The volume under consideration gives an excellent account of what is known of the molecular state of gases, dissolved substances and liquids, and it includes an extensive list of references to the literature of the subject. In an appendix is given a long list of results of investigations showing molecular complexity, and here another list of references is supplied.

H. L. W. 7. X-Rays and Crystal Structure; by W. H. and W. L. BRAGG. Pp. viii, 229, 75 figures, 4 plates. London, 1915 (G. Bell and Sons).—The theoretical work of Laue together with the experimental realization of his ideas by Friedrich and Knipping opened up, about two years ago, a new and very fruitful field of investigation which requires, for its proper understanding, a knowledge both of X-ray phenomena and of crystallography. "As these branches of science have never been linked together before, it is to be expected that many who are interested in the new development find themselves hampered by a tantalising ignorance of one or other of the essential contributory subjects." "In
this little book my son and I have first made an attempt to set out the chief facts and principles relating to X-rays and to crystals, so far as they are of importance to the main subject." "We have devoted the remaining and larger portion of the book to a brief history of the progress of the work, and an account of the most important of the results which have been obtained."

A more detailed idea of the contents of this most opportune volume may be derived from the titles of the chapters, which are: "I Introductory, II Diffraction of Waves, III The X-Ray Spectrometer, IV The Properties of X-Rays, V Crystal Structure, VI X-Ray Spectra, VII The Analysis of Crystal Structure I, VIII The Analysis of Crystal Structure II, IX The Relation between Crystal Symmetry and the Arrangement of the Atoms, X The Analysis of Crystals III, XI The Intensity of X-Ray Reflection," and "XII The Analysis of the Laue Photographs." The value of the text is greatly enhanced by the fact that its authors have both contributed largely to the progress of the subject and that W. L. Bragg has greatly simplified and illuminated the crystallographic problems by his conception of "reflecting" planes of atoms. H. S. U.

8. Elementary Chemical Microscopy; by ÉMILE MONNIN CHAMOT. Pp. xiii, 410, 139 figures. New York, 1915 (John Wiley and Sons, Inc.).-In the opinion of the author the advantages to be derived from the intelligent use of the microscope have been largely neglected or overlooked by the American chemist. Among the various causes which have conspired to produce this condition, the two which stand out most prominently are (i) lack of appreciation of the fact that a great variety of problems are solvable by means of the microscope, and (ii) the non-existence in English of an elementary but adequate textbook on the subject. The present volume is derived primarily from the mimeographed sheets which the author has written for his classes during the past fifteen years and it is designed to close the gap in the literature of the subject. As regards preliminary training the author says: "It is assumed that the students for whom this textbook is intended have had a course in crystallography and one in physics, including optics."

The first chapters are devoted to detailed descriptions and explanations of the manipulation of such pieces of apparatus as oculars, objectives, illuminating devices, ultramicroscopes, metallurgical microscopes, accessories, radiants, micrometric microscopes, polarizing systems, etc. "The instruments figured (and the methods described) have all been tested and tried by the author with but one or two exceptions." The remaining chapters deal with the practical applications of the methods and apparatus previously considered. In particular, pages 273 to 382 pertain to characteristic microchemical reactions of the common elements and acids when in simple mixtures. The last chapter deals with the preparation of opaque objects for the microscopi study of internal structure. In many cases the names of th manufacturers of the instruments described are indicated. The appendix comprises a fairly long table of melting-points of compounds suitable for microscopic work, the periodic table, and a list of reference books. The diagrams are large and clear, and the entire volume seems admirably adapted to meet all the requirements for which it was intended. H. S. U.

9. Hancock's Applied Mechanics for Engineers; revised and rewritten by N. C. RIGGS. Pp. xiii, 441, with 289 figures. New York, 1915 (The Macmillan Co.).—"In the revision of this text. although rather extensive changes in method of treatment have been made in certain parts, the general subject matter and order of arrangement have been, in the main, retained." The most important points of difference between the present edition and its predecessor (see vol. xxviii, page 78) may be noted as follows. The chapter formerly entitled "Dynamics of Machinery" is now called "Dynamics of a Rigid Body" and, because of its relatively greater difficulty, it has been transferred to a later position in the book. More extensive use is now made of graphical methods. The graphical and analytical methods are developed side by side and many problems are proposed for solution by both processes. The emphasis on the graphical methods has necessitated the introduction of much new material, especially in the construction of stress diagrams for trusses, and in the numerous applications of the equilibrium polygon. The problems illustrating the principles follow immediately after the development of the principles and are of such a nature as to require original thinking and to preclude the possibility of mere substi-tution of numerical data in the proper formulae. The number of new problems added is about two hundred. On the whole, the book has been appreciably improved by the process of revision. H. S. U.

10. Electricity for the Farm; by FREDERICK IRVING ANDERson. Pp. xxiii, 265, illustrated. New York, 1915 (The Macmillan Co.) .- "This book is designed primarily to give the farmer a practical working knowledge of electricity for use as light, heat, and power on the farm." The subject matter is presented in three Parts which deal respectively with water-power, with electricity, and with gasoline engines, windmills, storage batteries, etc. The text is elementary, practical, thorough and adequate. In other words, no previous acquaintance with scientific matters is presupposed. Typical examples of the design and installation of small electrical plants are given. The text includes tables of numerical data and simple formulae for calculating all necessary quantities, such as: the discharge of water from weirs, spouting velocity, "head," horsepower, pipe friction, Ohm's law, etc. The text-figures are numerous and well chosen, and the half-tone illustrations are attractive. The author's style is pleasing and the text reads like a novel in several places. The volume should be very helpful to all who live in the country and who desire to take advantage of the opportunities afforded by their surroundings. H. S. U.

## II. GEOLOGY.

1. Geology of the North American Cordillera at the Fortyninth Parallel; by REGINALD ALDWORTH DALY. Memoir No. 38, Geological Survey of Canada. Ottawa, 1912. In three parts, pp. 857, pls. 73, figs. 42, tables 55.—This report, a most important contribution to the geology of western Canada, was originally issued as Appendix 6, Report of the Chief Astronomer and Commissioner for Canada, International Boundary Surveys. In that form it was not accessible to many libraries and individual geologists. The Geological Survey has accordingly done an important service to geology in republishing it as one of their memoirs. As stated by Director Brock in the introductory note,— It must be referred to constantly in future work dealing with the geology of British Columbia, and were it not available in the publications of the Survey great loss and inconvenience would result.

The area surveyed consists of a belt 400 miles long, varying in width from 5 to 10 miles. The field work was carried on by Professor Daly from 1901 to 1906, over rugged or heavily wooded An additional difficulty lay in that for several mountains. seasons the geologist was in advance of the topographic mapping. Daly states that the quality of the work is between that of a detailed and a reconnaissance survey. It is sufficiently detailed, however, to show the character of the general geology. The geologic maps and sections in the atlas which constitutes Part III bring this out, but perhaps the most impressive feature of the report consists in the number of novel points of view and theoretical problems which the author has developed from the field studies. These have been in considerable part published by him elsewhere, but are here given in the field setting where they were developed. They will supply material for research along these lines for many years. The test of the value of these ideas con-sists in part in the degree to which they will ultimately become verified, or the basis at least of modifications of older views, but the value consists most largely in the degree to which they will stimulate further investigation. The report is far more valuable than if it had been restricted to mere descriptions of rocks and structure, and, as long as such memoirs as this of Professor Daly's are published, geologic science is in no danger of stagnation. J. B.

2. Florida State Geological Survey: E. H. SELLARDS, Ph.D., State Geologist, Sixth Annual Report, 1914. Pp. 451, figs. 90, and a Key Map to Mineral Resources of Florida.—The annual report for the year 1913 includes the following papers: Mineral industries and resources of Florida by E. H. Sellards (pp. 21-114); Some Florida lakes and lake basins by E. H. Sellards (pp. 115-160); The relation between the Dunnellon Formation and the Alachua Clays of Florida by E. H. Sellards (pp. 161-162); and the geography and vegetation of Northern Florida by R. M. Harper (pp. 163-343). The Director of the Florida Survey has been unusually successful in maintaining the two-fold function of the organization: economic and educational. The physiographic and economic publications in particular are to be commended.

3. Biennial Report of Topographic and Geologic Survey of Pennsylvania for the two years ending June 1, 1914. Pp. 232, pls. I-V.—Of 240 quadrangles into which the State of Pennsylvania has been divided, 144 have been covered by topographic maps on a scale of 1:62500 with 20-foot contours. Geologic surveys cover 31 quadrangles. A series of reports dealing with the mineral wealth of the state from year to year engages the chief attention of the staff, an emphasis on economic geology justified by the fact that 24 per cent of the total mineral production of the United States is credited to Pennsylvania. The present report includes papers on the Copper Development of the South Mountain Region by G. M. Bevier, and Mineral Production of Pennsylvania for 1912. Papers dealing with the slate industry and the clay industry are in process of preparation.

H. E. G.

H. E. G.

4. Geological Survey of Illinois: FRANK W. DEWOLF, Director. Bulletin No. 24, Some Deep Borings in Illinois, by J. A. UDDEN. Pp. 141, pls. I-IV (last three in pocket) .- The stratigraphic value of carefully collected samples obtained by drilling is evident. Particularly in regions of slightly dissected, flat-lying rocks a few well records correctly interpreted may yield more valuable geologic data than could be obtained by the study of many square miles of surface exposures. The relatively little attention given to this source of information doubtless results from unsatisfactory experience with logs as frequently recorded. Professor Udden shows, however, that modern methods of drilling are suitable for geologic purposes and he discusses methods of examination best designed to secure correct interpre-For the formations underlying the surface of Illinois the tation. thickness and number of strata have been determined on the basis of well sections, with the result that the lithologic variations and sequence of beds may be discussed on a quantitative basis.

H. E. G.

5. Publikationer fra det Danske Meteorologiske Institut, ved C. RYDER, Direktor, Aarboger. Isforholdene i de Arktiske Have (The State of the Ice in the Arctic Seas, 1914). 1915. Pp. xxiv, 5 maps.—Like the publications dealing with the annual fluctuations of the world's glaciers, the reports of the annual (in many cases monthly) distribution of ice in the arctic seas furnishes detailed elimatologic data of high significance. The value of the data is proportional to the number of years for which observations are recorded and it is to be hoped therefore that the work undertaken may be continued and its scope increased. It is gratifying to professional workers in geography that captains of sealers, fishing schooners, and freighters, as well as scientific explorers, should devote their attention to this series of well planned meteorological observations. H. E. G.

6. Dew-Ponds: History, Observation and Experiment; by EDW. A. MARTIN. Pp. 208, 12 ills. London, 1914 (T. W. Laurie). -Many shallow ponds on the chalk downs of England, situated at moderately high levels, retain a supply of water during the driest, hottest weather, when similar water bodies at lower levels and apparently more favorably situated are dry. Under the term "Dew-Ponds" these supposedly mysterious phenomena have received much attention in archeological, geographical and geological literature. When field study replaced deductive reasoning the "mystery" disappeared. Mr. Martin finds the annual deposit of dew in the region under discussion to be .77 inches, and that on only five occasions in three summer months was the water in the ponds below dew point. The "dew-ponds" are supplied by rain. During the dry season they decrease in size and occasionally dry up. In some instances the downland fogs make good the unequal relations existing between rainfall and evaporation. An analysis of the water reveals the presence of salt brought from the sea and salt particles serve as nuclei for the condensation of moisture in the downland air. H. E. G.

7. Union of South Africa, Department of Mines and Indus-tries. Annual Reports for 1913; Part V, Geological Survey, 1914. Pp. 119, 3 figs., plates I-IX, including 4 maps .- During the year 1913 the Geological Survey of South Africa issued two sheets of the Geological Map, viz: Lydenburg and Pienaars River (revision). The Pilandsberg and Olifants River sheets are ready for publication. The field work for the year included detailed studies of the Witwatersrand by E. T. Mellor, and a continuation of the survey of the Rustenburg district by H. Kynaston, Director. Areal mapping resulted in the following reports: The Geology of the Country north-east of Carolina, by A. L. Hall (pp. 31-50); The Geology of Portions of the Piet Retief, Wakkerstroom, and Utrecht Districts, by W. A. Humphrey (61-68); The Geology of a Portion of the Ngotshe Division of Northern Natal, by W. A. Humphrey (69-78); Summary of a Geological Survey of Part of Namaqualand, by A. W. Rogers (79-82); The Geology of Mount Currie and Umzimkulu (Cape) and Alfred County (Natal), by Alex L. duToit (83-102). H. E. G.

8. Fossil Birds in the Marsh Collection of Yale University; by R. W. SHUFELDT. Trans. Connecticut Acad. Arts and Sci., vol. xix, pp. 1-110, pls. i-xv, 1915.—Doctor Shufeldt has made a very notable contribution to our knowledge of fossil birds by the careful and painstaking way in which he has studied, figured and described the accumulation of avian material in the Peabody Museum. Bird fossils are very rare and almost always fragmentary, or, if a whole bone be present, it may be the sole representative of a skeleton, so that at best their study is a rather thankless task. Doctor Shufeldt has placed this material, which represents no fewer than thirty-two genera and forty-nine species, in the best possible condition as a basis for future reference. The Yale collection will therefore remain a standard of comparison for years to come. R. S. L.

## III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Report on the Starfishes of the West Indies, Florida, and Brazil, including those obtained by the Bahama expedition from the University of Iowa in 1893; by A. E. VERRILL. Bulletin from the Laboratories of Natural History, University of Iowa, vol. vii, No. 1, pp. 232; 29 plates. March, 1915.—This is a monograph of all the genera and species of starfishes (Asterioidea) found in the West Indian faunal area, from North Carolina to Rio Janeiro, in depths less than 150 fathoms, with a list of those known from deeper waters. Practically all of the 82 species are fully described, and nearly all are figured, with a few from Panama, etc., for comparison. The general figures are mostly from photographs, but eight plates consist of microscopic details, drawn by A. H. Verrill. It includes a very full Bibliography.

2. American Hydroids, Part III. The Campanularidæ and the Bonneviellidæ; by CHARLES C. NUTTING. Special Bulletin U. S. Nat. Museum, Smithsonian Inst., pp. 118, 4to, 27 plates. 1915.—This, like the two preceding numbers, is a monographic work including all the known species from both the Atlautic and Pacific Coasts, with detailed synonymy and fairly complete bibliography. Nearly all the species are illustrated by excellent figures. Eighty-two species of Campanularidæ are included, from North and South America.

3. Nahrungsmittelchemie in Vorträgen: herausgegeben von Dr. W. KERP. Pp. xxxii, 579. Leipzig, 1914 (Akademische Verlagsgesellschaft m. b. H.).-This large volume represents a new venture in the direction of technological literature. It includes the collection of lectures on the subjects of the chemistry and hygiene of foods delivered at the first "Fortbildungs-kursus" for food chemistry in Berlin, 1912. The individual essays, prepared by experts in various branches of this rapidly developing subject, present recent modifications and improvements in technique; reviews of new contributions to the underlying sciences upon which the food industries are based; and especially the changing viewpoints which progress in the arts and sciences have enforced upon the chemist in this domain. In illustration, chapters on the application of modern physical chemistry, serological studies, bacteriology, and microscopy may be cited. Questions of legal import and economic significance are also discussed from the standpoint of recent experience. The authors include Professors Abderhalden, Uhlenhuth, Buchka, Th. Paul, and Kerp, among the sixteen essayists. The book in no way aims to be a systematic treatise, but rather a guide to the newer features of the chemistry of foods, as well as to the sanitary problems involved, and to the most approved analytic procedures now available. Even the most cursory inspection will awaken a lively appreciation of the enormous field already covered by what was once a minor application of physiological chemistry. L. B. M.

## Obituary.

4. Leavening Agents: Yeast, Leaven, Salt-Rising Fermentation, Baking Powder, Aerated Bread, Milk Powder; by RICH-ARD N. HART. Pp. 90. Easton, 1914 (The Chemical Publishing Co.).—A brief review of the preparation and use of yeast in various industrial processes; of the nature of baking powders and the problems involved in their use; of aerated bread; and incidentally of milk powders which are rapidly finding use in everyday life. The little book is evidently intended for popular use. It contains occasional careless statements; such, for example, as the ability of yeast to turn red blood blue (p. 8). The most useful part is that devoted to the discussion of commercial yeast. L. B. M.

5. The Mining World Index of Current Literature. Vol. VI. Last Half Year 1914; by GEORGE E. SISLEY. Pp. XXVII, 234. Chicago, 1914 (Mining World Company).—This valuable index to the recent literature of mining, metallurgy, engineering, mining geology, mineralogy, etc. is on the lines laid down in earlier issues. It has, however, been amplified by the addition of a brief digest of many of the articles referred to; this should materially increase its usefulness.

6. The Museum of the Brooklyn Institute of Arts and Sciences. Science Bulletins, Vol. 2, No. 3. Long Island Fauna and Flora, III. The Frogs and Toads; by FRANK OVERTON. Pp. 21-40; 11 pls. November 3, 1914.

No. 4. A Report on the South Georgia Expedition; edited by ROBERT C. MURPHY. Pp. 40-102; plates 14-18. November 5, 1914.

7. Annual Report of the Board of Scientific Advice for India for the year 1913-14. Pp. 175. Calcutta, 1915.—This report gives the usual summary, in very concise form, of the work accomplished in India in the different lines of science, physical, natural, economic, etc.; a large amount of interesting matter is thus presented to the reader. Some eleven departments are enumerated, which are handled by six sub-committees; the Hon. L. J. Kershaw, Secretary to the Government of India is ex officio President of the Board.

### OBITUARY.

Mr. SANDERSON SMITH, malacologist, of Port Richmond, Staten Island, N. Y., died March 28, 1915, aged 83 years. He was born in Regents Park, London, May 14th, 1832. He received much of his early education at the Rectory School, conducted by the Rev'd C. M. Everest, in Hamden, Conn. Later he studied at the School of Mines, in London, three years. He early took up the study of conchology and published several papers on the East Coast Shells. Among his papers are the following :—

On the Mollusca of Peconic and Gardiner's Bays, Long Island, in the Annals of the Lyceum of Natural History of New York, vol. vii, 1860, accompanied by tables of distribution. Notice of a Post-pliocene Deposit on Gardiner's Island, N. Y., op. cit., vol. viii, 1865.

Report on the Mollusca of Long Island, N. Y., and its Dependencies (with Temple Prime), op. cit., vol. ix, 1870.

Catalogue of the Mollusca of Staten Island, N. Y. (with J. W. Hubbard), op. cit., vol. viii, 1865.

Mr. Smith was associated with the writer during the investigations of the marine faunæ off our coast, by the U. S. Fish Commission, nearly every season, from 1875 to 1887, and rendered valuable services in connection with all the dredging expeditions during all those years. He was a careful and very enthusiastic collector, especially looking after the smaller shells, but by no means confining himself to that group. Although unfortunate circumstances prevented his participating largely in the final working up of the collections, as planned, his name appears jointly with that of the writer, in connection with the names of a large number of the new species of deep sea shells discovered by us. He gave his services for this work as a volunteer, without pay, as did all the other zoologists. For some years he was engaged in arranging the collection of shells in the American Museum, of New York.

One of his most valuable works is the Lists of Dredging Stations in North American Waters, from 1867 to 1887, published in the Annual Report of the U. S. Commission of Fish and Fisheries for 1886. This includes all the physical data obtained, and embraces the dredging stations of the Challenger, the Blake, the Hassler, and various other expeditions, besides those of the Fish Hawk and Albatross, of the U. S. Fish Comm. Its compilation required a large amount of time and patient care.

Subsequently, with Richard Rathbun, he published in 1882 another similar list of all the dredging stations of the U. S. Fish Comm. vessels, from 1871 to 1879, including a large amount of valuable oceanographic data.

During the later years of his life he devoted a large amount of time to making very extensive collections of maps, charts, and engravings, which he arranged very systematically. These should prove very valuable to some large library.

Mr. Smith was socially inclined, very fond of children, and much liked by all his numerous friends. He did not marry.

A. E. V.

DR. W. GRYLLS ADAMS, emeritus professor of natural philosophy in King's College, London, died on April 10, at the age of seventy-nine years.

DR. EBERHARD FRAAS, the distinguished German paleontologist, died in Stuttgart on March 6.

M. EMILE-HILAIRE AMAGAT, the eminent French physicist, died in March last at the age of seventy-five years. His most important work was the successful researches into the properties and behavior of gases under high pressures. Α

Academy, National, meeting at Chicago, 134; Washington, 610; Memoirs, Vol. XII, part 1, 229; Proceedings, Vol. I, No. 1, 228.

Adaptation, Lloyd, 612.

- Adirondacks, age of igneous rocks, Cushing, 288. Allegheny Observatory, publications,
- 611.
- Allen, F. I., thaumasite, 134.
- Ampère molecular currents, Onnes, 313.
- Andersen, O., system anorthite-forsterite-silica, 407
- Anderson, F. I., Electricity, 680. Anticosti Island faunas, Twenhofel, 130.
- Arizona, Meteor Crater, Barringer, 482.

в

- Bailey, E. H. S., Food Products, 136. Barbour, E. H., new longirostral
- mastodon, 87; Carboniferous plant tissue, 173. Barus, C., repulsion of two metallic
- disks, 93.
- Berry, E. W., Eocene ancestor of the Zapodilla, 208.
- **Bigelow** on the solar constant, Very, 201.
- Birds, fossil, in the Marsh Collection, Yale University, Shufeldt, 683.
- Blackwelder, E., calcareous algæin the Middle Cambrian, Wyoming, 646.
- Blake, J. M., growing crystals for measurement, 567.
- Bliss, A. R., Jr., Qualitative Chemi-cal Analysis, 123.
- Bowen, N. L., silicate liquids, crys-tallization and differentiation. 175.
- Bradley, W. M., footeite and con-nellite, 670.
- Bragg, W. H. and W. L., X-Rays and Crystal Structure, 678.
- Brandegee, M. M., hydrochloric acid in estimation of organic oxygen, 398.
- British Museum, publications. 325. Brooklyn Institute, bulletins, 685.

Brown, E. W., simple apparatus for tidal analysis, 386.

Brown, T. C., development of the mesenteries in zooids of Anthozoa, 535.

C

Canada geol. survey, 481.

- Carnegie Foundation, Bulletin 8, 611. - Institution, Year Book No. 13, 484.
- Catskill Mts., physiography and geology, Rich, 137.
   Chamot, E. M., Chemical Micro-
- Chamot, E. scopy, 679.
- Chemical Technology, 5th ed., Lewkowitsch and Warburton, 122, 215. - Analysis, Qualitative, Bliss, 123.
- Chemie, Physikalische, der Zelle, Höber, 324.
- Chemistry, Physical, Findlay, 678; Gray, 677.
- Cyanogen Compounds, Williams, 476.

## CHEMISTRY.

- Acidimetric solutions, Dodge, 215. Acids, polythionic, determination, Jamieson, 639.
- Aluminium, separation, Minnig, 197.
- Atomic weights of carbon, sulphur, 213.
- Chloropierin, production of, Datta and Chatterjee, 475.
- Chromium sesquioxide, unstable, Mixter, 295.

Coal tar industry, Hesse, 121.

- Cobalt, electroplating with, Kal-mus, Harper, etc., 677.
- Cuprous and cupric sulphides, determination, Posnjak, 311.
- Elements, transmutation, Jorissen and Vollgraff, 476.
- Ethyl hydracrylate, hydrolysis, Drushel, 113.
- Gasolene vapor in air, determination, Burrell and Robertson, 475.
- Hydrochloric acid in estimation of organic oxygen, Drushel and Brandegee, 398.

Hydrogen, production, Seeker, 600.

\*This Index contains the general heads, CHEMISTRY, GEOLOGY, MINERALS, OBITUARY, ROCKS, ZOOLOGY; under each the titles of Articles referring thereto are included.

#### CHEMISTRY-cont.

Lead from Ceylon thorite, Soddy, 601.

- Magnesium, separation from lithium, Dinwiddie, 662. Mercuric oxide for standardizing
- volumetric solutions, Abelmann, 677.
- Nitrogen, fixation of atmospheric, Landis, 676.
- Potash from feldspar, Cushman and Coggeshall, 311.
- Rare Earths, Levy, 312.
- carbonate, Sodium molecular weight, Richards and Hoover, 213.
- sulphate, molecular weight,
- Richards and Hoover, 213. Thorium-D, volatility, Wood, 218. Tin, antimony, etc., analysis of alloys, Stief, 602. Tungsten and molybdenum, sepa-
- ration, Marbaker, 214.
- Vanadium, pentavalent, estimation, Oberhelman, 530.
- Water, qualitative test, Weaver, 312. Chlorophyll, absorption spectrum, Van Gulik, 604.
- Cline, J. H., extrusive basalt of Cambrian of Virginia, 665.
- Coast and Geodetic Survey, U. S., 225, 486.
- Commerce, Secretary of, annual report, 225.
- Connecticut geol. survey, 318.
- Cook, C. W., datolite, Great Notch, New Jersey, 642.
- Corals, development of structure, Brown, 535.
- Cross, W., petrographic classifica-tion. 657.
- Crowther, J. A., Molecular Physics, 314.
- Crystallization of silicate liquids, Bowen, 175.
- Crystals, growing, Blake, 567.
- structure shown by X-Rays, Bragg, 678.
- Culler, J. A., General Physics, 315. Cushing, H. P., age of igneous rocks of Adirondacks, 288.

## D

- Dana, James Dwight, lectures commemorating Centenary, 605.
- Danish Meteorological Institute, pub-
- Lications, 682.
  Davis, J. W., meteorites of Brenham, Kansas, 609.

- Derby, O. A., stem structure of Tietea singularis, 251.
- Dew-Ponds, Martin, 683.
- Dinwiddie, J. G., separation of magnesium, 662.
- Disks, metallic, repulsion of, Barus, 93.
- Dispersion experiment, Thompson, 218.
- Drushel, W. A., hydrochloric acid in estimation of organic nitrogen, 398; hydrolysis of ethyl hydracrylate, 113.

#### E

- Earths, Rare, Levy, 312. Edelman, P. E., Experiments, 128.
- Egypt, amethysts in, 483.
- Electrical measurements, Smith, 127.
- Electricity for the Farm, Anderson, 680.
- and Magnetism. Franklin a MacNutt, 314, 480; Nipher, 219. and
- Elektrische Spektralanalyse chemischer Atome, Stark, 480.
- Embryology, Heape, 485. Emmons, S. F., Memor Emmons, S ship, 229. F., Memorial Fellow-
- Evolution, Dynamic, Redfield, 324.

#### F

- Feeblemindedness, Goddard, 229.
- Field, R. M., Roentgen ray, use in paleontology, 543.
- Findlay, A., Physical Chemistry, 678.
- Finland, petrology of the Orijärvi region, Eskola, 221.
- Florida geol. survey, 681.
- Food Industries, Vulté and Vanderbilt, 136.
- Products, Bailey, 136.
- Foods, Wardall and White, 136. Foote, W. M., new meteoric iron from Sams Valley, Oregon, 80.
- Ford, W. E., footeite and connellite, 670.
- Fossils, Study of, Shimer, 322.
- Franklin, W. S., Electricity and Magnetism, 314, 480.

#### G

- Gaede, W., diffusion of gases through
- mercury vapor, 477. Gardner, J. A., Tertiary faunas of Yorktown and Duplin Formations, 305.
- Gases, diffusion through mercury vapor, Gaede, 477.

## GEOLOGICAL REPORTS.

Canada, 481.

- Connecticut, 6th biennial report, 318.
- Florida, 6th annual report, 681.
- Illinois, bulletin No. 24, 682; No.
- 28, 482, 607. Iowa, 132, 320. New Jersey, 132.

- Pennsylvania, report No. 9, 318;
- No. 10, 131 ; biennial report, 682.

South Africa, 683.

- South Dakota, 608
- United States, 35th annual report, 316; publications, 316.
- Vermont, 608.

West Virginia, 607.

Wisconsin, 132.

Geology, Problems of American, Rice, Adams, et al., 605.

### GEOLOGY.

- Algæ, reef of calcareous, Wyoming, Blackwelder, 646.
- Algonkian Algal Flora, Walcott, 221.
- Amphibian, from Coal Measures, Moodie, 509.
- Beatricea-like organism from Middle Ordovician, Raymond, 323.
- Brachiopoda of Mississippi Valley Basin, Weller, 129.
- Carboniferous Producti, British, Thomas, 130.
- Coleoptera, new Miocene, from Florissant, Wickham, 323. Cordillera, North American, geol-ogy, Daly, 681.
- Currents, bottom, in Lake Ontario, Kindle, 192.
- Debris, transportation by running water, Gilbert, 128.
- Equus scotti, etc., Troxell, 613. Eurypterid, new Ordovician, Shuler, 551.
- Fauna, fossil, of Conemaugh rocks, Price, 322.
- Faunas, Anticosti, Twenhofel, 130.
- Tertiary of Yorktown and Duplin Formations, Gardner, 305,
- invertebrate, Triassic marine Smith, 323.
- "Fern Ledges," New Brunswick, Stopes. 219.
- Flora, Carboniferous, of St. John, N. B., Stopes. 219.
- Algonkian Algal, Walcott, 221. Fossil Birds in the Marsh Collec-
- tion, Yale Univ., Shufeldt, 683.

- Glacial geology of Catskill Mts. Rich, 137.
- Gravels, fluviatile and marine, Gregory, 487.
- Limestone solution on the bottom of Lake Ontario, Kindle, 651.
- Mastodon, new, Barbour, 87. Mosasaur, new, from the Ft. Pierre, Loomis, 555.
- Mylodon harlani from Texas, Dill, 327.
- Permian reptiles, new genera, Williston, 575.
- Plant tissue, Carboniferous, Barbour, 173.
- Pleistocene sloth from Rock Creek, Texas, Lull, 327.
- Mammals of Iowa, Hay, 320.
- Rugosa corals, structure, Brown, 535.
- Tertiary faunas, Yorktown and Duplin Formations, Gardner, 305. Tetrabelodon lulli, Barbour, 87.
- Tietea singularis, Derby, 251.
- Vertebrate fossils of Texas, Lull, 327; Troxell, 613.
- Zapodilla, Eocene ancestor, Berry, 208.
- Geometry of Four Dimensions, Man-ning, 127.
- Geophysical Laboratory, thermal investigations of minerals, Rankin and Wright, 1; Bowen, 175; Andersen, 407.
- Gilbert, G. K., transportation of debris by running water, 128.
- Glaciers, periodic variations, 608.
- Goddard, H. H., Feeblemindedness, 229.
- Goldman, M. I., origin of Catahoula sandstone of Texas, 261.
- Gray, F. W., Physical Chemistry, 677.
- Gregory, H. E., shape of pebbles, 300; fluviatile and marine gravels, 487.

Η

Hancock's Applied Mechanics 680.

Hart, R. N., Leavening Agents, 685. Hawkins, A. C., datolite from New

Jersey, 473. Hay, O. P., Pleistocene Mammals of Iowa, 320. Heape, W., Embryology, 485. Hegner, R. W., Germ-cell Cycle in

- Animals, 324.
- Helium, absorption, Paschen, 123.
- Hydrogen and nitrogen, liquid, properties, Augustin, 603.

Ichikawa, S., etched figures of Japanese quartz, 455.

- Iddings, J. P., Volcanism, 318. Illinois geol. survey, 482, 607, 682. India, Board of Scientific Advice, report, 685.
- Infection and Resistance, Zinsser, 325.

Ions, mobilities in air, Wellisch, 583. Iowa geol. survey, 132.

- Pleistocene mammals, Hay, 320.

I

Jaggar, T. A., Jr., 1914 outbreak of Mauna Loa, 167.

Jamieson, G. S., determination of polythionic acids, 639.

### K

Kansas, Brenham meteorites, 609.

- Klndle, E. M., bottom currents in Lake Ontario, 192; limestone solution on the bottom of Lake Ontario, 651.
- Kraus, E. H., datolite, Great Notch, New Jersey, 642.

### L

Lake Ontario, bottom currents. Kindle, 192.

- limestone solution, Kindle, 651.

Leavening Agents, Hart, 685.

Levy, S. I., Rare Earths, 312.

Lewkowitsch, J., Chemical nology, 122, 215. Tech-

Library of Congress, 485.

Lloyd, S. J., radium content of Gulf of Mexico water, 580.

Logik, Arithmetik, etc., König, 486. Loomis, F. B., new Mosasaur from the Ft. Pierre, 555.
 Lull, R. S., Pleistocene ground sloth

from Rock Creek, Texas, 327.

#### M

MacDougal, D. T., the Salton Sea, 231.

- MacKenzie, J. D., primary analeite in Crowsnest volcanics, 222, 571.
- McNutt, B., Electricity and Magnet-ism, 314, 480.

Manning, H. P., Geometry, 127. Martin, E. A., Dew-Ponds, 683. Martin, L., Physiography, 132.

Mauna Loa, 1914 outbreak, Jaggar, 167.

- Mechanics, Applied, Hancock and Riggs, 680.
- Meteor Crater, Arizona, Barringer, 482.
- Meteorite, iron, from Sams Valley, Oregon, Foote, 80. eteorites of Brenham,
- Meteorites Kansas. Davis, 609.

iron, new, Farrington, 483.

Microscopy, Chemical, Chamot. 679. Milk, freezing point, 122. Mineralogie, Neues Jahrbuch, Fest-

schrift, 483.

Minerals, Useful, 133, 134.

### MINERALS.

- Amethysts, Egypt, 483. Analeite, Alberta, 222, 571. Anorthite, 416. Clinoenstatite, 418. Connellite, 670.
- Cristobalite, 417.
- Datolite, New Jersey, 473, 642.

- Empressite, Colorado, 223. Footeite, 670. Forsterite, 178, 416.
- Lawsonite, Cal., 105.

Olivine, 176.

- Pyroxene, 177.
- Quartz, Japanese, etched figures, 455.
- Spinel, 420.
- Jersey, 154. Tridy-Thaumasite, New Thorite, Ceylon, mite, 182, 417.
- Vanadic acid, supposed, 404.
- Mines, U. S. Bureau of, 224.
- Mining World Index, 685.
- Minnesota soils, radio-active, Sanderson. 391.
- Minnig, H. D., separation of aluminium, 197
- Mixter, W. G., unstable chromium sesquioxide, etc., 295. Molecular Association, Turner, 678. Moodie, R. L., Coal Measures Am-

phibian, 509.

#### N

Nahrungsmittelchemie, Kerp, 684. New Jersey geol. survey, 132.

- Nipher, F. E., Electricity and Magnetism, 219.
- Nutting, C. C., American Hydroids, 634.

#### 0

Oberhelman, G. O., estimation of vanadium, 530.

- Adams, W. G., 686. Amagat, E. H., 686. Auwers, G. F. J. A., 486.
- Bessey, C. E., 486. Borgmann, J., 230. Brackett, C. F., 326.
  Cooke, M. C., 230.
  Dunér, N. C., 230. Dyche, L. L.,
- 486.
- Fraas, E., 686.
- Geikie, J., 486.
- Harding, J. S., 326. Hittorf, J. W., 230. Hubrecht, A. A. W., 612
- Lea, A. S., 612. Lydekker, R., 612.
- Minot, C. S., 230. Muir, J., 230. Nares, Sir George, 326.
- Peale, A. C., 230. W., 326. Phillips, A.
- Rudler, F. W., 326.
- Sharp, B., 326. Smith, S., 685.

#### P

- Palaeontologische Zeitschrift, 131.
- Pebbles, shape of, Gregory, 300.
- Pennsylvania geol. survey, 131, 318, 682.
- Petrographic classification, Cross, 657.
- Physical Tables, Smithsonian. Fowle, 219.
- Physics, General, Culler, 315.
- Molecular, Crowther, 314
- Physiography, College, Tarr and Martin, 132.
- Poisons, Detection, Autenrieth, 612.

#### R

- Radio-active content of Minnesota soils, Sanderson, 391.
- Radium content of Gulf of Mexico water, Lloyd, 580.
- Rankin, G. A., ternary system CaO-
- Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, 1. **Rich, J. L.**, physiography and glacial geology of Catskill Mts., 137.

#### ROCKS.

- Basalt, extrusive in Virginia Cambrian, Watson and Cline, 665. Blairmorite, 222.
- Catahoula sandstone of Texas, origin, Goldman, 261.
- Igneous, of the Adirondacks, age, Cushing, 288.
- Monte Ferru, trachyte, basalt, etc., Washington, 513.

Petrographic classification, Cross, 657

- Petrography, Sardinian, Washington, 513.
- Petrology of the Orijärvi region, Finland, Eskola, 221.
- Volcanics, Crowsnest, MacKenzie, 222.
- Roentgen ray, use in Paleontology, Field, 543.
- Rogers, A. F., lawsonite, Cal., 105.

#### S

- Salton Sea, MacDougal, 231. Sanderson, J. C., radio-active content of Minnesota soils, 391.
- Sardinia, rocks of Monte Ferru,
- Washington, 513.
  Schaller, W. T., supposed vanadic acid, L. Superior, 404.
  Shimer, H. W., Study of Fossils, 2000
- 322.
- Shufeldt, Marsh collection of fossil birds, 683.
- W., Shuler, E. new Ordovician Eurypterid, 551.
- Silicate liquids, crystallization and differentiation, Bowen, 175.
- Silliman Lectures, Yale University,
- Iddings, 318; Rice, et al., 605. Smith, A. W., Electrical Measure-ments, 127.
- Smithsonian Institution, report of Board of Regents, 228; annual report of secretary, 227. - Physical Tables, Fowle, 219.
- Solar constant, Very, 201.
- South Africa geol. survey, 683.
- South Dakota geol. survey, 608.
- Spectra of the elements, high fre-
- quency, Malmer, 215. Spectrum, new type of band series. 604.
- Stanley, R., Wireless Telegraphy, 126.
- Stopes, M. C., Carboniferous Flora of St. John, N. B., 219.
- Strips, twisted, bifilar property, Buckley, 216.

#### т

- Tarr, R. S., College Physiography, 132.
- Ternary system, CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Rankin, 1; optical study, Wright, 1; see also Andersen, 407.
- Texas, Catahoula sandstone of, Gold-
- man, 261.
- fossils, Lull, - Vertebrate 327:Troxell, 613.

OBITUARY.

#### INDEX.

- Tidal analysis, simple apparatus for, Brown, 386. Troxell, E. L., Vertebrate fossils of
- Rock Creek, Texas, 613.

## U

United States Coast Survey, 486. - geol. survey, 35th annual report, 316 ; publications, 316.

## v

Vanderbilt, S. B., Food Industries, 136.

Vermont geol. survey, 608.

Verrill, A. E., Starfishes of the West Indies, etc., 684.

Very, F. W., solar constant, 201. Vision, intermittent, Thompson, 124. Volcanism, Iddings, 318.

#### w

Walcott, C. D., Pre-Cambrian Algonkian Algal Flora, 221.

- Warburton, G. H., Chemical Tech-nology, 122, 215. Wardall, R. A., Study of Foods. 136. Washington, H. S., rocks of Monte Ferru, Sardinia, 518.
- Watson, T. L., extrusive basalt of Cambrian of Virginia, 665.

Weller, S., Brachiopoda of Missis-sippi Valley Basin, 129.

- Wellisch, E. M., mobilities of ions
- West Virginia geol. survey, 607.
  White, E. N., Study of Foods, 136.
  Williams, H. E., Chemistry of Cyan-ogen Compounds, 476.
  Williams, W. Dermiser rentiles

Williston, S. W., Permian reptiles, 575.

Wireless Telegraphy, Stanley, 126.

Wisconsin geol. survey, 132. Wright, F. E., optical study of the ternary system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, 1.

#### х

X-Rays and Crystal Structure, Bragg, 678.

— in paleontology, Field, 543.

#### Z

Zinsser, H., Infection and Resistance, 325.

## ZOOLOGY.

Animals, Germ-cell Cycle, Hegner, 324.

British Museum Catalogues, 325.

Hydroids, American, Nutting, 684.

Insects, Injurious, Herrick, 323. Starfishes of the West Indies, etc., Verrill, 684.

See also GEOLOGY.

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tive Osteology. J-94. Casts of Reptiles, etc. Microscope Slides: J-135. Bacteria Slides. Taxidermy: J-138. Bird Skins. J-139. Mammal Human Anatomy: J-16. Skeletons and Models. General: J-100. List of Catalogues and Circulars. Mammal Skins.

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## CONTENTS.

Celation

ART. XLIII.—Vertebrate Fossils of Rock Creek, Texas; by	
E. L. TROXELL. (With Plate IX).	613
XLIV.—Volumetric Determination of Polythionic Acids by	
Potassium Iodate; by G. S. JAMIESON	639
XLVDatolite from Great Notch. New Jersev: by C. W.	
Cook and E. H. KRAUS	642
XLVL—Fully Exposed Reef of Calcareous Algæ(?) in the	
Middle Cambrian of the Teton Mountains ; by E	
BLACKWELDER	646
XLVII — Limestone Solution on the Bottom of Lake Ontario:	010
by F. M. KINDLE	651
XLVIII - Cortain Points in Potrographic Classification: hy	001
W Chose	657
VIIV Separation of Magnacium from Lithium by Magna	007
AIAA.—Separation of Magnesium from Entitum by Means	
O Devenue of Ammonium Carbonate in Alcoholic Solution; by J.	0.20
G. DINWIDDIE	662
LExtrusive Basalt of Cambrian Age in the Blue Ridge of	
Virginia; by T. L. WATSON and J. H. CLINE	665
L1.—Identity of Footeite with Connellite together with the	
Description of two new Occurrences of the Mineral; by	
W. E. FORD and W. M. BRADLEY	670

## SCIENTIFIC INTELLIGENCE.

Chemistry and Physics—Fixation of Atmospheric Nitrogen, W. S. LANDIS, 676.—Electroplating with Cobalt, H. T. KALMUS, C. H. HARPER, and W. L. SAVELL: Use of Mercuric Oxide for Standardizing Volumetric Solutions, M. A. ABELMANN: Manual of Practical Physical Chemistry, F. W. GRAY, 677.—Practical Physical Chemistry, A. FINDLAY: Molecular Association, W. E. S. TURNER: X-Rays and Crystal Structure, W. H. and W. L. BRAGG, 678.—Elementary Chemical Microscopy, E. M. CHAMOT, 679.— Hancock's Applied Mechanics for Engineers, N. C. RIGGS: Electricity for the Farm, F. I. ANDERSON, 680.

- Geology-Geology of the North American Cordillera at the Forty-ninth Parallel, R. A. DALY: Florida State Geological Survey, E. H. SELLARDS, 681.—Biennial Report of Topographic and Geologic Survey of Pennsylvania for the two years ending June 1, 1914: Geological Survey of Illinois, J. A. UDDEN: Publikationer fra det Danske Meteorologiske Institut, C. RYDER, 632. – Dew-Ponds; History, Observation and Experiment, E. A. MARTIN; Union of South Africa, Department of Mines and Industries: Fossil Birds in the Marsh Collection, C. W. SHUFELDT, 683.
- Miscellaneous Scientific Intelligence—Report on the Starfishes of the West Indies, Florida, and Brazil, etc., A. E. VERRILL, 684.—American Hydroids, Part III; The Campanularidæ and the Bonneviellidæ, C. C. NUTING: Nahrungsmittelchemie in Vorträgen, W. KERP, 684.—Leavening Agents, N. HART: Mining World Index, Vol. VI: Museum of the Brooklyn Institute of Arts and Sciences: Report of Board of Scientific Advice for India, 1913– 1914, 685.

313

Obituary-S. SMITH, 685.-W. G. ADAMS: E. FRAAS: E.-H. AMAGAT, 686. INDEX, 687.

.









