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JOURNAL OF SCIENCE.

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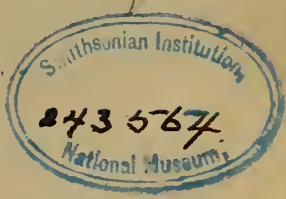
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T H E

# AMERICAN JOURNAL OF SCIENCE

[ F O U R T H S E R I E S . ]

ART. I.—*The Problem of the Cretaceous-Tertiary Boundary in South America and the Stratigraphic Position of the San Jorge-Formation in Patagonia*; by A. WINDHAUSEN, Buenos Aires.

## CONTENTS.

- Introduction: The Cretaceous-Tertiary problem in North and South America.
- Part I: Origin and history of Patagonian molluscan faunæ. Antarctica as a center of evolution for marine and terrestrial faunæ during the Cretaceous and Tertiary. The question of age, stratigraphic position and general faunistic character of the San Jorge-Formation.
- Part II: Stratigraphy of the San Jorge-Formation. Stratigraphic limits. Critical review of the exposures and sections in geographical order from north to south. The strata at the bottom and top of the marine San Jorge: Dinosaur-bearing Pehuenche Beds and the sediments with the ancient Patagonian mammal-fauna, the *Notostylops*, *Astraponotus* and *Pyrotherium* Beds (Casamayor and Deseado).
- Part III: Paleogeography of the San Jorge-Formation. Reconstruction of the shore-lines of the San Jorge-Sea. The great depression between the ancient Patagonian continental platform and the structural elements of Central and Northern Argentina. Characteristic features of sedimentation.
- Part IV: Paleontology of the San Jorge-Formation. Critical examination of the faunistic characters. The transgression of the San Jorge-Sea as a forerunner of the Patagonian Formation. Age of the San Jorge and position of Pehuenche and mammal-bearing horizons.
- Conclusions.
- Appendix: Table of the invertebrates found in the San Jorge at different localities.

## INTRODUCTION.

Critical treatment of the problem of the Cretaceous-Tertiary boundary has not yet led to conformity of opinions. It was, however, a necessary prelude to sum-

marize the stratigraphic and paleontologic evidence bearing on this important question, as has been done in the Bulletin of the Geological Society of America.<sup>1</sup>

The same difficulty in determining the general relations between the Cretaceous and Tertiary is encountered in three remote localities of the great American Continent. In California, in Chile and in Patagonia there has been said to exist a mixture of faunas at this critical boundary; but in all these localities there is obvious evidence of unconformity and a stratigraphic and paleontologic break closing Cretaceous time. On the other hand, the stratigraphy of the marine sediments covering the border of the Brazilian Shield over a large tract between the mouth of the Amazon River and Sergipe, is not yet entirely clear. The fauna of Pirabas (Pará) is said to contain both Cretaceous and Tertiary elements;<sup>2</sup> but according to J. C. Branner the oil-bearing shales with diatoms and the freshwater-deposits in the Bahia basin and more northward, may be considered as of Eocene age.<sup>3</sup> In a similar way, Hill<sup>4</sup> described from the Antilles sediments with *Rudistæ* and *Actæonella*, associated according to him with typical fossils of the Eocene. In such cases, where marine Paleocene or Eocene rests upon marine Cretaceous, it may be justifiable to infer the existence of a gradual transition from Cretaceous to Tertiary. In the Eastern Sahara and in Central Tunesia, where during this critical period the sea always maintained a constant depth, marine Eocene can be observed lying without hiatus upon marine Cretaceous; but in this case the appearance of nummulites may be considered as a conventional sign for the necessity of stratigraphic division.

In other cases, where the negative phase which followed the close of the Senonian Epoch, or its equivalents, was manifested by oscillatory movements, an obvious break separates the Upper Cretaceous from Tertiary sediments of marine character. The finest example illustrating this phenomenon is found on both borders of

<sup>1</sup> See volume 25, September, 1914.

<sup>2</sup> F. Katzer, Grundzüge der Geologie des unteren Amazonasgebietes (des Staates Pará in Brasilien), pp. 132 etc., Leipzig, 1903.

<sup>3</sup> The oil-bearing shales of the coast of Brazil. A paper read before the Am. Inst. of Mining Engineers, Canadian Meeting, August 1900, Author's edition.

<sup>4</sup> The geology and physical geography of Jamaica, Bull. Mus. Comp. Zool., Harvard College, vol. 34, 1899.

Laurentia, where recent results indicate a clear separation of Cretaceous and Tertiary sediments and their faunas, both in California to the westward of the Sierra Nevada and Cascade-Range, as well as in the region of the Atlantic and Gulf Coastal Plain. But in carrying on this study in the interior provinces of the ancient continental masses, along the borders of the epicontinental Laramie-Sea or in the region of the Patagonian mesetas, extraordinary difficulties are met with on account of the participation of terrestrial faunas. The abundance of facies, the changing and interwedging of terrestrial, lacustrine, brackish, littoral and marine sediments, the migrations of animals and plants, the movements of faunas and floras, afford a spectacle of kaleidoscopic variety. Thus, this period may be characterized as a phase of transformations and alterations, of destruction of the past and preparing of a new order of organic and inorganic life. The very complicated problem of correlating the manifold interior formations with the marginal events and the general geological time table, could not be displayed better than by the symposium of the Geological Society of America.

In South America, Steinmann was the first to point out the existence of an hiatus between Cretaceous and Tertiary sediments. In Chile he determined the Senonian age of the ammonite and baculite-bearing beds of the Quiriquina Isle, and proved the strata of the Navidad Beds (Piso de Navidad) to be the most ancient marine deposits of that country (Upper Oligocene or Miocene).<sup>5</sup> Between these two groups of marine sediments a wide hiatus corresponds to a long continental period with heavy denudation. Recently Brüggén, with special reference to the fauna of Algarrobo (near Valparaiso), has dispelled the last doubts about the existence of this unconformity.<sup>6</sup>

In Patagonia the interpretation of the analogous phenomena is also beset by many difficulties, and both the stratigraphic and paleontologic research require revision.

In the southern part of Patagonia, Steinmann<sup>7</sup> in 1883

<sup>5</sup> Steinmann, Deecke und Möricke, Das Alter und die Fauna der Quiriquina-Schichten in Chile, N. Jahrb. Min., Beil.-Bd., 10, 1896.—Möricke und Steinmann, Die Tertiärbildungen des nördlichen Chile und ihre Fauna, *ibid.*, Beil.-Bd., 10, 1896.

<sup>6</sup> El Cretaceo del Algarrobo i las supuestas relaciones entre las formaciones cretacea i terciaria de Chile. Santiago-Valparaiso, 1915.

<sup>7</sup> Reisenotizen aus Patagonien, N. Jahrb. Min., 2, 255, 1883.

pointed out the fact that an obvious hiatus separates the folded, bended and metamorphosed sediments (the so-called "clayslate-formation" of Darwin<sup>8</sup>) in the interior of the Patagonian Cordillera from the Tertiary Formations in the zone of the mesetas (tableland). Having found fossils at various localities, Steinmann assumed that the folded and metamorphosed sediments are partly of Early and Middle Cretaceous and partly of Upper Cretaceous age. By the term "Patagonian Tertiary" was meant chiefly the marine deposits of the so-called "Patagonian Formation" or "Patagonian Beds" (later called by Wilckens also "Patagonian Molasse") which are an equivalent of the Navidad Beds in Chile and have been correlated by Ortmann with the Lower Miocene on the basis of collections made by the Princeton University Expedition to Patagonia.<sup>9</sup>

In contrast to Steinmann, Hauthal<sup>10</sup> and Ameghino<sup>11</sup> emphatically defended the idea of a gradual transition from Cretaceous to Tertiary in Patagonia, Hauthal from a stratigraphic and Ameghino from a paleontological point of view. Going back to the observations of Steinmann, Wilckens proved the improbability of these opinions and made a summary of Patagonian stratigraphy, which will always remain a standard work.<sup>12</sup> Starting from the same point of view as Hauthal and Ameghino, H. v. Ihering<sup>13</sup> assigned an Eocene age to the Patagonian Formation and opposed the determination of age given by Ortmann.

This position of H. v. Ihering was maintainable as long as no other invertebrate fauna of Early Tertiary age was known from the Patagonian mesetas. The marine molluscan fauna of Roca in the Rio Negro, discovered by

<sup>8</sup> Geological Observations on Coral Reefs, Volcanic Islands and on South America, being the Geology of the Voyage of the Beagle, etc., pp. 140, etc., London, 1851.

<sup>9</sup> Reports of the Princeton University Expeditions to Patagonia, 1896-1899. Volume 4, 1902.

<sup>10</sup> Über patagonisches Tertiär, etc., Zeitschr. deutsch. Geol. Gesellsch., 50, pp. 436-440, Berlin, 1898.

<sup>11</sup> L'âge des formations sédimentaires de Patagonie, Anales Sociedad Científica Argentina, vols. 50-54, Buenos Aires, 1903.—Les formations sédimentaires du Crétacé Supérieure et du Tertiaire de Patagonie, Anales Museo Nacional de Buenos Aires, (3), vol. 8, 1906.

<sup>12</sup> Die Meeresablagerungen der Kreide- und Tertiärfornation in Patagonien, N. Jahrb. Min., Beil.-Bd., 21, 1905.

<sup>13</sup> Les mollusques fossiles du Tertiaire et du Crétacé Supérieur de l'Argentine, Anales Museo Nacional de Buenos Aires, 7, 1907.

Roth<sup>14</sup> in 1896, and described for the first time by Burckhardt,<sup>15</sup> was supposed to be of Upper Cretaceous age and was even placed in the Cenomanian by Ameghino. Roth believed that this fauna had only a local character and considered the corresponding sediments as marine intercalations in the "Areniscas Abigarradas," sandstones of continental origin, representing in large parts of Patagonia the negative phase of the Upper Cretaceous. The mistaken assertion that ammonites were present in these sediments (Ameghino) appeared for a long time as another proof of a Cretaceous age. It is true that Wilckens rightly perceived the connection of the Roca Beds (Piso Rocanense, Rocaneano) of the Rio Negro valley with the equivalent formations of Southern Patagonia (Salamanqueano, Sehueneano) and classified all these formations under the general name of his "San Jorge-Formation," but adhered, just as did v. Ihering, to an Upper Cretaceous age of this fauna.<sup>16</sup>

On the basis of a series of observations in the field, the author of this paper showed in 1912-14 that the sediments of the Roca Beds must be regarded as deposits of a widespread transgression covering the Upper Cretaceous sandstones (Areniscas Abigarradas) over large areas of Patagonia.<sup>17</sup> In the light of these new observations the Roca Beds cannot be regarded as mere transitory intercalations in these sandstones, but are rather the witness of the first transgression which, coming from the Atlantic side, spread over the Patagonian Continent, remnant of the older Brazilo-Ethiopian Continent of Mesozoic times. In the sense of the theory of Haug, the folding of the great Andine geosyncline at the western border of this old continent was coördinated with the sinking and breaking down of the corresponding continental area in

<sup>14</sup> Apuntes sobre la geología y paleontología de los Territorios del Rio Negro y Neuquén, Revista del Museo de La Plata, 9, pp. 141 etc., 1899.

<sup>15</sup> Le gisement supracrétacique de Roca, Revista del Museo de La Plata, 10, pp. 207 etc., 1902.

<sup>16</sup> v. Ihering, however, partly admitted the possibility of correlating the San Jorge with the lowest part of the Tertiary, and Wilckens in conversation during the last years was inclined to revise its earlier published views.

<sup>17</sup> A. Windhausen, El yacimiento de Rafaelita de Auca Mahuida, Informes preliminares de la Dirección Gral. de Minas etc., vol. 1, Buenos Aires 1912.—Contribución al conocimiento geológico de los Territorios del Rio Negro y Neuquén etc., Anales del Ministerio de Agricultura, Sección Geología etc., vol. 10, No. 1, Buenos Aires, 1914.—Einige Ergebnisse zweier Reisen in den Territorien Rio Negro und Neuquén, N. Jahrb. Min., Beil.-Bd., 38, 1914.

the west and consequently the formation of the South Atlantic basin. In the same way, it is proven that the claim that ammonites had been found in these beds was utterly unfounded and that these sediments cannot be correlated with the ammonite- and baculite-bearing Senonian sediments of Southern Patagonia (Lago Argentino, Ultima Esperanza etc.).

Further collections and studies of the sediments of the Roca-Salamanqueano or San Jorge-Formation have convinced me that this fauna is to be regarded as the hitherto missing one of the Early Tertiary of the Patagonian and South Atlantic region and that in it we must see the forerunner of the Patagonian Formation. But the interest offered by this fauna does not end with these facts. In contrast with Chile, where a long denudation period covers the whole time between the Senonian of Quiriquina and the Navidad Beds, we find in Patagonia not only in evidence an Early Tertiary marine fauna, but also a series of continental deposits with terrestrial faunas at the bottom and top of these marine sediments. Thus, the study of the San Jorge is connected with the problem of the stratigraphic position and age of the dinosaur-bearing horizons and the oldest mammal-bearing sediments of Patagonia. Furthermore, our present knowledge of this subject will enable us to attempt to reconstruct the limits of the San Jorge-Formation, and connectedly to study a number of general geologic and paleontologic questions of great importance for this part of South America. The San Jorge-Formation and its faunistic, stratigraphic, diastrophic and paleogeographic conditions are a cardinal point in the problem of the Cretaceous-Tertiary boundary in Patagonia. Moreover, a parallelism of geologic history in the north and south of the American Continent is indicated by the terrestrial faunas of this period. In both cases the appearance of placental mammals bears the same relation to the marine sediments. Just as on the Laurentian Continent, on the borders of the retreating Laramie-Sea, so in Argentina, an analogous association of animals can be seen on the borders of the overlapping and invading epicontinental San Jorge-Sea. In both cases, the diastrophic events of special significance are in direct relation to these phenomena: in the north there is the great Laramide-revolution, and in the south the orogenetic movements in the

Andine geosyncline with the formation of the South Atlantic basin.

PART I.—*Origin and history of Patagonian Molluscan Faunas.*

In contrast with the northern hemisphere, where the negative phase of the Wealden can be observed from the Vistula River to Dakota,<sup>18</sup> the period which corresponds to the Jurassic-Cretaceous boundary and a great part of the Lower Cretaceous signifies in the southern hemisphere one of the culminating points of marine faunistic development; for in the creation of a South Andine province not only Mediterraneo-European, Central Asiatic and Boreal faunal elements were associated, but there was a further evolution of independent and characteristic elements in this local biologic center.<sup>19</sup>

The Upper Jurassic and Lower Cretaceous types of the South Andine faunas are spread over a wide area from Texas and Mexico to the extreme south, passing the Equator and into southern latitudes with rare uniformity. They occur on the western border of the ancient Brazilo-Ethiopian Continent, showing little or no visible dependence on either latitude or climate. Uhlig pointed out the probability that the center of evolution of this South Andine fauna had to be looked for south of the Brazilo-Ethiopian Continent, in the vicinity of the Antarctic, and he assumed that future investigators with a better knowledge of physical and biological conditions in this province would characterize its fauna as an "Austral Fauna."

On the basis of Favre's<sup>20</sup> publication, we may suppose that within the area of this province (the Chile-Pata-

<sup>18</sup> E. Suess, *Antlitz der Erde*, III 2, p. 91, Leipzig and Vienna, 1909.—See also the symposium held by the Geological Society of America with remarks on this matter by Osborn, Lee, Mook, Lull, Berry and Stanton, *Bulletin of the Society*, vol. 26, Sept., 1915.

<sup>19</sup> As such characteristic elements of the South Andine province may be regarded for instance: *Steuerocheras* Cossm. (= *Odontocheras* Steuer) or *Hatchericheras* Stanton. See the remarks of Uhlig on the South Andine elements in his two publications: *Fauna der Spiti-Schiefer des Himalaya, ihr geologisches Alter und ihre Weltstellung*. *Denkschriften d. Akad. der Wissensch., Wien, Math.-Nat. Klasse*, vol. 85, pp. 597 etc., 1910.—*Die marinen Reiche des Jura und der Unterkreide*, *Mitt. Geol. Gesellsch., Wien*, 4, pp. 423 etc., 1911.

<sup>20</sup> *Die Ammoniten der unteren Kreide Patagoniens*, *N. Jahrb. Min., Beil.-Bd.*, 25, 1908.—See also T. W. Stanton, *The marine Cretaceous invertebrates*, *Reports of the Princeton University Expeditions to Patagonia*, 1896-1899, vol. 4, 1901.

gonian Andine zone) the marine faunistic development closed in the Barremian with the *Crioceras* of the Lago Chacabuco and Rio Caracoles, giving way to a negative phase which is represented in Patagonia by the Variegated Sandstones of the Upper Cretaceous ("Areniscas Abigarradas"); while in the northern hemisphere the invasion of the Gault-Sea and, in a larger degree, the Cenomanian transgression indicated a positive phase.<sup>21</sup> During this epoch was prepared the home of the Patagonian terrestrial faunas, while this continent was yet a part of the Brazilo-Ethiopian (Gondwana) Continent. A little later, in North America, the brackish Laramie-Sea began to take on the character of an inland sea of the Laurentian Continent, and the latter became not only one of the four great "asylums" in the sense of E. Suess,<sup>22</sup> but also the oldest known home of placental mammals.

Passing over the periphery of the Cenomanian transgression, the Senonian Sea with rare uniformity invaded parts of the northern as well as of the southern hemisphere. The world there experienced a positive movement of universal character. From Greenland (Disko Island) in the north, the Aral Sea in the east, and from the Pacific (California) and Atlantic borders (Maryland, New Jersey) of Laurentia, crossing the Mediterranean region (Mexico, Antilles) and Brazil (Pirabas, Sergipe), this positive movement of the Senonian extended to the Chile-Patagonian region (Quiriquina, Lago Argentino, Fireland) and even far to the extreme Antarctic south. From the latter region the meritorious *Swedish Antarctic Expedition* (1901-1903) has brought an abundance of marine faunas, in no way inferior to the South Andine fauna of the Tithonic and Lower Cretaceous. Thus, for the second time in the course of earth history, Antarctica became a center of independent, rich and singular marine life; but of course under climatic conditions quite different from the present ones. There are well-founded reasons for the belief that the sediments at the bottom of the present Antarctic Sea, or parts of the Antarctic Continent cover numerous intermediate stages of a very interesting marine life development, which will likely be cleared up

<sup>21</sup> This transgression reaches in the south the Columbian and Peruvian coasts.

<sup>22</sup> *Antlitz der Erde*, III 2, pp. 760 etc.



by future exploration. Concerning the evolution of South American terrestrial faunæ, H. v. Ihering<sup>23</sup> has the merit of having emphasized the great importance of "Archinotis," the sunken Antarctic Continent of the past. The idea of Gaudry,<sup>24</sup> that the manifold Patagonian faunas required for their evolution a much larger area than that existing at the present time, thus finds a certain validity. In the same way, Ameghino claimed a greater Patagonia of the past. The known part of the homes of the fossil Patagonian faunas does not have the features of an "asylum" in the sense of Suess. As in the case of New Mexico, where occur the placental mammals of Laurentian correlation, Patagonia is only the border of an old continent of the past. Antarctica thus reveals itself during Cretaceous and Tertiary time as an important center for the evolution of the terrestrial as well as the marine faunæ of Patagonia.

Towards the close of the Cretaceous, perhaps when the Senonian Sea still partly covered the southern margin of the old Brazilo-Ethiopian Continent,<sup>25</sup> this continental area experienced one of the greatest diastrophic events of its history; on its western border, in the zone of the Andine geosyncline took place the first phase of orogenic movements characterized by lateral pressure.<sup>26</sup> Thus ended the series of marine Jurassic and Cretaceous transgressions from the west side and thus were initiated the events leading to the present geologic structure. The breaking down of large parts of the old continent and the consequent formation of the South Atlantic basin may be primarily regarded as the result of this phenomenon, which opened the way for a series of marine transgressions from the Atlantic side, and in great part determined the geologic and physiographic character of the present Patagonia, outside the Cordillera.

These transgressions of Tertiary time stretched over an ancient basement, the structural and genetic knowledge of which has not reached the settled stage. With regard

<sup>23</sup> Archhelenis und Archinotis, Leipzig, 1907.

<sup>24</sup>Étude sur une portion du Monde Antaretique, Annales de Paléontologie 1, fasc. 3, 1906. (Cited according to E. Suess, Antlitz der Erde, III 2, p. 772.)

<sup>25</sup>Hauthal, Wilckens und Paulcke, Die Obere Kreide Südpatagoniens und ihre Fauna, Berichte Nat. Gesellsch. Freiburg i. Br., 15, 1907.

<sup>26</sup>H. Keidel, Die neueren Ergebnisse der staatlichen geologischen Untersuchungen in Argentinien, Comptes rendu du XI-ème Congrès Géol. Internationale, p. 1137, Stockholm, 1910.

to such portions of basal structures as for instance the widespread sheets of Patagonian quartz porphyry, investigations justifying any pronouncement as to origin and age are lacking.<sup>27</sup>

At many points, especially in Northern Patagonia, the leveling of the old base line and the sedimentation of the continental Variegated Sandstones of the Upper Cretaceous are the events preceding the main Atlantic transgressions, which on this surface laid down their sediments. In other cases, the extension of the transgressions was obviously dependent on ancient orographic elements of Paleozoic structure (now partly in the underground). The estuary of the La Plata River formed the Neogene gateway of marine invasion. It will be proved in Part III that the northern limit of the San Jorge-Sea was formed by the socle (or floor) of the Sierras of Buenos Aires, further by an old granitic mass in the heart of the Pampa; also that there was renewed activity along the ancient tectonic line between the Precordilleran elements and the mass of Pampine Sierras, forming a large depression, in which brackish sediments were deposited. Furthermore, it is extraordinarily important that the line of the Rio Negro-valley, where the San Jorge-transgression entered by a northern branch, has the character of a tectonic chief line, being the limit of the old mass in the underground of Patagonia.

Obviously, the oldest of these marine transgressions from the Atlantic basin is of special interest, as it marks

<sup>27</sup> It is not the aim of this paper to go into a discussion of character and age of the old root forming the foundation of Cretaceous and Tertiary formations of Patagonia. F. Ameghino (*Les formations sedimentaires*, pp. 35 etc., fig. 3) gave in 1906 a sketch of the then known exposures of old rocks in the Patagonian mesetas, and recently R. Wichmann gave for the First Congress of Natural Science in Tucuman (November, 1916) a brief review on the same subject, with special reference to Northern Patagonia. The chief components of this old basement are gneiss, mica schists, phyllites and grauwackes, strongly inclined and folded and with transverse cleavage, showing also intrusions of granitic rocks, frequently accompanied by injections of quartz. Upon the base-leveled surface of these old rocks rest large sheets of quartzporphyry and generally the exposures of the latter are more numerous than those of the older rocks. This basement comes to the light as window-like apertures among the Cretaceous and Tertiary strata. There are reasons for the assumption that faults of a considerable degree cross this ancient platform. Its age is uncertain, but there is a great similarity to the Caledonian or Hercynian structure of the so-called "Pampine Sierras" of Central Argentine. In the map accompanying this paper, the old rocks of the continental platform and the quartzporphyry sheets are comprised under the same symbol, all outcrops being purposely enlarged.

not only the beginning of modern geologic history in this part of South America, but is correlated with vaster diastrophic events. Until now, however, neither the fauna of the Roca Beds in the north nor that of the Salamanca Beds in the south has afforded the data for more closely fixing the age and stratigraphic position of the San Jorge. This formation has thus fluctuated between the Upper Senonian and the Patagonian Formation, the Lower Miocene age of which (determined by Ortmann in 1902) was recently confirmed by the studies of Loomis.<sup>28</sup> Indeed, v. Ihering,<sup>29</sup> in his description of this fauna, doubted the convenience of correlating the San Jorge either with the Upper Cretaceous or with the Lower Tertiary.

In the first paleontologic monograph on the Roca Beds, C. Burekhardt tried to establish faunistic relations with the Danian of the Brazilian coast<sup>30</sup> and North Africa, and also with the Arrialoor Group of India. This interpretation was not accepted by subsequent writers,<sup>31</sup> quite in the degree to which they fail in solving the San Jorge-problem. Thus, we see that this formation with a relatively small and poor fauna has lacked the general paleontologic connection requisite to a more satisfactory establishment of its physical, stratigraphic and biologic conditions. But it seems to me that a better interpretation can now be given to the available facts.

Ortmann<sup>32</sup> can claim the merit of having pointed out as the most striking feature of the fauna of the Patagonian Beds the relationship to the marine invertebrate faunæ of New Zealand and Australia; though the theory of a connection of southern continental masses towards the close of Mesozoic time, or at the beginning of the Tertiary, is in a general form a postulate of several zoogeographic systems, and is closely allied to H. v. Ihering's theory of "Archinotis." Ortmann emphasized the fact that the marine fauna of the Patagonian Beds proves the existence of a vast continental mass,

<sup>28</sup> The Deseado Formation of Patagonia, Amherst, Mass., 1914.

<sup>29</sup> Les mollusques des terrains cretaciques superieures de l'Argentine orientale, *Anales Museo Nacional de Buenos Aires*, (3) 9, pp. 193 etc., 1903.

<sup>30</sup> Ch. A. White, *Contribuções a paleontologia do Brazil*, *Archivos do Museu Nacional do Rio de Janeiro*, vol. 7, 1887.

<sup>31</sup> Apart from various reports of H. v. Ihering, may be mentioned: J. Boehm, *Über Ostreen von General Roca am Rio Negro*, *Zeitschr. Deutsch. Geol. Gesellsch.*, 55, *Protokol.*, p. 71, Berlin, 1903.

<sup>32</sup> Reports of the Princeton Univ. Exped. etc., vol. 4, pp. 310 etc.

connecting South America with Australia, New Zealand and (?) Africa. According to him, this fauna is littoral and migrated along the shelf of a continent, or at least over a shallow sea between large islands of more or less continental character. Hence the surprising resemblance between the Australo-New Zealand and Patagonian molluscan faunas. In connection with this phenomenon attention may be called to the fact that in the Santa Cruz Beds an increasing relationship of the Patagonian terrestrial faunas to that of Australia has been observed, while more and more exchanges of faunas between these provinces are postulated.

On the other hand, a peculiar contrast results from a comparison of the older Patagonian transgressions with the last one, which is represented by the Paraná Formation (Piso Paranaense, Formación de Entre Rios etc.) determined by Borchert<sup>33</sup> as of Pliocene age. Here the fauna is entirely different from that of the Patagonian Formation. It resembles the Upper Tertiary faunæ of Europe and the present molluscan faunas of South America and the Caribbean Sea. The Paraná Formation is in open contrast to the foregoing marine invasions of Patagonia; and thus is afforded an exact proof that diastrophic events of special importance took place in the period between the Patagonian and Paraná-Formation. We may draw the inference that the peculiarity of the fauna of the Patagonian Beds and its Australo-Antarctic origin have been caused by restriction towards the north, by a barrier like the "Archhelenis" of H. v. Ihering, which separated the South Atlantic basin from the northern marine provinces, and made impossible a free circulation of streams and currents between this basin and "Thetys."

Presumably two facts explain the approximate form and location of the barrier in question. First, the older transgressions were in the strict sense of the word limited to Patagonia; and while the old mass in the sole of the Sierras of Buenos Aires formed the northern limit of the corresponding epicontinental seas, the Paraná Formation represents the only transgression that passed over this limit, invading the mouth of the La Plata River and advancing far to the north into the region of the

<sup>33</sup> Die Molluskenfauna und das Alter der Parana-Stufe, N. Jahrb. Min., Beil.-Bd., 14, 1901.

Paraná and Paraguay Rivers. Second, Keidel's discovery of the connections between the Sierras of Buenos Aires and the South African mountains<sup>34</sup> establishes (apart from a stratigraphic analogy concerning the Paleozoic) a connection of the Permian orogenic movements in both parts of the southern hemisphere.

These well-founded observations will, I believe, justify an attempt at reconstruction of this barrier, the "Arch-helenis" in the sense of H. v. Ihering. Evidently, the southern limit of this bridge between South America and Africa coincided approximately with the 38th degree S. L.<sup>35</sup>

Furthermore, the geologic age of the Paraná Formation affords the evidence for fixing those diastrophic events which caused the breaking down of the Afro-American barrier and, consequently, the formation of the Middle Atlantic basin.<sup>36</sup> This occurred approximately at the time of the Miocene-Pliocene boundary. A general study of the Chilean Tertiary confirms such opinion; for the emergence of the Mid-American landbridge (Isthmus of Panama) and the definite closing of the old marine animal route from the South American westcoast to Eurasia, were merely connected events, plainly recorded and attested by many facts.<sup>37</sup> This was the period, when

<sup>34</sup> La geología de las Sierras de la Provincia de Buenos Aires y sus relaciones con las montañas de Sud Africa y los Andes, *Anales Minist. de Agricultura, Secc. Geología*, 11, No. 3, Buenos Aires, 1916.

<sup>35</sup> In a recent paper, W. D. Matthew (*Climate and Evolution, Annals New York Academy of Sciences*, 24, 1915) opposes assumptions of "barriers and bridges," also certain geotectonic hypotheses. It is true that former speculations on migrations of fauna and flora have been very liberal in the construction of such bridges, but those attempts cannot be compared with the present case, in which stratigraphic, geotectonic and paleontologic facts agree perfectly in the assumption of a continental mass lying in the Middle Atlantic regions. Where this sunken continental mass connected with the present South American Continent is clearly indicated by the absence of Early Tertiary sediments over a large tract of the present coast.

<sup>36</sup> These epirogenetic movements seem to have been allied with the orogenic movements which led to the formation of the Sierras of Buenos Aires. According to Keidel, these sierras as orographic elements were formed in the Tertiary, perhaps by large overthrusts coming from the southwest; but it has not been hitherto possible to get a closer determination of age. I believe that the history of Tertiary transgressions may be profitably used for this object. This method would indicate an approximately Upper Miocene age of these movements.

<sup>37</sup> The fauna of the Navidad Beds (Upper Oligocene or Miocene) is of an essentially Atlantic character. The vast Oligocene and Miocene strata of the Peruvian coast are in obvious relation to the Atlantic Ocean and especially to the Caribbean province. Later, in the Coquimbo Beds (Pliocene) the faunistic character changed on the entrance of Indopacific

the final stage in the formation of the Atlantic basin was reached. The great meridional lines of its present forms were here definitely fixed.<sup>38</sup> That the Paraná Formation does not agree in faunistic character with the older transgressions, cannot be surprising; it is an Atlantic formation in every respect.

In the light of these facts, the fauna of the San Jorge loses all strangeness of character. The assumption of Burckhardt that this fauna was more or less similar to that of the Upper Cretaceous strata of the Brazilian coast (Maria Farinha near Pernambuco) was not supported by v. Ihering's studies.<sup>39</sup> It is improbable that a direct connection existed between the San Jorge-transgression and the Brazilian province. Any movement or migration of this period must have followed along the old route of marine wanderings along the westcoast and across the Isthmus of Panama and the region of the Caribbean Sea. Even if greater knowledge and further comparison of faunas should indicate genetic connections with the North African province, the exchange of marine faunas must have taken place along this same route. The assumption of a direct Atlantic connection does not agree with the known facts.

Perhaps future collections of fossils and critical comparisons of the San Jorge will prove a certain preponderance of relationship to the Australian and New

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elements, and a strong similarity is noted with living types of the Pacific fauna. This may be regarded as evidence that the Centro-American landbridge became steady approximately in Miocene time, whereas before there existed a free circulation between the South American westcoast and the Atlantic north of the Equator. Special currents might favor a preponderance of Atlantic elements in the Navidad Beds.—According to Donald F. Macdonald the landbridge of Panama appeared for the first time in the Oligocene; but until the present there has been a change of submergences and upliftings. At all events, it can be proved that, beginning approximately with the close of the Miocene, the existence of a threshold is strongly marked by the above changes of marine faunas on the South American westcoast.

<sup>38</sup> According to De Geer, the continent that occupied the northern portion of the Atlantic was submerged in the Neogene, opening the way for the waters of the Arctic Ocean to the Atlantic basin. It may be, that this phenomenon is parallel and contemporaneous to the alluded occurrences in the Atlantic of the southern hemisphere. See De Geer, *Kontinentale Niveauperänderungen im Norden Europas*, *Compte rendu, Congrès Géologique Internationale*, pp. 849 etc., Stockholm, 1910.

<sup>39</sup> For instance *Cardita morganiana* Rathb. has been cited very frequently as a proof of correlations between the Upper Cretaceous deposits of Brazil and Argentine; but v. Ihering has shown that the *Cardita* of the Roca Beds cannot be compared with the alluded *Cardita morganiana*.

Zealand provinces. But in general, future studies will attach more importance to the independence and peculiarity of the faunistic elements, and these features may be regarded as due to a relatively isolated development in the South Atlantic and Antarctic regions. Thus, for the third time in the course of earth history, Antarctic becomes the center of singular marine life. The apparent poverty of the San Jorge-fauna cannot be adjudged an original and peculiar feature, being rather the consequence of insufficient collections and bad preservation of the fossils. The real wealth of this fauna is very likely buried in the depths of the Antarctic Ocean. In the succession of marine faunas that sprang from this biologic center of the far south, the San Jorge-fauna is as important as the foregoing Lower Cretaceous and Senonian faunæ. It indicates one of the culminating points of marine biologic evolution.

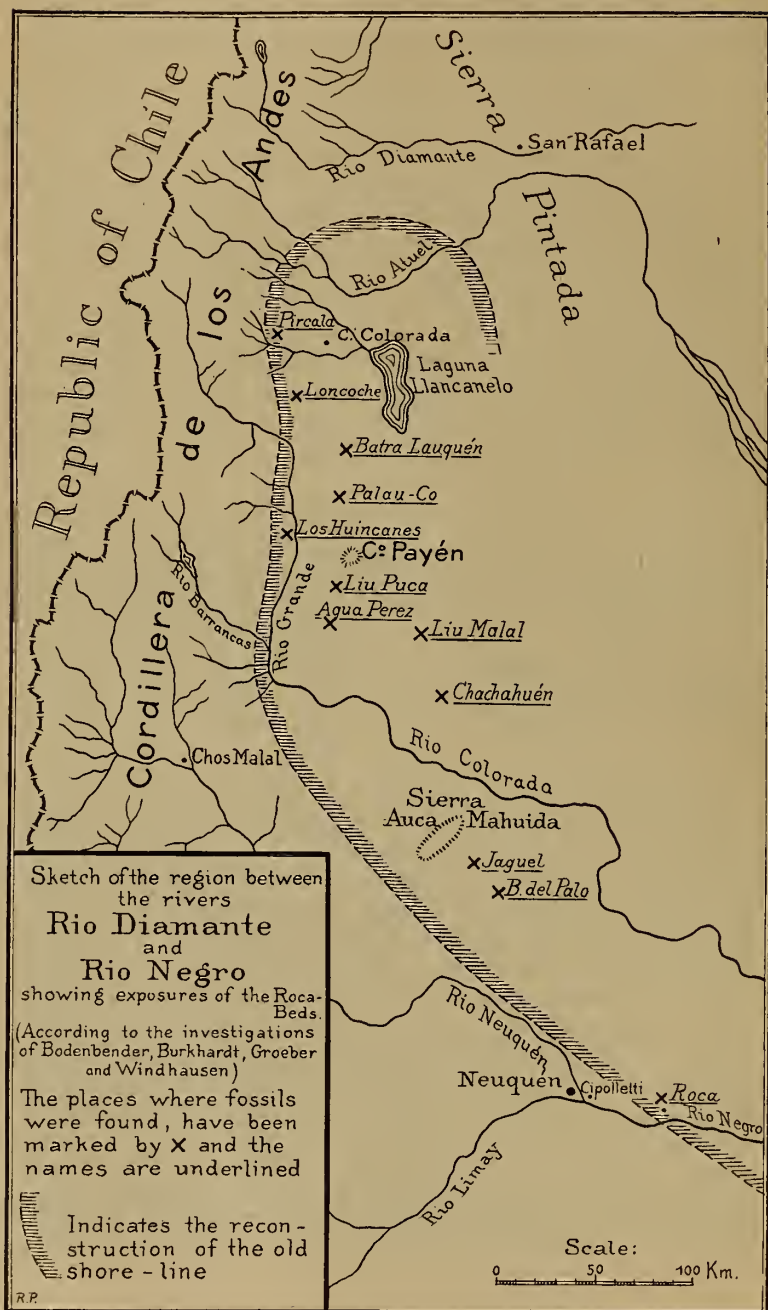
#### PART II.—*Stratigraphy of the San Jorge-Formation.*

According to the definition of Wilckens,<sup>40</sup> the San Jorge-Formation comprises the marine deposits firstly in the neighbourhood of the village of General Roca in the Rio Negro, secondly in the region of the Gulf of St. George,<sup>41</sup> and thirdly the strata with *Lahillia luisa* Wilck. in the region of the Lago Argentino and Seno de la Ultima Esperanza (Santa Cruz). But while the two first of these formations are in obvious contrast to their base, namely the continental Variegated Sandstones of the Upper Cretaceous, the so-called Luisaen is, even according to Wilckens himself, closely allied with the ammonite- and baculite-bearing deposits of the Upper Senonian. There is a gradual transition from the lower horizons with ammonites and baculites to the upper ones with *Lahillia luisa*; and the impoverishment of the ammonite-fauna progresses little by little from top to bottom, although in the strata with *Lahillia luisa* some ammonites still occur. Wilckens instances three or four mollusca as common types of the Luisaen and the Roca-Salamanca; but there can be no doubt that great faun-

<sup>40</sup> Die Meeresablagerungen der Kreide- und Tertiärformation in Patagonien, pp. 135 etc.

<sup>41</sup> The so-called Salamanca-Beds which received its name from the Salamanca-Peak, located about 10 miles at the north of Comodoro Rivadavia (Chubut).

FIG. 1.





istic and lithologic differences separate the Luisaen from the Roca-Salamanca-Beds, and that evidence cannot be found for contemporaneity or equivalence of these formations.<sup>42</sup> Since, as mentioned above, no ammonites occur at Roca, the most important evidence for all earlier opinions as to the age of Roca has disappeared.<sup>43</sup> Furthermore, it will be shown in this paper that equivalent deposits of the Roca-Salamanca-Beds also exist in Southern Patagonia, but these deposits are obviously separated from the Luisaen by a faunistic and stratigraphic break. Consequently, the denomination "San Jorge-Formation" as applied in this paper, is not entirely identical with what Wilckens understands by it. I wish to apply this name to the marine deposits of the Roca-Salamanca-Beds and related formations, the age of which will be discussed further on, but special attention may be called to the fact that the strata with *Lahillia luisa* Wilck. are excluded from my definition.

To the hitherto known exposures of these deposits will be added in this paper some new data about the Roca-Beds in the region of the Rio Grande and around the Cerro Payén, and further in the Bajo de Gualichú, northwest of San Antonio at the mouth of the Rio Negro. For information about these localities, I am gratefully indebted to my colleagues, Dr. Groeber and Dr. Wichmann, who kindly allowed me to take advantage of still unpublished observations. Furthermore, some new observations I made on a trip to Roca in September, 1916, complete the evidence brought out in my previous publications and bring the discussion of the Roca question up to the present.

In attempting a critical examination of the various sections from a stratigraphical point of view and according to their geographical distribution, we may start in the north, in the region of Cañada Colorada, a small village situated in the northern part of the Province of Mendoza, at the foot of the Cordillera. Bodenbender<sup>44</sup>

<sup>42</sup> v. Ihering has called the Luisaen a formation of more archaic character and he always considered it as older than Roca-Salamanca.

<sup>43</sup> Windhausen, Einige Ergebnisse zweier Reisen in den Territorien Rio Negro und Neuquén, p. 344.

<sup>44</sup> Sobre el terreno jurásico y cretáceo de los Andes Argentinos entre el Rio Diamante y el Rio Limay. Boletín Academia Nac. de Ciencias en Córdoba, 12, 1892.—Sobre el carbon y asfalto carbonizado de la Provincia de Mendoza, *ibid.*, 13, 1893.

and Burckhardt<sup>45</sup> described several localities in this district (Arroyo Pequenco, Arroyo Loncoche etc.) where glauconitic marly limestones of a green color and gray marls with typical fossils of the Roca-Beds have been observed. Burckhardt divided the sediments in the syncline Cañada Colorada-Pircala into two parts and distinguished Senonian and Danian; but there can be no doubt that this complex of sediments must be assigned entirely to the Roca-Beds. Behrendsen<sup>46</sup> in his paleontologic study of the material collected by Bodenbender, compared these fossils with the so-called Cretaceous fauna described by C. A. White<sup>47</sup> from Maria Farinha near Pernambuco. Behrendsen tried to establish relationship between the Brazilian coast terrane and the Paleocene of Mons, laying stress upon the appearance of several *Cerithium* in Brazil. These, according to his interpretation, have great similarity to certain *Cerithium* of the European Paleocene. He further instanced three *Cerithium* sp. found at Los Huincanes by Bodenbender, but it seems probable that this classification may result from a bad state of preservation.

From a critical and summary examination of the various sections published by Burckhardt and Bodenbender, we get the following character and sequence for the Roca-Beds of Cañada Colorada: Upon reddish and gray sandstones with intercalations of variegated marls of the Upper Cretaceous, there rests a complex of sediments which in general consists of yellow limestones with marly intercalations of a clear color carrying the molluscan fauna; but there also occur limestones with bryozoa, corals and remains of fish. This complex of sediments has a thickness of about 240 feet and, towards the top, goes over into slaty marls with banks of sandstone and limestone. Gerth<sup>48</sup> who recently made more systematic explorations in this region, also observed brackish and lacustral deposits at the base of the Roca-Beds near to Malargüe.

<sup>45</sup> Profils géologiques transversaux de la Cordillère Argentino-Chilienne, Anales del Museo de La Plata, Sección Geologica y Mineralogica II, pp. 53 etc., La Plata, 1900.

<sup>46</sup> Zur Geologie des Ostabhanges der Argentinischen Cordillere, Zeitschr. deutsch. Geol. Gesellsch., 43, 1891; 44, 1892.

<sup>47</sup> Contribuções a Paleontologia do Brazil, Archivos do Museu Nacional do Rio de Janeiro, 7, 1887.

<sup>48</sup> Die Pampinen Sierren Centralargentiniens, Geologische Rundschau, 4, pp. 577 etc., 1913.

With regard to the region east of the Rio Grande (36° and 37° S. L.), Bodenbender expressed the opinion that the vast plateaus which constitute the characteristic physiographic element of this region, consist chiefly of sediments of the Roca-Beds lying under thick sheets of andesitic rocks. The investigations of Groeber in this portion of Argentina have confirmed Bodenbender's assumption, as sediments and fossils have been found in numerous localities to the north, west and south of the Cerro Payén. The fossils found by Groeber have been partly identified with well-known forms of the Roca-Beds; partly they will considerably enlarge the paleontological knowledge of this formation.

A rapid change of facies and the lack of constant and easily recognizable horizons of fossils are the most characteristic features of deposits originating like these in a shallow sea. In general, according to Groeber, the entire series of Roca-sediments in this region may be divided into a lower chalky or sandy part with fossils and local intercalations of gypsum and in an upper part with gray reddish nonfossiliferous marls. The thickness, in accordance with the frequent change of facies, is very variable. The sandy facies with gypsum shows in general a thickness reaching 450 feet, whereas in the chalky facies the thickness is frequently reduced to 30 feet. The whole complex rests unconformably upon the upper marly formations of the Upper Cretaceous Variegated Sandstones. Sometimes brackish deposits with *Paludina* appear at the base. The breccias, tuffs and sheets of the so-called Andesitic Series (a very thick complex of volcanic material to which Groeber is inclined to assign an approximately Oligocene age) have been laid down upon the eroded surface of these sediments.

To the south of the Rio Colorado, widespread deposits of the Roca Beds have been observed by the writer in the surroundings of the Sierra Auca Mahuida and may be divided in two horizons, just as in the region north of the Rio Colorado.<sup>49</sup> In the lower horizon of clayey sediments with much gypsum ("Capas del Jaguel") fragments of *Perna* have been found and, a little higher up, the typical fauna, especially *Ostrea Ameghinoi* Th., bryozoa and corals. An upper nonfossiliferous horizon is formed by marls with sandy intercalations.

<sup>49</sup> See Windhausen, *El yacimiento de Rafaelita de Auca Mahuida etc. and Einige Ergebnisse zweier Reisen in den Territorien Rio Negro und Neuquén*, pp. 343 etc.

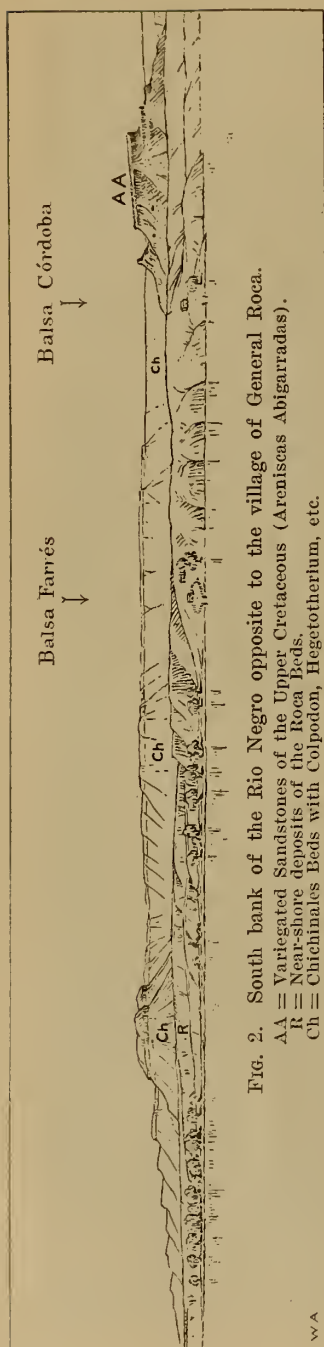


FIG. 2. South bank of the Rio Negro opposite to the village of General Roca.

AA = Variegated Sandstones of the Upper Cretaceous (Areniscas Abigarradas).  
 R = Near-shore deposits of the Roca Beds.  
 Ch = Chichinales Beds with Colpodon, Hegetotherium, etc.

In reviewing the principal stratigraphic features of the region from Cañada Colorada to the Sierra Auca Mahuida, there can be distinguished a chalky-sandy gypsum-bearing division with marine as well as brackish fossils and above these a complex of variegated marls with sandy intercalations and no fossils. At the foot of the Sierra Auca Mahuida clayey sediments with gypsum of great thickness begin to interwedge at the base of the chalky-sandy division, and this clayey horizon can be observed as far as the village of General Roca. At the bottom as well as at the top of the whole complex in the region of the Rio Grande, Groeber observed obvious unconformities.

The geologic conditions of the surroundings of General Roca may be summarized according to my last investigations as follows: On the north bank of the Rio Negro, the marine fossiliferous strata of the Roca Beds are well exposed at various localities, especially on the heights of a long spread terrace situated about 10 miles north of Roca. But nowhere can the base upon which these strata are resting, be seen. In these sections a clayey gypsum-bearing horizon with *Gryphaea Burckhardti* Boehm and fish teeth ("Capas del Jaguel") is followed by a layer with *Nautilus Valencienni* Hupé, and upon this layer rest chalky and marly sediments with the known fauna of Roca-invertebrates. This complex may be approximately 100 feet thick.

Upon these marine sediments lie clear tuff-bearing sandstones containing opalized trunks of trees and further testifying to a terrestrial origin. On the south bank of the Rio Negro these terrestrial sediments are of great

thickness and constitute a very important physiographic element. They are exposed on a long tract always along the heights of the river bank. Following the example of Doering,<sup>50</sup> Wichmann proposed for these sediments the denomination "Capas de Chichinales" (Chichinales Beds).<sup>51</sup> In the Rio Negro-valley they begin near Chichinales (about 40 miles east of Roca) and, crossing the junction of Rio Neuquén and Rio Limay, they spread as far as the lower course of the Rio Limay.<sup>52</sup>

These Chichinales Beds rest to the north of Roca upon the eroded surface of the marine Roca Beds, whereas to the south of the village they lie on a base which offers high interest in a stratigraphic as well as tectonic sense. These relations can be studied in the surroundings of the two ferryboats (balsas) opposite to the village (see fig. 2).

Close upon the bank of the Rio Negro the sharp slope of the Variegated Sandstones (marked AA in fig. 2) obviously has the character of a fault-scarp, and about two miles southward this tectonic line disappears under the terrace of the Chichinales Beds (marked Ch). Eastward from this line, typical marine sediments appear and occupy the place of the Continental Variegated Sandstones. They consist in soft clayey, sandy and gypsum-bearing sediments with the character of Bad Lands. With regard to their lithologic appearance, these sediments can be compared only with the "Capas del Jaguel" in the region of the Sierra Auca Mahuida (marked R in the figure). There can be no doubt that these strata on the south bank of the Rio Negro also belong to the Roca Beds, and their character as deposits of sand and mud indicates clearly their near-shore origin. I do not hesitate to hold the fault-scarp that represents the eastern limit of the Variegated Sandstones in this region as the ancient shore-line of the Roca-Sea.

Consequently, the following stratigraphic, tectonic and physiographic elements appear on the south bank of the

<sup>50</sup> Expedición al Rio Negro, vol. 3, Geologia, Buenos Aires, 1882.

<sup>51</sup> Contribución a la geología de la región entre el Rio Negro y Valcheta, Anales del Ministerio de Agricultura, Buenos Aires. In press.

<sup>52</sup> In the sections published by Roth (Rev. Museo La Plata, 9, pp. 149, 169, etc., plate I) these sediments have been compared with the "Arenisca del Rio Negro" (Rio Negro-Sandstone) that in the lower course of the Rio Negro is widely spread and is correlated with the marine Entre Rios-Formation (Paraná Beds). Roth's erroneous interpretation appeared in my previous papers as I too believed that the Rio Negro-Sandstone existed in this region. But this is not so.

Rio Negro: 1. A portion of the continental Variegated Sandstones, obviously belonging to the upper part of this series. 2. The fault that determines the scarp of these sandstones. 3. The near-shore deposits of mud and sand which lie to the east of the above fault-line and indicate the ancient beach of the Roca-Sea. 4. A peneplain, spread over this old relief, indicating by its imperfect stage but a short period of erosion. 5. The Chichinales Beds, deposited upon this old surface. 6. The later erosion of the Rio Negro which first cut down its way in the Chichinales Beds and then advanced deeper into the basal relief.

It is self-evident that the determination of the age and origin of the Chichinales Beds assumes special importance in connection with the events of earth history which are recorded in the above section. In September, 1916, the writer succeeded in finding in the middle horizon of these sediments some fragments of *Colpodon*, *Hegetotherium* and turtles, also those of a great edentate. The thickness of these sediments may be estimated at about 300 feet. Carlos Ameghino, to whom I am indebted for the classification of these fossil remains, expressed the theory that strata with *Notostylops* and *Pyrotherium* might be found below this horizon. This theory is very acceptable for several reasons, as not only a complex of about 120 feet lies under the referred horizon with *Colpodon* etc., but also because the general and lithological character of this lower division of the Chichinales Beds bears a great similarity with the classic section that Florentino Ameghino referred to as existing on the southern shore of Lake Colhué Huapi (or Colhuapi), where the strata with *Colpodon* appear above the strata with *Notostylops* and *Pyrotherium*.<sup>53</sup>

Therefore, about Roca as well as in the region of Lake Colhué Huapi observations agree as to the Tertiary age of the alleged mammalian faunas, alike whether the marine Roca and Salamanca Beds, resting at the base of these sections, are correlated with the Upper Cretaceous (Danian) or the lower horizon of the Tertiary.

The position and determination of age of the dinosaur-bearing horizons and the fixing of their limits towards the top and towards the base is not so clear at present. No doubt the chief deposit of dinosaur bones is found in

<sup>53</sup> Les formations sédimentaires, p. 112, fig. 31.

the variegated Keuper-like marls of the so-called Pehuénche Beds (Piso Pehuénche, Doering and Ameghino), which may be considered either as the highest part of the Variegated Sandstones of the Upper Cretaceous (Areniscas Abigarradas) or perhaps as basal formations of the Roca Beds. In these strata, Dr. Wichmann collected in 1912, on the southern shore of the Rio Negro, a nearly complete dinosaur skeleton, now in the National Museum at Buenos Aires.<sup>54</sup> According to a communication from Carlos Ameghino, this skeleton does not belong to a *Titanosaurus*, as has been assumed before, but to a Sauropod of the family of the *Diplodocidæ*.

Florentino Ameghino claimed that remains of *Pyrotherium* and dinosaurs had been found in the same layer, nearby in the region west of the junction of the rivers Neuquén and Limay, thirty miles west of Roca.<sup>55</sup> This association of dinosaurs and mammals was one of the chief supports for a Cretaceous age of the ancient Patagonian mammalian faunas. *A priori* it is necessary to call attention to the fact that this report is to be judged in the same manner as the unfounded statement that ammonites occur at Roca.<sup>56</sup> With regard to the alleged occurrence of dinosaurs and mammals to the west of Confluencia (junction of Rio Neuquén and Limay) an exact statement about the locality has never been made. Lydekker<sup>57</sup> as well as Smith Woodward<sup>58</sup> have turned their attention exclusively to the paleontologic side of this matter, without going into studies of a stratigraphic kind. As the Roca-Sea never invaded the region to the west of Confluencia, it is obvious that the mammal-bearing Chichinales Beds in the lower course of the Rio

<sup>54</sup> See Wichmann, Las capas con Dinosaurios en la costa Sur del Rio Negro frente a Gral. Roca, Revista "Physis," vol. 2, pp. 258 etc., Buenos Aires, 1916.

<sup>55</sup> L'âge des formations sédimentaires de Patagonie, pp. 19, 20 of the abstract.—Les formations sédimentaires, p. 77. See also on the same subject: Wilckens, Die Meeresablagerungen etc., pp. 151, 152.

<sup>56</sup> These ammonites really came from the Upper Jurassic beds in the Preandine zone (Cerro Lotena) and had been mixed with collections from Roca, due to the inexperience of the collector. There can be no doubt that the same occurred with the bones of dinosaurs and of *Pyrotherium* from different localities and horizons.

<sup>57</sup> Contributions to a knowledge of the fossil vertebrates of Argentina, Anales del Museo de La Plata, Paleontologia Argentina, 2, La Plata, 1893. Supplemental observations on the extinct ungulates of Argentina, *ibid.*, 3, La Plata, 1895.

<sup>58</sup> On two Mesozoic crocodylians, Anales del Museo de La Plata, Paleontologia Argentina, 4, La Plata, 1896.

Limay rest directly upon the Pehueneche Beds with dinosaurs. This fact explains why a non-geologist might consider these sediments of quite different age as a uniform formation. Further, the lithologic character and color of the Chichinales Beds depends a great deal on their base, and consequently in regions where they rest upon variegated sediments, they bear a great similarity to their base in color and material.

Summarizing our present knowledge, we may establish the following table of formations for the region to the south and north of the village of General Roca:

Boulder or shingle formation of the Tehuelche Beds ("Rodados Patagonicos").

Sandy elays, tuffs and tuff-bearing sandstones with <i>Colpodon</i> , <i>Hegetotherium</i> and turtles; probably in a lower level also with <i>Pyrotherium</i> etc. Intercalations of sandstones with opalized trunks of trees (palms).	}	Chichinales Beds (terrestrial).
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*Unconformity.*

*Peneplain.*

Dolomitic limestone, marls and limestones with marine invertebrates ( <i>Ostrea Ameghinoi</i> etc.). Gypsum-bearing elays with <i>Gryphaea burckhardti</i> and fish-remains. Near-shore deposits of fine sand and clay at the south bank of the Rio Negro.	}	Marine Roca Beds (transgression).
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*Unconformity.*

Crossbedded sandstones. Sandstones of brown color with braekish mollusca. Keuper-like deposits with dinosaurs ( <i>Diplodocida</i> ). Fossil wood.	}	Pehueneche Beds (laeustrian and braekish deposits).
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Variegated Sandstones of the Upper Cretaceous (Areniseas Abigarradas).	}	Continental deposits.
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Advancing south or southeast, the next locality where deposits of the San Jorge have been found is in the depression of the Bajo de Gualichú, a few miles to the south of the Isle Choele-Choel, formed by two branches of the Rio Negro. Ameghino<sup>59</sup> has already reported the appearance of some Roca fossils here and Wichmann,

<sup>59</sup> Les formations sedimentaires, etc., p. 53.



on the occasion of his investigations in the lower Rio Negro-valley, visited this place (1913) and made a collection of fossils. According to him, the San Jorge is exposed in the bottom of this depression; strata of the Patagonian Formation appear in the slopes of the walls, while above this a second terrace is formed by deposits of the Rio Negro Sandstone.

The stratigraphy of the so-called Salamanca Beds in the surroundings of the Gulf of St. George is based chiefly upon the various reports of Ameghino and v. Ihering. Besides this several sections have been described in the publications of Stappenbeck<sup>60</sup> and of Loomis<sup>61</sup> and the aforementioned critical study of Wilkens is of much importance. Tournouer<sup>62</sup> issued a detailed stratigraphic study of the occurrence of vertebrates in several places in this district, but he gave less attention to the marine deposits.

Just as in the region of General Roca, an impartial examination of the stratigraphic conditions in the surroundings of the Gulf of St. George will lead to the conclusion that the Salamanca Beds are a deposit due to a widespread marine transgression, and obviously overlap the Variegated Sandstones of the Upper Cretaceous, or its highest part, the dinosaur-bearing deposits of the Pehuenche Beds. Towards the top these marine Salamanca Beds are cut by a peneplain and upon this surface have been laid down the terrestrial deposits with *Notostylops*, *Astraponotus* and *Pyrotherium*. No more than in Roca are there reasons for assuming in this district an intercalation of these marine sediments in the Variegated Sandstones. Ameghino,<sup>63</sup> who described two sections of the southern shore of Lake Colhué Huapi, is inconsistent in this regard. Although the two sections proceed from nearly the same place, in the first one the layer with *Ostrea pyrotheriorum* has been drawn as a light intercalation, while in the second section the same layer appears as a constant and normally stratified sediment, resting with regularity upon the Pehuenche Beds

<sup>60</sup> Informe preliminar relativo a la parte Sudeste del Territorio del Chubut, Anales Ministerio de Agricultura, Sección Geología etc., vol. 4, No. 1, Buenos Aires, 1909.

<sup>61</sup> The Deseado Formation of Patagonia, 1914.

<sup>62</sup> Note sur la géologie et la paleontologie de la Patagonie, Bull. Soc. Géologique de France, (4), vol. 3, pp. 463 etc., 1903.

<sup>63</sup> Les formations sédimentaires, p. 63, fig. 9 and p. 112, fig. 31.

with dinosaurs. In another section<sup>64</sup> the Salamanca Beds begin at the shore of the gulf in a normal position above the Pehuenche and are overlain by the mammal-bearing sediments; for more than 30 miles inland, on the west bank of the Rio Chico, the Salamanca Beds retain the same thickness.

Compared with Roca and Gualichú, the Salamanca sediments seem a little different; a remarkable preponderance of sands and clays and a decrease of the chalky component is apparent. Further, a special feature seems to be the abundance of *Ostrea pyrotheriorum*, which is represented by a vast number of specimens and plays here the same part as *Ostrea ameghinoi* in the northern half of the San Jorge-Sea.

As to the existence of *Notostylops* and *Pyrotherium* Beds about the Gulf of St. George, it may be noted that this region also belongs to the series in which contemporaneity of dinosaurs and mammals was emphasized by Ameghino.<sup>65</sup> There can be no doubt that in the treatment of this subject wrong inferences were drawn from some partly correct observations. For the interpretation of stratigraphic sections it is necessary to start from a general base and establish harmony between stratigraphic correlations, diastrophic phenomena and faunistic movements.

It has been demonstrated that the chief deposits of dinosaur-remains are in the highest horizons of the Variegated Sandstones, the marly-clayey formations of the Pehuenche Beds. Whether it is assumed that the bones are rolled (as Lydekker suggested) or relatively *in situ*, is, therefore, a secondary question. The most important fact is, that in Patagonia just as in other parts of the world the dinosaurs became the most striking element of the terrestrial faunas in the Upper Cretaceous. Nor is it improbable that at least certain groups of this abundant reptile life survived the diastrophic events at the close of Cretaceous time and even resisted the invasion of the San Jorge-Sea, since large parts of Patagonia remained outside of this transgression. We can even imagine that some further biological evolution affected the surviving remains of this fauna. Thus may be explained the occurrence of dinosaurs at the base of

<sup>64</sup> Ibidem, p. 113, fig. 32.

<sup>65</sup> Les formations sédimentaires, p. 113, fig. 32.

the terrestrial deposits, which contain the most ancient mammals of Patagonia. Outside the limits of the San Jorge-Sea (which means in large parts of Patagonia, as will be proved in Part III) the mammal-bearing strata rest directly on the chief dinosaur-bearing horizon, the Pehuenche Beds, and the hiatus separating both formations may easily be overlooked. The case already studied in the region of Confluencia thus repeats itself. The normal sequence of strata is preserved chiefly in the marginal regions of the present Patagonia and is represented by the Pehuenche-San Jorge-Casamayor and Deseado.<sup>66</sup>

The cases instanced by Ameghino may be briefly reviewed. The section from the southern shore of Lake Colhué Huapi,<sup>67</sup> with the association of mammals, turtles, serpents and dinosaurs in the same layer of the *Notostylops* Beds, has been mentioned. Further, Ameghino<sup>68</sup> cited Roth as witness to strengthen his own assumptions, and Roth himself mentioned the occurrence of dinosaurs with *Notostylops*.<sup>69</sup> According to the statement of Ameghino, remains of *Genyodectes serus* A. S. Woodw. have been found by Roth about 30 feet above a layer with mammals of the *Notostylops*-fauna. In the same manner the great turtle, *Miolania argentina* A. S. Woodw., appeared in a locality about two miles north of Lake Colhué Huapi together with the same fauna of mammals.

It seems to me remarkable that the contemporaneity of dinosaurs and *Notostylops*-fauna has been put forward in the above mentioned reports, but the finding of *Pyrotherium* together with dinosaur bones has never been confirmed. No study or work in reference to the *Pyrotherium* Beds in Patagonia has ever been more thoroughly gone into than by the Amherst Expedition, and therefore it is of fundamental importance that Loomis flatly denies the association of dinosaurs and the Deseado fauna. This seems to indicate that the Cretaceous reptile fauna sent some survivors into the time of the *Notostylops* Beds (Casamayor), but these remains did not last up to the time of *Pyrotherium*. It is impossible to

<sup>66</sup> It seems to me convenient to apply the denominations Casamayor and Deseado for the *Notostylops*, *Astraponotus* and *Pyrotherium* Beds, as has been done by Loomis, following the example of Tournouer and Gaudry.

<sup>67</sup> Les formations sédimentaires, p. 112, fig. 31.

<sup>68</sup> Ibidem, p. 80.

<sup>69</sup> Beitrag zur Gliederung der Sedimentablagerungen in Patagonien und der Pampasregion, N. Jahrb. Min., Beil.-Bd., 26, p. 95, 1908.

maintain from these facts a Cretaceous age of the Patagonian mammal faunas, as Ameghino did. *The mammalian faunas did not live in Cretaceous time, but a small surviving part of the reptile fauna reached into the period of prevailing mammalian faunas.*<sup>70</sup> It seems to me characteristic that no reference has been made to the appearance of *Sauropoda* in association with mammals, and wherever cases of contemporaneity of mammals and dinosaurs in Patagonia have been instanced, these latter belonged to the carnivorous *Theropoda*. There are reasons for supposing that at least the *Sauropoda*-group became entirely extinct in the Cretaceous.<sup>71</sup>

In other words, from the preceding explanations there results a remarkable simplification of the stratigraphic scheme and of some paleontologic questions. The pretended complexity of the alleged phenomena disappears, if the San Jorge-transgression is put in the right place and appreciated as an important factor in the stratigraphic division.

Among the other sections of general interest in the region of the Gulf of St. George, we may briefly review those described by Stappenbeck. This author gave a detailed classification of Salamanca Beds in the valley of the Rio Chico about 20 miles down the river from the

<sup>70</sup> This is also apparently the opinion of Dr. W. D. Matthew in the above mentioned symposium of the Geological Society, p. 401. See also the review of this problem by E. Hennig, *Naturwiss. Wochenschrift. N. F.*, 13, No. 52, 1914.—W. T. Lee, Recent discovery of dinosaurs in the Tertiary, *this Journal*, vol. 35, May, 1913.

<sup>71</sup> After having written these lines, I received the paper of W. D. Matthew, *Climate and Evolution* (*Annals New York Acad. of Sciences*, vol. 24, 1915) in which the question of the age of Argentine geologic formations in comparison with European and Northamerican standards has also been thoroughly treated. In the chapter "Synchronism and Homotaxis" the author suggests the idea that the peculiar contradictions between Ameghino's time demarcations and the generally adopted schemes might be due to the fact that "the data on which they rest do not prove contemporaneity but homotaxis. Granting that two faunas in widely remote regions contain the same proportion of extinct species, granting that they represent equivalent stages of evolutionary progress, they are not thereby shown to be contemporaneous, unless they are at the same distance (measured not in miles but in difficulty of advance) from the main center of dispersal of the fauna they contain." From this point of view, Dr. Matthew draws the inference that "the late Tertiary mammals of the southern continents will approximate in homotaxis the Middle or Early Tertiary mammals of Holarctica; and the Middle Tertiary southern faunas will approximate the Early Tertiary or Late Cretaceous faunas of the north." I trust that the new data published in this paper may help to show that it is not necessary to look for explanations, which have an obviously artificial character. The Cretaceous age of the Patagonian mammalian faunas is not supported by a single valid fact. Those paleontologists who like Gaudry, Schlosser and Philippi defended the Tertiary age of these faunæ, are now completely justified by the results of this research.

outlet to the sea, and the essential part of this section consists of marly sands and clear sandstones with intercalations of clay. The boundary between the Salamanca and the overlying terrestrial deposits is formed, according to Stappenbeck, by a sheet of black bituminous clay. As to the Casamayor and Deseado Beds, this author has given two sections. One of these is identical with the classic section from the southern shore of Lake Colhué Huapi, published by Ameghino, while the second one is the continuation of the alleged section of Rio Chico and comprises a complex of crossbedded yellow and green sands, sandstones and clayey intercalations, which may be about 300 feet thick.

The work of the Amherst Expedition to Patagonia has been extraordinarily successful in a paleontologic sense, and a rich collection of the so-called *Pyrotherium* fauna was obtained in a locality 3 miles east of Rio Chico and to the west of Puerto Visser. Loomis published two typical sections that comprise deposits of the Salamanca, of the overlying terrestrial horizons and even of the Patagonian Formation. As to the interpretation of these sections I do not agree entirely with Loomis. In the chief section of the so-called "Deseado exposure," this writer laid emphasis on the existence of an unconformity between the terrestrial deposits with *Notostylops* and *Pyrotherium* and the overlapping Patagonian Formation; but in the other two sections he did not distinguish the marine fossil-bearing Salamanca from the overlying terrestrial sediments which according to him contain turtles, fossil wood and "fragments of some sort of a bone." As the name "San Jorge-Formation" was created by Wilckens only for the marine deposits between the previously mentioned limits, the sections of Loomis cannot be assigned entirely to the San Jorge. The middle parts of the sections A and B belong to the *Notostylops* and *Pyrotherium* Beds, and the section of figure 2 is identical with the section published by Ameghino in "Les formations sédimentaires," p. 113.<sup>72</sup> It seems to me a feature of special importance that in the two sections A and B the terrestrial deposits rest upon apparently different levels of the marine Salamanca, and in each case Loomis gives a separate list of fossils, although all the specimens belong without excep-

<sup>72</sup> See Carlos Ameghino, Le Pyrothérium, l'étage Pyrothéréen et les couches à *Notostylops*, Un reponse a Mr. Loomis. Revista "Physis," vol. 1, No. 7, Buenos Aires, 1914.

tion to the Salamanca-fauna. On the basis of analogous observations in the Rio Negro-valley, I assume the existence of an hiatus in the Loomis-sections, separating marine Salamanca from terrestrial *Notostylops* Beds. I suppose, this hiatus in section A lies above the layer 7 and in section B above the layer 4, corresponding to a peneplain of widespread distribution; the same peneplain has also been found in the neighborhood of General Roca. It cuts the sediments of the San Jorge obliquely to its different levels.

The lithologic character of the Salamanca in the sections of Loomis is determined by sandy clays and green slates and limestones with the known fauna. A connected sequence of strata cannot be obtained from the two sections, because the peneplain cuts different levels and the basement is not visible. Furthermore, a somewhat irregular sedimentation is a characteristic feature of near-shore deposits, and to these also belong the Salamanca Beds in the surroundings of the Gulf of St. George. In case A, a complex of about 200 and in case B, of about 120 feet in thickness can be observed. It is interesting that *Ostrea guaranítica* has been found by Loomis in those places, a few feet above the *Ostrea pyrotheriorum*. In this way, further evidence is given for the equivalence and contemporaneity of the so-called Schueneen with Roca and Salamanca Beds.

The *Notostylops* and *Pyrotherium* Beds (Casamayor and Deseado) in the sections of Loomis consist of alternating yellow gypsum-bearing clays, green cross-bedded sands and coarse sandstones with opalized wood. In contrast to Roca the volcanic component has been greatly reduced. To a large extent these terrestrial deposits may doubtless be considered as accumulations in depressions and troughs, but nevertheless they are deposits of a widespread distribution corresponding to a general period of accumulation. It seems to me that Carlos Ameghino (loc. cit.) is right in laying stress on this latter fact. Such a surprising abundance of fossil remains as in the Deseado exposure of Loomis is an exceptional case, but the same formation with scarcer or without any organic remains is spread over a large area in Patagonia. Just as the peneplain above the Salamanca indicates a denudation period of general character, it is necessary to assign a regional character to the period of accumulation which is represented by the alleged terrestrial deposits.

Advancing farther to the south with the comparative review of the Roca-Salamanca-deposits, apparently the region of Lake Pueyrredon is another stage on this way. Hatcher collected to the southwest of this lake, in sediments far beneath the Santa Cruz Beds, a specimen of *Gryphaea tarda* Hutt., a species from New Zealand. But according to v. Ihering<sup>73</sup> this shell has to be assigned to *Gryphaea burckhardti* Boehm. Ameghino<sup>74</sup> as well as v. Ihering<sup>75</sup> suggests that the whole series of sediments from the Lower Cretaceous up to the Tertiary might be represented in the region of this lake.

It is known, furthermore, that in the upper course of the Rio Sehuen (Santa Cruz) deposits of the so-called Sehueneen are exposed, and Ameghino and v. Ihering have several times pointed out this fact. In 1908, Ameghino reported the finding of *Loncosaurus argentinus* Amegh. near Par Aik together with the existence of *Ostrea guaranitica* Ih. In 1907, v. Ihering<sup>76</sup> also published a few details, while in his molluscan catalogue<sup>77</sup> he added three other species to the known ones. Thus, at present the following five species establish correlations between these exposures and the Roca-Salamanca-Beds:

*Ostrea Clarae* Ih.

*Ostrea guaranitica* Ih.

*Corbula sehuena* Ih.

*Potamides patagonensis* Ih.

*Struthiolaria* sp.

By these species the Sehueneen is sufficiently characterized as a part of the San Jorge-Formation, particularly as Loomis recently found *Ostrea guaranitica* also in the Salamanca of the surroundings of the Gulf of St. George. The appearance of the freshwater-shell *Diplodon (Unio) colhuapensis* was noted by v. Ihering. Hauthal found this shell at the Rio Sehuen and it also appears in the sediments around the Gulf of St. George, but I suppose that it proceeds from the Pehuenche Beds beneath the San Jorge.

Farther to the south, the oyster-banks of brown color

<sup>73</sup> Les mollusques fossiles, pp. 6 and 32.

<sup>74</sup> Les formations sedimentaires, p. 53.

<sup>75</sup> Les mollusques fossiles, p. 32.

<sup>76</sup> Ibidem, pp. 49 etc.

<sup>77</sup> Katalog der Mollusken aus den Kreide- und Tertiärablagerungen Argentinens, enthalten in der Sammlung des Verfassers, Notas preliminares editadas pela redacção da Revista do Museu Paulista, vol. 1, fasc. 3, Sao Paulo, 1914.

above the strata with *Lahillia luisa* in the region of the Cerro Cazador near the Lago Argebtino must be taken as deposits of the San Jorge. Unfortunately the data published by Hauthal and Wilckens<sup>78</sup> are insufficient, and Hauthal's attention was mainly absorbed by the discovery of the marine Senonian strata at the bottom of these sediments. However, from these reports springs the important fact that the strata in question are in obvious contrast to its base. According to Wilckens, the ammonite- and baculite-bearing deposits of the Upper Senonian pass over little by little into the strata with *Lahillia luisa*, and there the cephalopoda-fauna experiences a gradual impoverishment. Above that follow sediments of quite a different character in a lithological as well as faunistic sense: a complex of soft brownish sandstones with *Ostrea ultimæ spei*, *Ostrea Ameghinoi* and other shells, but without ammonites and baculites. Wilckens points out the fact that this fauna is not identical either with the Upper Senonian mollusca or with the fauna of the Patagonian Formation. This faunistic and stratigraphic break at the bottom as well as at the top indicates important events of earth history. As the other molluscan genera referred to by Wilckens agree with forms represented in the San Jorge, there are well founded reasons for supposing a direct connection of these deposits with the San Jorge. It is desirable that future investigators dedicate special attention to the study of these fossil-bearing horizons above the Upper Senonian.

<sup>78</sup> Hauthal, Wilckens und Pauleke, Die obere Kreide Südpatagoniens, etc.

Fig. 3 (p. 33).

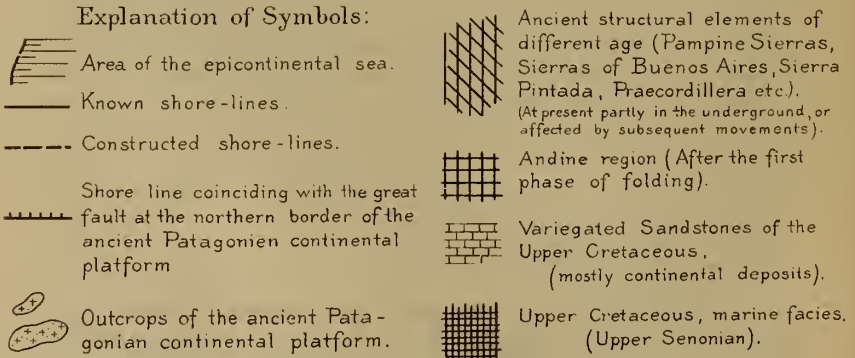
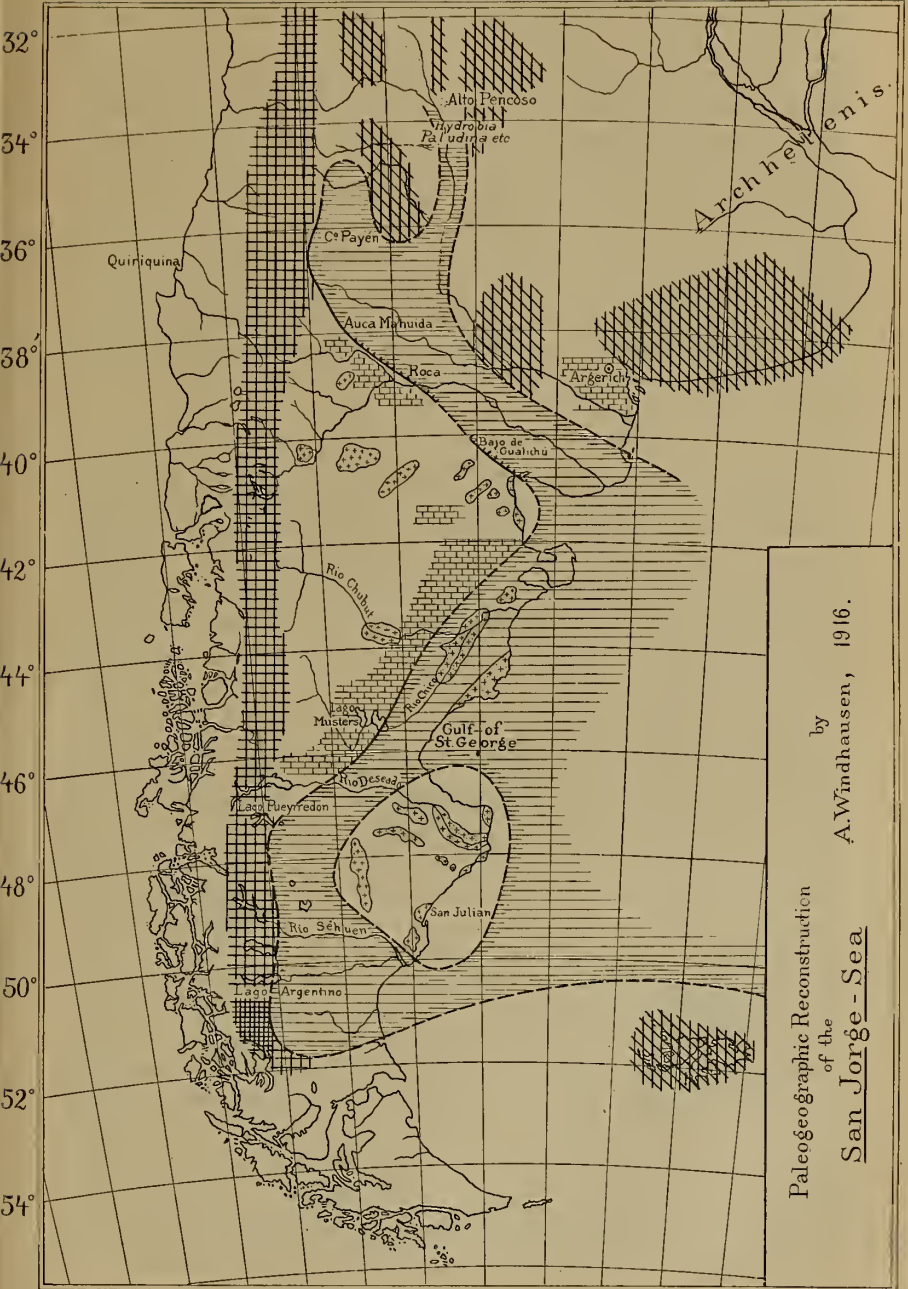




FIG. 3.

74° 72° 70° 68° 66° 64° 62° 60° 58°



Paleogeographic Reconstruction  
 of the  
San Jorge - Sea  
 by  
 A. Windhausen, 1916.

80° 78° 76° 74° 72° 70° 68° 66° 64° 62° 60° 58°

Accordingly, the latter case is in contrast to the others, inasmuch as in the northern and central parts of Patagonia, the San Jorge overlaps the Upper Cretaceous Variegated Sandstones, or perhaps in special cases directly the old platform of paleozoic or archaic age. The Upper Senonian transgression at Lago Argentino is due to the submergence of a small continental border, and not only the equivalent deposits at Quiriquina, but also their faunistic character, show the Pacific way, and origin of this transgression. Thus, near the southern point of the South American Continent can be observed the interesting case of the overlapping of marine formations, one of which came from the Pacific, the other from the Atlantic side, indicating in this way diastrophic events of fundamental importance.

### PART III.—*Paleogeography of the San Jorge-Formation.*

In the foregoing chapter it was necessary to go into a somewhat detailed examination of local stratigraphic relations. Upon the basis of this knowledge it is possible to determine the ancient shore-lines of the San Jorge-Sea; and it will now be shown that, at least in the northern part, the ancient structural elements influenced in a remarkable manner the limits of this epicontinental sea (see fig. 3).

In the north, the sea ended in the region of the Rio Atuel. In the surroundings of Cañada Colorada we have studied the most northerly deposits of this period, the base of which is formed by brackish horizons. Close to the north bank of the Rio Diamante ( $34^{\circ} 40' S., L.$  and  $69^{\circ} 30'$  west of Greenwich) there bends down the great granitic batholith, which from here strikes north across the Paso del Portillo,<sup>79</sup> the zone of Cerro Tupungato, and enters the region of the Cerro del Plata.<sup>80</sup> On the flanks of this great batholith, south of the Rio Diamante, the Variegated Sandstones of Cretaceous age rise up from the foot of the Cordillera towards the heights of the mountain. To the east of this region, on the other side of a large plain appears a new and strange orographic element, the so-called Sierra Pintada, forming a counterpart of the Cordillera in a SE.-NW. direction. This range extends at an acute angle to the very base of the Cordil-

<sup>79</sup> See Darwin, *Geological observations etc.*, pp. 175 etc.

<sup>80</sup> Stappenbeck, *Geología de la falda oriental de la Cordillera del Plata*, Anales Ministerio de Agricultura, Buenos Aires. In press.

lera, where it is truncated by a large fault; to the south, after gradually receding, it disappears under widespread sheets of basaltic and andesitic rocks.<sup>81</sup> The antecedent valleys of the Rio Diamante and Rio Atuel show that during a great part of the Tertiary the Sierra Pintada underwent a slow and gradual rising movement. The unconformity at the base of the Gondwana Series and the existence of Permian Glacial Conglomerates characterize this range as an intermediate link, joining the Precordillera of San Juan and Mendoza with the Sierras of Buenos Aires.<sup>82</sup> In the great acute-angled depression between it and the Andine structural element, where at present the most striking hydrographic element is represented by the Laguna Llanquanelo, ended the transgression of the Roca-Sea. On one side this sea of the past washed the foot of the High Cordillera, approaching the flanks of that great batholith, and on the other side towards the east the sea ended at the southern foot of the Sierra Pintada among hundreds of small islands and peninsulas. From this point of view, we may perhaps consider the Laguna Llanquanelo as a relic of that period.

In the region of the Cerro Payén, according to the investigations of Groeber, the course of the shore was a little to the west of the Rio Grande. Here too the sea ended at the first folds of the Cordillera. Direct observations of a small portion are still lacking, but there are reasons for assuming that the shore was stretched more or less midway between Chos Malal and Auca Mahuida. The writer has seen deposits of the Roca-Beds not far from the bend of the Rio Neuquén, and from here to the region of the village of General Roca, the course of the Rio Neuquén and Rio Negro indicate the western shore-line of the Roca-Sea.

On the Rio Neuquén we enter into the region of the great fault noted in Part II as an ancient San Jorge shore-line. Although we cannot well dispense with direct observations in the tableland to the south of Roca, it may from the general study of tectonic and morphologic phenomena be justifiable to combine the Neuquén line with the fault-scarp at the northern border of the

<sup>81</sup> Stappenbeck, *Apuntes hidrogeológicos sobre el Sudeste de la Provincia de Mendoza*, Boletín 6B, Dirección Gral. de Minas etc., Buenos Aires, 1914.

<sup>82</sup> These characteristic features of the structure of the Sierra Pintada had been observed by the writer in 1909-10, but an interpretation was not possible, until Keidel discovered the relations between the Sierras of Buenos Aires and the Precordillera of San Juan and Mendoza.

ancient Patagonian platform. From San Antonio to the region south of Gualichú, this line may be perceived orographically by a remarkable difference of level in the Rio Negro-valley, if it is compared with the elevation, that is situated a little south from here. While in the Bajo de Gualichú deposits of the Roca Beds and Patagonian Formation are filling the depression, southward from here at a much higher level, granites, slates, diabase and quartz porphyry indicate the ancient Patagonian platform.<sup>83</sup> In the direct northwest prolongation of this line is met near Roca the alleged breaking down of the Variegated Sandstones, and there this fault is to be regarded as a posthumous one above the ancient Patagonian land-mass hidden in the underground. But this fault does not end at Roca; from there it goes over to the northern side of the valley crossing it obliquely. At the north of Cipolletti as far as Tratayén, near the great bend of the Rio Neuquén, this tectonic line determines the western bank of the Rio Neuquén. In the region of Tratayén the existence of this line is recorded by special erosion phenomena, which have been caused originally by tectonic events.<sup>84</sup> Probably this line does not end here, but goes on to the north, contributing not far from here to the formation of a great depression around the so-called Ojo de Agua.<sup>85</sup>

Everywhere observations indicate that the Neuquén line is the west or southwest margin of the Roca-transgression. To the west or southwest of this line deposits of the Roca Beds are not found.<sup>86</sup> Thus, *from San*

<sup>83</sup> This fault-scarp is orographically indicated by the so-called Subida del Indio.

<sup>84</sup> Windhausen, *Contribución al conocimiento geológico de los Territorios del Rio Negro etc.*, plate IV, fig. 3.

<sup>85</sup> The Topographic Section of the Argentine Geological Survey has proved that there are very remarkable depressions in the Territory of Neuquén. For instance the bottom of the Ojo de Agua (20 miles NW. of the Añelo at the great bend of the Rio Neuquén) is 225 meters above the sea, while the bottom of the valley of the river near the Añelo is 400 meters above the sea-level. Likewise the writer has observed very deep depressions surrounding the Sierra Auca Mahuida. All these phenomena cannot be considered as merely physiographic features, but must be assigned to tectonic movements connected with ancient structural elements in the underground.

<sup>86</sup> The strata that unconformably overlap the Upper Jurassic and Cretaceous sediments at the eastern wing of the Cerro Lotena, have been correlated by the writer with the Roca-Beds (*Contribución al conocimiento etc.*, p. 11 and plate III, fig. 1). That could be considered as inconsistent with the above statement. But Keidel, who studied a more extensive zone to the east of the Cerro Lotena, assigns these strata to the base of the Variegated Sandstones. This interpretation is probably the correct one.

*Antonio on the Atlantic coast as far as the region northward from the great bend of the Rio Neuquén, the shoreline of the Roca-Sea coincides with the tectonic line at the northern border of the ancient Patagonian platform.*<sup>87</sup>

In this way, is fixed the southern shore of a branch of this sea. We will now examine the conditions found to the north and northwest and also determine that boundary.

At the east of the Sierra Pintada the line of the Rio Salado represents an old boundary, such as has already been pointed out several times in this paper. It must be regarded as a graben-like depression between the Pre-cordillera-Sierra Pintada and the more ancient mass of the Pampine Sierras, the most western portion of which, the Sierra of San Luis and adjacent parts, is here ended by longitudinal as well as transverse faults.

The strata with *Hidrobia*, *Corbicula*, *Cyrena* etc. in the depression of the Alto Pencoso (southwest of the Sierra of San Luis) as well as deposits of the same character in the intermountain troughs between the Sierras of Famatina and Velasco have likely been connected with the San Jorge-transgression by small and shallow branches.<sup>88</sup> The depression of the Rio Salado may have represented the eastern limit of the sea during this period. A little more southward, in the region where Rio Atuel and Rio Salado take the name of Rio Chadi Leufú, lies the base-leveled root of an ancient range built up by gneiss, crystalline slates, granites, amphibolites and continental sandstones. In the underground of the

<sup>87</sup> Accordingly, in the central parts of Neuquén, where the Patagonian mesetas begin to emerge as a new element, the northern portion of the Patagonian landmass may be still regarded as an essential part of the underground. Outcrops of this old mass in the form of gneisses, granites, etc., are known in this region from the following localities: near Piedra Pintada (Roth), to the north of the Cerro Lotena (Keidel) and to the south of the Rio Limay (Rovereto, *Studi di Geomorfologia Argentina. La Valle del Rio Negro. Boll. Soc. Geol. Ital., vol. 31, p. 181, Rome, 1912*). This mass resisted in the period of Andine folding against the regional forces of folding, producing in this way a deviation of folds and, in some cases, a certain disturbance of normal tectonic conditions. This is a simple explanation of the departing strike in several parts of Neuquén (Cerro Lotena, Sierra Vaca Muerta, Covunco etc.) while the peculiar parallelism of certain chief hydrographic lines in this region is apparently connected with this phenomenon.

<sup>88</sup> Gerth, *Constitución geológica, hidrogeología y minerales de aplicación de la Provincia de San Luis, Anales Ministerio de Agricultura, Secc. Geología etc., 10, No. 2, Buenos Aires, 1914.*—See also the paper of the same author: *Die Pampinen Sierrren Centralargentiniens, Geolog. Rundschau, 4, pp. 577 etc., 1913.*

Pampa this range is known from the Rio Colorado as far as the southern limit of the Province of Cordoba.<sup>89</sup> It is apparently cut off by transverse faults at the south of the Rio Colorado, between the 66th and 64th degrees west of Greenwich. There is no doubt that the southern border was more elevated in the past and influenced the extension of the San Jorge-Sea.

Towards the east, the Sierras of the Province of Buenos Aires represent the remains of a region which has to be regarded as part of a continental mass during this same period.<sup>90</sup> The studies of Keidel revealed a part of the structure of this region and opened the way to future investigations. Its internal structure was determined by Permian movements, the regional character of which Keidel emphasized. These movements here created a zone which for a considerable length of time was one of the most prominent centers of regional erosion. Doubtless its area was considerably larger than the present one, which physiographically is represented only by the two ranges shrunk up and folded by Tertiary movements. Certain connections of this region are known, westward with the Precordillera of San Juan and Mendoza, and eastward with the mountains of South Africa. It has, however, been pointed out in Part I, that the floor ("sole") of these ranges formed a firm barrier to the older Patagonian transgressions. It did not submerge before the close of the Miocene, probably at the time of uplifting and folding of these ranges, and the formation of the Middle Atlantic basin was a consequence of the breaking down of this barrier. For the scope of this paper it is sufficient to repeat these facts and to maintain the assertion that no trace of the San Jorge can be found in the regions northward from here.<sup>91</sup> Further, it is remarkable that traces of Roca-deposits

<sup>89</sup> See Stappenbeck, Investigaciones hidrogeológicas de los valles de Chapalcó y Quehué y sus alrededores, Boletín 4B, Dirección Gral. de Minas etc., Buenos Aires, 1913.

<sup>90</sup> Compare what has been said about the theory of "Archhelenis" in Part I.

<sup>91</sup> The presence of *Ostrea guaranítica* in Misiones reported by Ameghino (Les formations sédimentaires, p. 43) is doubtful. In the same manner must we regard the assertion of v. Ihering (Katalog der Mollusken etc., pp. 21, 22) that fragments of *Ostrea guaranítica* and *Ostrea neuquena* were found at Arroyo San Juan, Puerto de Santa Ana, Misiones. There are really no deposits with oysters in this region, and the specimens in question are not correlated either with the so-called "Formación Guaranítica" or with the origin assigned to them.

are entirely lacking in the borings of Argerich. The strata of the Patagonian Formation in these borings, between 630 and 1800 feet, go over into red and white clays and then into loess-like sediments, that have been correlated by Stappenbeck and Wichmann<sup>92</sup> with the Cretaceous. But these relations as well as the origin of the artesian water in this region have not yet been perfectly cleared up. In case the above interpretation should be right, it would be necessary to suppose, that in the depression situated at the foot of the continental mass ("Archhelenis"), there existed a zone of a considerably strong accumulation. Consequently this zone could not be reached by the Roca-Sea, and the subsequent transgression of the Patagonian Formation resulted from a later depression.

Summarizing, we may assert that the San Jorge-transgression in its northern half was represented by a branch, which in the region of the present mouth of the Rio Negro entered into a graben-like depression along a SE.-NW. strike. This depression was limited towards the southwest by the great fault bordering the ancient Patagonian mass, and towards the north and northwest by old structures, partly belonging to the Pampine Sierras, partly to the Precordilleran-Sierras of Buenos Aires element. The prolongation of this latter element towards the east formed a barrier, which may be regarded as the northern limit of the South Atlantic basin and which at the same time confined the extension of the Roca-Sea towards the north.

It is next in order to set forth the limits of the San Jorge-Sea to the south across the Patagonian Continent.

The most westerly exposure of the fossil-bearing San Jorge sediments is in the Valle de las Plumas of the region of the Rio Chubut. We see deposits of an almost continuous chain extending from the lower valley of the Rio Chubut and its junction with the Rio Chico to Lake Colhué Huapi (or Colhuapi). There, "un peu a l'Ouest de Rio Chico," Ameghino<sup>93</sup> also placed the ancient shore of the San Jorge-Sea. Similarly, Stappenbeck<sup>94</sup> is inclined to extend the ancient San Jorge shore-line across the region of Lake Musters; while Ameghino's sections

<sup>92</sup> Personal communication.

<sup>93</sup> Les formations sédimentaires, pp. 93, 98.

<sup>94</sup> Personal communication.

from this lake<sup>95</sup> demonstrate the complete lack of the Salamanca Beds, not their partial denudation. These facts prove that in all probability the shore of the San Jorge-Sea stretched from the Gulf of St. Mathias south-southwesterly to Lake Musters. The masses of quartz porphyry on the Rio Chico and around the Bay of Camerones were probably islands.

Towards the south, the shore-line is more hypothetical. Fossils, indicating a normal San Jorge-facies, were reported from the upper course of the Rio Schuen. *Ostrea Ameghinoi* Ih. occurs on Lake Pueyrredon, as claimed by v. Ihering on the basis of Hatcher's collections. Accordingly, a slight western embayment towards this lake is indicated with a subsequent more or less north-south course along the Cordillera as far as the Rio Schuen. In the far south, at the Cerro Cazador, brown oyster-banks above the strata with *Lahillia luisa* indicate a neighboring San Jorge shore. Evidently too, as elsewhere, the large masses of quartz porphyry to the south of the Gulf of St. George, in the lower valley of the Rio Deseado and more southward as far as the Bajo de San Julian, were San Jorge-islands. According to Delhaes,<sup>96</sup> the Patagonian Formation of this region rests directly on Rhaetic sediments with *Estheria mangaliensis* Jones. This fact may be regarded as evidence that the Patagonian overlapped a relief, essentially different from the base of the underlying San Jorge.

As to the southern extension of the American Continent, in the southern part of Santa Cruz, the Magellan-Territory and Fireland, there is no indication of a sea corresponding to the close of the Cretaceous or beginning of the Tertiary.<sup>97</sup> The most noteworthy event following the first and chief phase of Andine folding was the intrusion and cooling down of the great batholith of the Coast-Cordillera.<sup>98</sup> For the Antarctic regions, Nordenskjöld<sup>99</sup>

<sup>95</sup> Les formations sédimentaires, p. 86, fig. 19.

<sup>96</sup> Ein Rhätvorkommen an der patagonischen Küste, Centralblatt f. Min. etc., pp. 776 etc., 1912.

<sup>97</sup> Among the many publications issued about the geology of Fireland, may be mentioned the report of Felsch, where special attention was given to the hiatus between the Cretaceous and Tertiary. See Felsch, Informe sobre el reconocimiento jeológico de los alrededores de Punta Arenas, Santiago de Chile, 1913.

<sup>98</sup> See Quensel, Geologisch-Petrographische Studien in der Patagonischen Cordillera, pp. 14 etc., Upsala, 1914.—Besides Hauthal and Wilckens (Ob. Kreide Südpatagoniens etc., p. 17) reported that in the region of Lago



laid emphasis on the existence of a great hiatus between the Cretaceous and Tertiary, with special reference to the Seymour and Cockburn Islands. There as well as in Fireland, the great hiatus, at least in part, corresponds to the San Jorge and thus indicates the bounding continental area.

Consequently, we must infer, that in accordance with the general strike of the southern Cordillera, the coast of the San Jorge from the southern Santa Cruz took a decidedly easterly direction. The southern point of South America and the Falkland Islands were not reached by this transgression. At present nothing can be said about the extension into far southern regions, but the results of future Antarctic expeditions are awaited. It is interesting to see, that the eastern or southeastern course of this coast seems to parallel the line of the so-called "Southern Antilles" in the sense of Arctowsky and Suess; but it would be hasty to draw any further inferences.<sup>100</sup>

Thus, according to the foregoing explanations, the San Jorge-Sea is directly traced from the 33rd to the 52nd degree S. L. Apart from the brackish deposits in the intermountain troughs between Sierra Famatina and Sierra Velasco, which may have been connected with the Alto Pencoso at the foot of the Sierra of San Luis, we do not know any deposits of this epoch from the central or northern Argentina. It is not possible to decide, whether the brackish sediments with *Cyrena*, *Corbicula* etc. of Santa Maria in the Province of Catamarca can be correlated with the transgression of the San Jorge-Sea.<sup>101</sup> But *à priori* it is not improbable that future investigations may show more deposits of this

Argentino are found sheets and dikes of diorite separating the Upper Cretaceous from the Lower Tertiary.

<sup>99</sup> Die geologischen Beziehungen zwischen Südamerika und der angrenzenden Antarktis. *Compte rendu de la XI-ème Session Congrès Géologique Internationale*, p. 759, Stockholm, 1910.

<sup>100</sup> Observations sur l'intérêt que présente l'exploration géologique des Terres Australes, *Bull. Soc. Geol.* (3), 23, pp. 589 etc., 1895. See also: J. G. Andersson, On the geology of Grahams Land. *Bull. Geol. Inst., Upsala*, 1906.—Wilckens, Zur Geologie der Südpolarländer, *Centralblatt f. Min. etc.*, pp. 173 etc., 1906.—Suess, *Antlitz der Erde*, III, pp. 552 etc.—Recently F. Kühn (El arco de las Antillas Australes, *Anales Museo Nacional de Buenos Aires*, 28, pp. 391 etc., 1916) has given a summary of this question.

<sup>101</sup> See Stelzner, *Beiträge zur Geologie der Argentinischen Republik*, p. 126, Cassel und Berlin, 1885.—See also J. Rassmuss, *Rasgos geológicos generales de las Sierras Pampeanas*, *Boletín 13B, Dirección Gral. de Minas etc.*, Buenos Aires, 1916.

kind in the large depressions between the various chains of the Pampine Sierras. If so, a widespread brackish epicontinental sea may have connected through the Alto Pencoso with the San Jorge-Sea.

It is obvious that the known San Jorge represent only a very small remnant. Its real marine life is hidden beneath the South Atlantic or remains unseen in the Antarctic. In the north but a relatively small branch is known, which resembled an inland sea, like for instance the present Baltic Sea. In the south, the connection with the open ocean was wider and more extensive; but our knowledge does not pass the limits of the littoral zone.

The manner in which the northern branch of the San Jorge-Sea was bounded by old structural elements, finds certain Central European analogies. Between the Baltic Shield on the one side and the Variscian Mountain on the other, lay the region of Mesozoic and Cenozoic transgressions alternating with periods of folding. Just as the old horsts play a part in the folding of the great Central European geosyncline, so between the ancient Patagonian mass on one side and the Permian and Prepermian structural elements on the other, can be observed the process of preparation and creation of a new geosyncline. It is, too, conceivable that in the geologic future this geosyncline may develop as a counterpart of the great Andine geosyncline of the Mesozoic. But, at present neither the magnitude of sedimentation nor the consequent subsidence is observable; while apart from the relatively feeble movements of the later Tertiary, no process of folding has affected this geosynclinal area.

The sediments of the San Jorge may be divided into two different lithologic facies, agreeing also with some faunistic features: In the north are the Roca-Beds and in the south the Salamanca. The northern facies is characterized in its lower half by a clayey, gypsum-bearing component. Gypsum of considerable thickness occurs in the region of the Rio Grande and near Roca. The clays ("Capas del Jaguel" in the surroundings of the Sierra Auca Mahuida) and the gypsum are at least in part of terrigenous origin and must be regarded as derivations of the San Jorge sea-bottom. The lithologic character of the northern half then depends in a great measure on the nature of the earlier Jurassic and Cretaceous continental surface. The facies of limestones with

Pelecypoda, Gastropoda, corals and Bryozoa may be regarded as a characteristic deposit of the San Jorge. They indicate the culminating phase of the transgression, but prove a very moderate depth. The green sands and soft sandy clays which are quite extensive about the Gulf of St. George indicate a near shore and these deposits might well be called "meeressand." The entire lack of coast conglomerates is explained by the character of the base, which over a large area is composed of the Variegated Sandstones of the Upper Cretaceous. These sandstones almost invariably have a fine or middle grain, and their derivatives were deposited as fine-grained mud and sand on the submarine continental slope.

#### PART IV.—*Paleontology of the San Jorge-Formation.*

The general faunistic character of the San Jorge has already been dealt with in Part I. A relatively secluded evolution in the South Atlantic and Antarctic regions is the most important factor aiding us to understand the paleontologic position.

The former interpretation of the San Jorge-fauna was influenced by the indefensible stratigraphic division into various members, really only differences of facies. Further, an unbiased interpretation was rendered very difficult by acceptance of a Cretaceous age. The most peculiar view was maintained by Ameghino who would prove the Cretaceous age of the Patagonian mammal faunas, correlating for this purpose the Roca and Salamanca with the Middle Cretaceous. The asserted presence of ammonites brought confusion to its culminating point.

The table of invertebrates found in the San Jorge at different localities, as given in the appendix to this paper, is only of a preliminary character.<sup>102</sup> This table has been drawn up on the basis of all the information contained in the bibliography and collections made on various occasions during recent years. The catalogue of v. Ihering (1914) has also been consulted, as it contains further information about the appearance of certain fossils. A few localities, from which Dr. Groeber brought

<sup>102</sup> The writer has in hand a revision of the whole San Jorge-fauna and hopes to publish it soon.

some material, have been comprised under the name "Region of the Rio Grande," the fossils from there having been classified by the writer. For the data about Gualichú I am indebted to Dr. Wichmanni. The following localities are united under the title "Region of the Gulf of St. George": Salamanca Peak, Malaspina, Mamelones de Piñedo, Monte Mayor, Colhue Huapi and Valle Alsina. Apart from the invertebrates given in this appendix, the following faunistic elements have been mentioned by various writers: bryozoa, corals, stalks of Crinoidea, crayfish-claws and remains of fishes, especially teeth.

The table in the first place shows the uniformity of the San Jorge in a faunistic sense, in spite of the irregularity of the collections and the imperfection of the material. In the second place it points out the existence of a *Tertiary element* of considerable extent. The following genera have to be regarded as Tertiary:

<i>Aturia</i>	<i>Siphonalia</i>
<i>Calyptraea</i>	<i>Malletia</i>
<i>Turritella</i>	<i>Hinnites</i>
<i>Struthiolaria</i>	<i>Lutraria</i>
<i>Trophon</i>	<i>Balanus</i> <sup>103</sup>

For the present it is not possible to decide as to the occurrence of *Cerithium*, asserted by Behrendsen,<sup>104</sup> who for this reason correlated this fauna with the European Paleocene. Ortmann and v. Ihering<sup>105</sup> have especially pointed out the absence of *Cerithium* in the ancient Patagonian fauna. Further *Dosinia* is very frequent in the Tertiary of Chile and New Zealand, and according to v. Ihering<sup>106</sup> it has to be regarded as an ancient element of the coasts of Archinotis. Accordingly, this form must also be assigned to the Tertiary element.

On gathering the various data scattered in the publications of Ameghino and v. Ihering, the following species are found represented in the San Jorge as well as in the Patagonian Formation:

<sup>103</sup> See about the Tertiary age of *Balanus*: Ch. Darwin, A monograph on the fossil Balanidæ and Verrucidæ of Great Britain, Paleontological Society, London, 1854.

<sup>104</sup> Zur Geologie des Ostabhanges etc., second part, p. 30.

<sup>105</sup> Les mollusques fossiles, p. 492.

<sup>106</sup> Ibidem, pp. 298 etc.

<i>Bouchardia patagonica</i> Ih.	<i>Myochlamys patagonensis</i> Ih.
<i>Turritella chilensis</i> Sow.	<i>Venus (Chionc) eupyga</i> Ih.
<i>Gryphaea burckhardti</i> Boehm	<i>Pododesmus Valehetanus</i> <sup>107</sup> Ih.
<i>Malletia ornata</i> Ih.	<i>Modiola andina</i> Ortm.

Besides

*Cardita patagonica* Ih.

and

*Struthiolaria ornata* Ih.

species of the Patagonian Formation are represented in the material proceeding from the region of the Rio Grande. From the same point of view it is very remarkable that v. Ihering<sup>108</sup> regarded the following species of the San Jorge as forerunners of forms of the Patagonian Formation: *Ostrea rionegrensis* as forerunner of *O. hatcheri* and *Venericardia palaeopatagonica* as forerunner of *V. inaequalis*.

Special interest is offered by the genus *Panopaea*. According to Wilckens,<sup>109</sup> *Panopaea inferior* Wilck. is represented in the Upper Senonian of South Patagonia as well as in the Roca Beds, and I am inclined to hold this form as identical with *Panopaea nucleus* Ih. of the Patagonian Formation; or at least it must be admitted that *P. inferior* Wilck. is the forerunner of *P. nucleus* Ih. On the other hand, v. Ihering in his catalogue of 1914 (p. 63 and plate II, fig. 8) describes and figures a new *Panopaea* of the Salamanca-Beds (Rio Chico): *P. Thomasi* Ih. This form appears identical with *P. inferior* Wilck. I believe that this species passes from the Upper Senonian into the San Jorge and from there into the Patagonian Formation, thus representing one of the most persistent forms of this region.

Without recourse to the very defective statistical method, it seems to me that the foregoing data indicate a strong Tertiary element in the San Jorge-fauna. The sole elements, that perhaps could be regarded as Cretaceous, are the genera *Exogyra*, *Gryphaea* and *Trigonia*; but none of these is decisive. The former two, although scarce, are known from Tertiary formations, while *Tri-*

<sup>107</sup> See Les mollusques fossiles, p. 32. According to v. Ihering this shell was found near Roca and at Lake Pueyrredon.

<sup>108</sup> Les mollusques fossiles, p. 489.

<sup>109</sup> Die Meeresablagerungen etc., p. 143.

*gonia* already appears in the Liassic of Chile<sup>110</sup> and must be regarded as a persistent form of this province. Consequently the appearance of *Trigonia* is not surprising. As to the character of the fishes referred to by Ameghino<sup>111</sup> it may be considered as especially interesting that v. Ihering<sup>112</sup> points out the slight value of fish remains for the decision of stratigraphic problems. He recalls that G. de Alessandri<sup>113</sup> on the basis of fish remains assigned an Eocene age to the Paraná or Entre Rios-Formation, whereas there can be no doubt at all about the Later Tertiary age of this formation. On the other hand, I found in the Roca-Beds near General Roca a tooth of *Odontaspis cuspidata* Ag., a fish of the European Eocene. Therefore it seems to me better to omit entirely the fish elements.

According to v. Ihering,<sup>114</sup> a general Antarctic fauna spread at the beginning of the Tertiary from New Zealand to Chile and Patagonia and had as its most characteristic elements the genera *Struthiolaria*, *Malletia* and *Lahillia*. The former two of these are represented in the San Jorge-fauna, and the genus *Lahillia* may likely be found in the future, when collecting work will be more extensive. From the elements that have been indicated by v. Ihering as most characteristic parts of this fauna, the following genera (more than the half of the whole list) are also represented in the San Jorge-fauna:

<i>Scalařia</i>	<i>Mytilus</i>
<i>Calyptraea</i>	<i>Venericardia</i>
<i>Turritella</i>	<i>Phacoides</i>
<i>Struthiolaria</i>	<i>Cardium</i>
<i>Bulla</i>	<i>Panopaea</i>
<i>Cucullaea</i>	<i>Corbula</i>
<i>Arca</i>	<i>Lima</i>
<i>Ostrea</i>	<i>Nucula</i>
<i>Myochlamys</i>	

Wilckens,<sup>115</sup> discussing this statement, expressed the

<sup>110</sup> W. Mörcke, Versteinerungen des Lias und Unteroolith von Chile. N. Jahrb. f. Min., Beil.-Bd., 9, 1894.

<sup>111</sup> Les formations sedimentaires, p. 70.

<sup>112</sup> Die Conchylien der patagonischen Formation, N. Jahrb. Min., 2, p. 42, 1899.—See also Ameghino, Mammifères cretacés de l'Argentine, Bol. Inst. Geografico Argentino, vol. 18, p. 115 of the abstract.

<sup>113</sup> Ricerche sui pesci fossili di Parana, Atti R. Accademia Scienze, Torino, vol. 31, 1896.

<sup>114</sup> Les mollusques fossiles etc., p. 498.

<sup>115</sup> Die Mollusken der Antarktischen Tertiärformation, Wissenschaftl. Erg. der Schwedischen Südpolar-Expedition 1901-1903, 3, Lief. 13, p. 39, Stockholm, 1911.

opinion that the Early Tertiary fauna of the Antarctic regions had not been preserved. This opinion could be maintained, as long as the San Jorge-fauna was imperfectly known. Now, on the basis of the results of this study, I do not hesitate in declaring that *the San Jorge-fauna, as a fauna of Antarctic origin, is identical with the hitherto missing fauna of the Early Tertiary.* Not only the diastrophic events, but also the fossils characterize the San Jorge-Formation as a forerunner of the Patagonian Formation. It therefore lies at the base of the Tertiary.

On the other hand, the comparative studies of Wilckens proved, that there exist certain relations between the gastropoda and pelecypoda of the San Jorge and the Upper Senonian of South Patagonia and Antarctica. These correlations are not only indicated by some common species, but also by the general character and the generic composition of both faunas. This fact may be appreciated as evidence, that in the regions at the south of the present South America there existed during several geologic periods, a prominent center of evolution for marine fauna. This biological center maintained its character with peculiar tenacity. It gave to the northward invading transgressions new forms continuously creating varieties, modifications and species, but always maintaining the essential character of the original fauna.<sup>116</sup> In this well-defined sense it may be justifiable to suppose a gradual transition from Cretaceous to Tertiary. Weighing the participation of different elements, there is a remarkable preponderance of the Tertiary element in the San Jorge-fauna. The entire absence of ammonites and baculites may be considered as the most important fact in this sense.

Unfortunately, the slight relations of this fauna to

<sup>116</sup> Two examples may be cited to illustrate the isolated evolution and persistence of certain forms in this region. The genus *Tylostoma* (*Pseudotylostoma* v. Ihering) is already represented in the Lower Cretaceous (Barremian) of Neuquén by a species *T. aequiaris* Coq. The *Tylostomas* in the Tertiary of this province may be regarded as direct descendants of that form. Further, the so-called *Exogyra ostracina* Lam. var. *mendozae* Ih. (which I regard as a new form) is very probably a descendant of *Ostrea minos*, a form which also appears in the Lower Cretaceous of Neuquén. A future revision of the San Jorge will certainly add many more examples of this kind. Such a revision will show a continuous evolution of this molluscan fauna, which originally came from Upper Jurassic-Cretaceous elements of the South Andine province (see Uhlig, l. c.) and gradually developed itself into a characteristic fauna of the Antarctic regions. In spite of this gradual evolution, the faunistic break between the Cretaceous and Tertiary cannot be clearer than it is in this province.

foreign provinces prevent a closer fixing of its stratigraphic position at the base of the Tertiary. Affinity with Brazil cannot be maintained as v. Ihering proved. Neither can we find relations to the Chilian Tertiary; while there Patagonian and Paraná Formation have their respective equivalents in the Navidad and Coquimbo Beds, we do not know any marine deposits in Chile that could be correlated with the San Jorge. The relations to Madagascar, which have been emphasized by Ameghino<sup>117</sup> and v. Ihering<sup>118</sup> from the point of view of the Cretaceous age to the San Jorge, are of too general a character. The Eocene sediments as well as the formations of the Cretaceous-Tertiary boundary of Madagascar are still very imperfectly known.

Consequently, there only remain the comparisons with Australia and New Zealand, which have been emphasized by Ortmann and v. Ihering with special reference to the Patagonian Formation. But it is not possible to build up on these resemblances a stratigraphic division of a European kind. Marshall<sup>119</sup> in his chapter on the Oamaru-System of New Zealand points out in the first place the great difference of individual opinions. Further, he calls attention to the difficulties that crop up, when the molluscan fauna of such a remote region is compared with the well-limited periods of the European time table in order to establish homotaxial relations. Just the same difficulties are met with in determining the age of South American mammalian faunas, the evolution of which has been influenced by a long lasting isolation.

A lower limit in the determination of the age of the San Jorge is afforded by the close of the great transgression in the Upper Senonian. The regression of the Upper Senonian sea was caused by the movements that led to the breaking down of the ancient Brazilo-Ethiopian (Gondwana) Continent, although some remains of it lasted until the end of the Miocene.<sup>120</sup> These movements were manifested in an orogenetic sense by the first folding of the Cordillera, in an epirogenetic sense by the formation of the South Atlantic basin and the posthumous reopening of the great graben-like depression

<sup>117</sup> Les formations sedimentaires, p. 511.

<sup>118</sup> Les mollusques fossiles, p. 58.

<sup>119</sup> New Zealand and adjacent Islands, Handbuch der Regionalen Geologie, 7, 1, Heidelberg, 1911.

<sup>120</sup> Compare what has been said about "Archhelenis" in Parts I and III.



between the Patagonian continental platform and the structural elements to the north. These are the events that characterize the Cretaceous-Tertiary boundary. They are manifested by the hiatus between the San Jorge and its base. If any sediments should be correlated with this epoch, the upper part of the dinosaur-bearing Pahuénche-Beds and their lacustrine and brackish formations could perhaps be regarded as contemporaneous. Further, the freshwater beds of Lonquimay, first described by Burckhardt,<sup>121</sup> again recently by Felsch,<sup>122</sup> may have been deposited in this period. All these events are approximately contemporaneous with the highest part of the Cretaceous (Danian) and the lowest part of the Paleocene, perhaps the whole Paleocene. The Puerco Beds in New Mexico, the Lance in Wyoming and the Hell Creek Beds in Montana might be correlated with them. Then, *the San Jorge-transgression coincides with the Upper Paleocene or with the Lower Eocene and has to be parallelized with the Libyan Formation, the London Clay or the Kirthar Group of India.* We have recognized that this period was followed by one of regional denudation, which—although lasting only a short time—would, however, require a part of the Eocene, perhaps the whole Eocene. The Casamayor and Deseado (*Notostylops* and *Pyrotherium*) would then come into the Oligocene. This determination agrees not only with the ideas of Loomis and other competent paleontologists about the age of the Deseado fauna; but a series of geologic and physiographic phenomena would also harmonize. The Patagonian Formation, that unconformably follows upon these strata, remains in the Lower Miocene, where the studies of Ortmann fixed it, a long time ago.

Future investigations may produce some small displacements in this scheme, but they will not affect the result that the San Jorge has to be regarded in a diastrophic as well as in a paleontological sense as a forerunner of the Patagonian Formation. The San Jorge marks in Patagonia the beginning of the Tertiary era. It is a link similar in importance to the two other Tertiary transgressions, the Patagonian and the Paraná.

<sup>121</sup> Coupe géologique de la Cordillère entre Las Lajas et Curacautin, Anales Museo La Plata, Secc. Geologica etc., 3, pp. 43 etc., La Plata, 1900.

<sup>122</sup> Las pizarras bituminosas de Lonquimay, Boletín Sociedad Nac. de Minería, No. 220, 32, November and December, 1915. (3) vol. 27, Santiago de Chile.

Thus, the chief result of this paper emphasizes a principle expressed by Pompeckj<sup>123</sup> in the following words: "The great transgressions did not conquer large areas during a short geologic time-unit, but gradually advanced step by step through several geologic periods." The transgression of the San Jorge leveled the way for the subsequent transgressions. Just as we observe on the western border of this continent, in the region of the great Andine geosyncline, from the Liassic through the Dogger and up into the Tithonic and Lower Cretaceous, a gradual acceleration of the transgressions, an enlarging of areas and an increasing of faunistic wealth, so the importance of Tertiary transgressions increased by degrees. These phenomena manifest a law of rhythmical movements; but the explanation of the causes of this rhythm is still as obscure as is the great problem of the primitive causes of crustal movements.

#### CONCLUSIONS.

1. In Patagonia the Cretaceous and Tertiary are obviously separated by a stratigraphic as well as faunistic break.

2. The hiatus at the Cretaceous-Tertiary boundary corresponds to the first phase of the Andine orogenic movements. These movements in the epirogenetic sense caused the breaking down of the Brazilo-Ethiopian Continent, the formation of the South Atlantic basin and the posthumous reopening of the graben-like depression between the Patagonian continental platform and the structural elements of Central and Northern Argentina.

3. The formation of the South Atlantic basin opened the way for the Tertiary transgressions spreading over the Patagonian Continent. The San Jorge-Formation must be regarded as the first of these.

4. The paleogeographic reconstruction of the San Jorge-Sea shows that the shore-lines were in a remarkable manner influenced by ancient structural elements. The northern branch of this sea entered the region of the present mouth of the Rio Negro by way of the graben-like depression at the northern border (fault-scarp) of the Patagonian mass and reached as far as the Rio Atuel. The most southerly deposits of the San Jorge have been observed in the region of the Lago Argentino.

<sup>123</sup> Die Meere der Vorzeit, Göttingen, 1909.

5. The extension of the San Jorge-Formation is limited to Patagonia, just as is the subsequent Patagonian Formation. The ancient mass in the floor of the Sierras of Buenos Aires ("Archhelenis") formed the northern limit of these two epicontinental seas. It was not until the time of the Paraná-Formation (Pliocene) that this mass broke down, opening the way for the Paraná-Sea, that invaded the mouth of the La Plata River and advanced far to the north into the region of the Paraná and Paraguay Rivers.

6. In the paleontologic sense, the San Jorge is of Tertiary character being the forerunner of the Patagonian Formation. Its fossils, however, exhibit a number of similarities to the Pelecypoda and Gastropoda of the Upper Senonian of South Patagonia. It can be proved that all these faunas sprang from the same South Atlantic-Antarctic center, representing a continuous evolution of the original stock. Other affinities of the San Jorge are slight.

7. The age of the San Jorge is Upper Paleocene or Lower Eocene. It may be contemporaneous with the Libyan Formation in Africa, the London Clay in Europe and the Kirthar Group in India.

8. Above the marine deposits of the San Jorge can be observed a peneplain of regional character. Upon this surface have been laid down the sediments with the earliest Patagonian mammal-fauna (*Notostylops*, *Astraponotus* and *Pyrotherium* Beds of Ameghino or Casamayor and Deseado of Loomis). The age of these deposits is fixed as Oligocene, in accordance with the assumptions of many paleontologists. The subsequent Patagonian Formation retains its place in the Lower Miocene.

9. The association of dinosaurs and mammals in Patagonia can be interpreted only by assuming that some branches of dinosaurs (*Theropoda*) still persisted in the Tertiary. The dinosaurs mainly occur in the upper part of the Variegated Sandstones (Pehuenche Beds) of Cretaceous age. The Pehuenche Beds and the mammal-bearing horizons are clearly separated by the interwedging of marine San Jorge and the peneplain cutting into it; but in those regions where the San Jorge fails, the hiatus between Pehuenche and Casamayor or Deseado requires closer attention.

TABLE OF INVERTEBRATES FOUND IN THE SAN JORGE FORMATION AT DIFFERENT LOCALITIES.

	Region of Cañada Colorado (Pircala, Arroyo Pequeño)	Region of the Río Grande	Region of the Sierra Auca Manúda	Surroundings of the village of General Koca, Río Negro	Bajo de Guailichú	Region of the Gulf of St. George	Río Chico, Chubut	Upper course of the Río Sehuen, Santa Cruz
<i>Echinoidea.</i>								
<i>Linthia joannis boelhi</i> Opp. ....				×				
<i>Hemiaster</i> sp. ....					×			
<i>Cyphosoma</i> sp. ....					×			
<i>Vermes.</i>								
<i>Serpula</i> sp. ....		×						
<i>Brachiopoda.</i>								
<i>Bouchardia patagonica</i> Ih. ....		×				×		
<i>Discina</i> sp. ....						×		
<i>Terebratula</i> sp. ....					×			
<i>Terebratella</i> sp. ....					×			
<i>Cephalopoda.</i>								
<i>Nautilus (Aturia) valencienni</i> Hupé. ....				×		×		
<i>Nautilus roemeroi</i> Ih. ....				×				
<i>Gastropoda.</i>								
<i>Calyptrea</i> cf. <i>pileolus</i> d'Orb. (= <i>aperta</i> [Sol.] Boehm) ....				×	×			
<i>Natica</i> sp. ....					×			
<i>Pseudotylostoma roemeroi</i> Ih. ....	×			×				
<i>Paludina</i> sp. ....	×	×						
<i>Scalaria</i> sp. ....					×			
<i>Turritella ameghinoi</i> Ih. ....		×			×		×	
“ <i>doeringi</i> Boehm. ....	×	×		×	×			
“ <i>aff. multistriata</i> Reuss. ....				×	×			
“ <i>malaspina</i> Ih. ....						×		
“ <i>affinis</i> Müll. ....				×				
“ <i>chilensis</i> Sow. ....						×		
<i>Melania cullia</i> Ih.* ....							×	
<i>Potamides patagonensis</i> Ih. ....						×		×
<i>Aporrhais patagonensis</i> Ih. (= <i>rocai</i> Boehm) ....				×	×			
<i>Aporrhais rothi</i> Ih. ....				×	×			
<i>Aporrhais chubutensis</i> Ih. (= <i>striatissima</i> Ih.) ....				×			×	
<i>Aporrhais cosmanni</i> Ih. ....		(X)?		×	×		×	
“ <i>gregaria</i> Wilck. ....				×				
<i>Strutholaria prisca</i> Ih. ....				×	×			
“ <i>ornata</i> , var. <i>densistriata</i> Ih. ....		×						
<i>Cantharidus</i> aff. <i>striolatus</i> Stol. ....				×				
<i>Trophon</i> sp. ....					×			
<i>Fusus</i> sp. (fide Burckhardt). ....	×							
<i>Siphonalia</i> sp. ....					×			
<i>Bulla</i> sp. ....					×			
<i>Pelecypoda.</i>								
<i>Ostrea ameghinoi (rocana)</i> Ih. ....	×	×	×	×	×	×	×	
“ <i>hemisphaerica</i> d'Orb. ....			×	×	×	×		
“ <i>neuquena</i> Ih. ....			×	×	×	×		
“ <i>rionegrensis</i> Ih. ....	×		×	×	×	×		
“ <i>clarae</i> Ih. ....	×		×	×	×			×

\* This form is uncertain; it seems that it proceeds from the strata beneath the San Jorge, the Pehuenche Beds.

	Region of Cañada Colorada (Pircaia, Arroyo Pequeño)	Region of the Río Grande	Region of the Sierra Aca Mañuda	Surroundings of the village of General Roca, Río Negro	Bajo de Gua- liehu	Region of the Gulf of St. George	Río Chilo, Chubut	Upper course of the Río Sehnen, Santa Cruz
<i>Ostrea wilckensi</i> Ih.				×	×			
“ <i>guaranitica</i> Ih.						×		×
<i>Gryphaea rostrigera</i> Ih.				×		×	×	
“ <i>concors</i> Ih.						×	×	
“ <i>pyrotheriorum</i> Ih.						×	×	
“ <i>rothi</i> Boehm.			×	×	×			
“ <i>burckhardti</i> Boehm.	×	×	×	×	×			
<i>Exogyra ostracina</i> Lam., var.								
<i>mendozana</i> Ih.	×	×						
<i>Exogyra callophyla</i> Ih.				×	×	×	×	
<i>Perna</i> sp.			×					
<i>Lima</i> sp.		×						
<i>Hinnites</i> sp.		×						
<i>Pecten</i> sp.			×					
“ <i>piconus</i> Ih.						×		
<i>Chlamys patagonensis</i> d'Orb., var. <i>negroina</i> Ih.		×		×				
<i>Myochlamys salamanca</i> Ih.				×		×		
<i>Pododesmus</i> ( <i>Placunanomia</i> ) <i>valchethanus</i> Ih.					×			
<i>Plicatula</i> aff. <i>multicostata</i> Forb. (fide Burckhardt)	×							
<i>Mytilus</i> sp.		×						
<i>Modiola rionegrensis</i> Ih.				×				
“ <i>andina</i> Ort. **				×				
<i>Nucula dynastes</i> Ih.				×	(X)?			
<i>Malletia ornata</i> Ih.				×				
<i>Arca</i> sp.		×						
<i>Cucullæa</i> ( <i>Arca</i> ) <i>tehuelcha</i> Ih.				×	×			
“ <i>rocana</i> Ih.				×				
<i>Trigonia</i> sp.				(X)?				
<i>Cardita</i> ( <i>Venericardia</i> ) <i>ameghin-</i> <i>orum</i> Ih.				×				
<i>Cardita</i> ( <i>Venericardia</i> ) <i>iheringi</i> <i>Boehm.</i>	×	×		×	×			
<i>Cardita</i> ( <i>Venericardia</i> ) <i>burmeisteri</i> <i>Boehm.</i>		×		×	×			
<i>Cardita</i> ( <i>Venericardia</i> ) <i>palæo-</i> <i>patagonica</i> Ih.				×	×	×	×	
<i>Cardita</i> ( <i>Venericardia</i> ) <i>patagonica</i> Ih.		×						
<i>Cardium</i> ( <i>Hemicardium</i> ) <i>rocanum</i> Ih.				×				
<i>Phacoides</i> (? <i>Cardium</i> ) <i>rocana</i> Ih.				×				
<i>Dosinia burckhardti</i> Ih.		×		×				
<i>Chione</i> ( <i>Venus</i> ) <i>eupyga</i> Ih.				×				
<i>Cytherea chalconica</i> Ih.				×		×		
<i>Tellina burmeisteri</i> Ih.		×		×				
<i>Solecurtus</i> sp.		×						
<i>Lutraria ameghinoi</i> Ih.				×				
<i>Panopæa inferior</i> Wilck. (=P. <i>thomasi</i> Ih.)				×			×	
<i>Corbula sehuena</i> Ih.							×	×
<i>Entomostraca.</i>								
<i>Balanus</i> sp.					×			

\*\* This shell has also been found at the Lake Pueyrredon, according to Ortman and v. Ihering.

ART. II.—*On the Rate of Solution of Silver in Chromic Acid*; by R. G. VAN NAME and D. U. HILL.

(Contributions from the Kent Chemical Laboratory of Yale Univ.—cexevi.)

In a recent study of the rates of solution of metals in oxidizing solutions, the results of which have already been published in this Journal,<sup>1</sup> it was found that when two or more metals under like conditions dissolved at different rates, these rates could be brought into closer agreement by increasing the acidity. The only exception to this empirical rule was observed in the case of silver dissolving in a chromic acid solution containing sulphuric acid. When the sulphuric acid was 0.25 molar the ratio of the rate of solution of cadmium to that of silver was found to be 1.64, while in the presence of 5 molar sulphuric acid this ratio was 2.19, a larger difference in the stronger acid. A conspicuous feature of the experiments with silver in the 5 molar sulphuric acid was the fact that the initial velocity constant of the series was much higher than the succeeding ones, as seen in the following example:<sup>2</sup>

$$k = 1.53 \quad 1.26 \quad 1.20 \quad 1.18 \quad 1.21 \quad 1.23 \quad 1.25$$

This was not the case in the 0.25 molar acid, though the constants showed a slight tendency to decrease as the experiment progressed.

On account of these peculiarities the case seemed to merit a further investigation, which has now been carried out, with the results described below. For this work no changes were made in the apparatus, experimental conditions, or procedure described in the former article. All experiments were at 25°.

At the outset it seemed possible that the effects noted might be due in part to the formation of an interfering coating on the dissolving disk of metal, and as chlorine might act in this manner great care was taken to have the reagents used free from traces of chloride. Later, however, it was found that the addition of small amounts of hydrochloric acid (two or three drops) to the solution at the beginning of the experiment had no measurable effect upon the reaction velocity, since the silver ions

<sup>1</sup> Vol. xlii, 301, 1916.<sup>2</sup> Table X, Exp. 18.

entering the solution quickly precipitated all the chloride in the body of the liquid, and so rendered it innocuous. On the other hand a larger amount of chloride (1 cm<sup>3</sup> of strong hydrochloric acid in 600 cm<sup>3</sup> of solution) soon produced a coating of silver chloride on the disk, and the reaction velocity dropped to zero in a few minutes. Following are the velocity constants obtained in an experiment under these conditions, the duration of the reaction periods being ten minutes each, and the normal value of *k* about 1.95.

$$k = 1.08 \quad 0.09 \quad -0.04 \quad -0.02 \quad 0.12 \quad -0.02 \quad 0.02$$

Further evidence against the hypothesis that coatings on the disk were responsible for the irregularities noted in experiments under normal conditions, was obtained by removing the disk after each reaction period and immersing it for several minutes in strong ammonia before replacing it. This procedure was employed in a number of experiments, but produced no appreciable change in the velocity constants.

The possibility that the depression of the reaction velocity might be caused by the accumulation of silver salt in the solution was also investigated. Such an effect could not, of course, be due to a simple displacement of the equilibrium, as in the case of silver in ferric sulphate,<sup>3</sup> because the reaction between chromic acid and metallic silver is not reversible, but might be produced in some other way. It was found, however, that no measurable change in the reaction velocity was produced by dissolving in the solution at the outset two grams of silver sulphate, an amount considerably larger than that produced during an average experiment. Three successive experiments which illustrate this point are recorded in Table I.

TABLE I.  
Silver (Sample A) in Chromic Acid.

		Sulphuric acid 5 molar.							
Exp. 1.	<i>k</i> =	2.20	2.11	1.88	1.83	2.08	1.92	1.95	Av. 2.00
Exp. 2.	<i>k</i> =	2.27	2.07	1.78	1.90	1.79	1.95	1.88	Av. 1.95
Exp. 3.	Two grams of Ag <sub>2</sub> SO <sub>4</sub> added at outset.								
	<i>k</i> =	2.12	1.88	1.90	2.02	1.93	1.97	1.99	Av. 1.97

At an early stage of the work it became clear that the cause of the variations lay in the metal itself. Two

<sup>3</sup> Loc. cit. p. 310.

samples of silver were used, designated below as Samples A and B, respectively, both obtained from the firm which had furnished the sample used in the former investigation. The rates of solution of these three specimens were all very different, Sample A giving an average velocity of about 1.95, and Sample B of 1.60, under conditions where 1.22 had been obtained in the former work. Moreover, the same sample gave different results according to the amount of metal which had been removed in the preliminary treatment with nitric acid, for the outer layer, owing probably to differences in physical structure produced by the greater stresses undergone in the process of rolling, generally showed a much higher rate of solution than the metal beneath. The following experiment illustrates the behavior of a silver disk which had had only a very light etching with nitric acid before the experiment. After the fourth reaction period (each of 10 minutes) this disk was removed and another disk substituted which had been cleaned as usual with boiling caustic soda, but had undergone no subsequent etching with acid.

*Silver, Sample B. Sulphur acid 5 molar.*

$k = 2.23 \quad 1.62 \quad 1.68 \quad 1.64$ ; (new disk)  $2.24 \quad 2.02 \quad 1.87$

The high initial value of  $k$ , followed by a more or less rapid fall to a comparatively constant final rate, is characteristic. It was only this final rate which was in any way definite and reproducible, and even this often varied considerably for samples cut from different parts of the same sheet. The more serious initial irregularities could of course be avoided by strong preliminary treatment with nitric acid.

For these reasons, in attempting to compare rates of solution of silver in the 0.25 and 5 molar acid we have found it best to use the same disk first in one solution for three or four reaction periods and then in the other. The results of a series of experiments so conducted, in each of which the solution was changed either once or twice, are recorded in Table II.

According to these figures the reaction is about 2.9 times more rapid in the weak than in the strong acid, while the former investigation gave a value of about 3.5 for this ratio. The new result is undoubtedly more correct as the older one was obtained before the sources of



TABLE II.

*Silver (Sample B) in Chromic Acid.*

Reaction periods usually 10 minutes with 5 molar  $H_2SO_4$ ,  
and 7 minutes with 0.25 molar  $H_2SO_4$ .

$H_2SO_4$										Average
1	5.0 molar	.....	1.72	1.74	1.57					1.68
	0.25 molar	.....	4.92	4.71	4.71	4.59	4.81			4.75
2	5.0 molar	.....	1.63	1.46	1.57					1.55
	0.25 molar	.....	4.59	4.50	4.81	4.27	4.67	4.53	4.49	4.55
3	0.25 molar	.....	5.03	5.22	4.91	5.07				5.06
	5.0 molar	.....	1.69	1.51	1.47	1.69	1.44	1.52	1.50	1.55
4	5.0 molar	.....	1.63	1.62	1.54	1.63	1.55			1.59
	0.25 molar	.....	4.36	4.69	4.61	4.82	4.94	4.89	4.76	4.73
	5.0 molar	.....	1.79	1.68	1.60	1.53				1.63
5	0.25 molar	.....	4.74	4.75	4.67	4.78				4.74
	5.0 molar	.....	1.63	1.65	1.44	1.65				1.59
	0.25 molar	.....	4.50	4.20	4.38	4.57				4.41

error were fully understood. The mean value of the constant  $k$  is 4.70 for the weaker, and 1.60 for the stronger acid. Combination of these results with those formerly obtained for cadmium under like conditions, gives for the ratio Cd: Ag the value 1.50 in the 0.25 molar acid, and 1.67 in the 5 molar acid. This still constitutes an exception to the empirical rule that the agreement should be closer in the stronger acid, but the exception is a much less conspicuous one than the former results indicated.

Considering these results from the standpoint of the diffusion theory the most interesting and important fact brought out is the proof of the existence in the case of silver of such large differences in the rate of solution depending upon the physical state of the metal. In the light of that theory we can distinguish, as shown in the former article, two classes of cases, those in which the reaction velocity is determined entirely by the rate of diffusion, and those in which the chemical stage of the reaction also exerts its influence upon the observed result. Differences in the physical state of the metal could affect the reaction velocity in the former case only in so far as they produced considerable variations in the roughness of the surface, for theory and experience alike go to show that slight variations would be without appreciable effect. Moreover, such changes would account, in general, only for an increasing reaction velocity, since it is only in the rarest cases that the surface of the metal would grow smoother as it dissolved, while the progres-

sive changes in the rate of solution of silver observed in the present work, have nearly always been in the opposite direction,—that of decreasing reaction velocity. They are therefore of a kind which would be expected to occur, if at all, only in the cases of the second class, that is, in those in which the rate of the chemical reaction proper has an influence upon the result. As was shown in our former article, it is to this class that the case of silver in chromic acid belongs.

The opposite proposition should also be true. Variations in the rate dependent upon the physical state of the metal and not caused by roughness or impurities should not occur in cases where the rate is governed solely by diffusion. On this point the evidence is rather limited. In our work on the rates of solution of metals we have usually confined our experiments with a given metal to specimens cut from one and the same sheet, so that the conditions were not very favorable for detecting variations of the kind in question, but so far as our experience goes, it confirms the truth of the above proposition. One case, however, which is clearly of the first class, has been much more fully investigated. This is the reaction between cadmium and dissolved iodine, which has been the subject of several papers from this laboratory.<sup>4</sup> Although the cadmium used in these investigations was rolled out into sheets in small quantities at various times, and without any attempt at uniformity of treatment, no characteristic differences were observed in the rates of solution of the numerous different samples so prepared, nor between the behavior of the superficial and the interior layers of metal in a single specimen.

<sup>4</sup> This Journal, 32, 207, 1911; 36, 543, 1913; 43, 449, 1917.

ART. III.—*Early Silurian Rocks of the Northern Peninsula of Michigan*; by T. E. SAVAGE and H. F. CROOKS.

The main body of Silurian rocks in the northern peninsula of Michigan extends in a broad arcuate belt from Garden Peninsula east to Drummond Island in St. Marys River, and represents a northeastward continuation of strata of corresponding age from eastern Wisconsin. The Silurian rocks of northern Michigan have recently been classified by Smith<sup>1</sup> as follows:

Smith's subdivisions of the Silurian rocks of Northern Michigan.

"Silurian."	{	Monroe formation
		(including the Salina).
		Upper Monroe or Detroit River series.
		Sylvania sandstone or middle Monroe.
		Lower Monroe or Bass Island series.
		"Niagara" formation.
		Engadine dolomite or upper "Niagara".
{	Manistique series.	
	Fiborn limestone.	
	Hendricks dolomite or lower "Niagara".	

Smith's classification was made chiefly on the basis of lithology, and is only in part consistent with the paleontologic evidence which the strata afford. Recent studies of the early Silurian rocks of northern Michigan by the writers have brought out the fact that the two lower members of the "Niagara formation" as defined by Smith (the Hendricks dolomite and Fiborn limestone) in this part of Michigan are equivalent in age to the Mayville limestone of Wisconsin.

The Hendricks dolomite and Fiborn limestone are exposed in superposition in the Hendricks quarry and test pit of the Union Carbide Company, in sec. 6, T. 44 N. R. 9 W. This is the type locality for the Hendricks dolomite, and a detailed section of the strata exposed at this place is given below:

<sup>1</sup> Smith, R. A., Mich. Geol. and Biol. Surv., 1915, Pub. 21, Geol. Ser. 17, pp. 148 and 149.

Section of strata exposed at Hendricks quarry and test pit.

FIBORN LIMESTONE:—		Thickness	
		Feet	Inches
24.	Dolomite, gray, thin bedded; vesicular .....	6	
23.	Dolomite, gray, fine grained, badly disintegrated, in places cherty .....	4	
22.	Limestone, brownish-gray to gray, compact, very fine grained, earthy, with sharp conchoidal fracture; the basal part containing crystals of calcite .....	18	

HENDRICKS DOLOMITE:—

21.	Limestone, white, fissile, fossiliferous, with some black streaks, weathering into laminae 1/4 to 2 inches thick .....	8	
20.	Limestone, lithographic; similar to the 18 foot stratum above .....	1	
19.	Limestone, grayish-white, fissile, thin bedded, stylolites structure prominent .....	1	4
18.	Limestone, yellowish-white, hard, massive .....	2	8
17.	Dolomite, yellowish-brown, fossiliferous, massive, crystalline .....	5	9
16.	Limestone, yellowish-brown, soft .....	1	

Downward continuation of section in the test pit.

15.	Limestone, white, with black streaks 1/4 to 2 inches apart; in upper 1 foot there is a tendency to part along bedding planes .....	8	10
14.	Limestone, lithographic, similar to No. 22 .....	1	
13.	Limestone, white, dense, with black streaks .....	2	8
12.	Limestone, whitish, dense, with no streaks .....	1	9
11.	Limestone, yellowish-brown above, passing into gray at the base where it becomes more massive, and contains numerous small solution cavities .....	6	
10.	Limestone in three layers, respectively 9, 13 and 15 inches thick, brownish-gray, fine grained, separated from one another by thin clay bands .....	3	
9.	Limestone, lithographic at base, passing upward into a cherty shale .....	1	6
8.	Shale band .....		3
7.	Limestone, grayish-white .....		7
6.	Shale band .....		6
5.	Limestone, magnesian, grayish-white, crystalline .....	2	
4.	Dolomite, white, highly crystalline .....		9
3.	Limestone, grayish-white .....	1	6
2.	Limestone, white, crystalline .....	1	
1.	Dolomite, gray to white, crystalline, massive, breaking angularly, and exhibiting no bedding. To floor of crusher pit .....	2	

The following species of fossils were collected from the Hendricks dolomite and Fiborn limestone at the Hendricks quarry.

Fossils from the Hendricks dolomite at Hendricks quarry:

Stratum No. 17	{	<i>Zaphrentis</i> sp. <i>Camarotæchia?</i> <i>winiskensis</i> Whiteaves
Stratum No. 19	{	<i>Atrypa putilla</i> (Hall and Clarke) <i>Camarotæchia?</i> <i>winiskensis</i> Whiteaves <i>Cyclonema</i> cf. <i>daytonensis</i> Foerste <i>Illænus</i> sp.
Stratum No. 20	{	<i>Atrypa putilla</i> (Hall and Clarke) <i>Camarotæchia?</i> <i>winiskensis</i> Whiteaves <i>Spirifer</i> sp. <i>Leperditia hisingeri</i> var. <i>fabulina</i> Jones <i>Illænus</i> sp.

The Fiborn limestone in the upper part of the quarry furnished the following species:

*Actinostroma* cf. *tenuiflatum* Parks  
*Favosites forbesi* var.  
*Zaphrentis* cf. *stokesi* Edwards and Haime  
*Atrypa putilla* (Hall and Clarke)  
*Camarotæchia?* *winiskensis* Whiteaves  
*Orthis flabellites* Foerste  
*Plectambonites* cf. *transversalis* var.  
*Schuchertella* cf. *propinqua* (Meek and Worthen)  
*Spirifer* sp.  
*Isochilina grandis* var. *latimarginata* (Jones)  
*Leperditia hisingeri* var. *fabulina* Jones

The presence of *Camarotæchia?* *winiskensis* as a common fossil in these strata is somewhat surprising and very significant, for it is a northern species not previously recognized in the United States.

The ostracods *Leperditia hisingeri* var. *fabulina*, and *Isochilina grandis* var. *latimarginata* are also species that have been described from the Saskatchewan region. *Schuchertella propinqua* occurs in the Edgewood formation in Illinois, and *Atrypa putilla* is a good guide fossil of the Edgewood. *Plectambonites transversalis* var., *Orthis flabellites* and *Spirifer* sp. are not inconsistent with the reference of these rocks to the Edgewood forma-

tion. On the whole this fauna seems to be much more closely allied to that of the Edgewood formation than to any other.

From the fossil lists given above it will be seen that the species of fossils occurring in the Fiborn limestone are quite similar to those in the Hendricks dolomite, but in the former shells of ostracods and coralla of *Favosites forbesi* var. are more numerous than in the latter.

The Fiborn limestone facies appears to represent a large lens of fine-grained limestone that appears to be confined to northern Michigan. This well marked phase has not been recognized farther west in Wisconsin, or farther east in Ontario. It may be noted in the detailed section that occasional layers of fine-grained, non-magnesian limestone, similar to the Fiborn, also occur lower down, in the Hendricks dolomite. The fauna of the Fiborn limestone shows it to be closely allied to the Hendricks dolomite, and it probably represents a local facies of that formation. The fossils of the Manistique series of Smith, which succeeds the Fiborn limestone, are characteristic Niagaran species.

The thickness of the Fiborn limestone varies from place to place, but is not known to exceed 30 feet, and is generally considerably less. The complete thickness of the Hendricks dolomite is known in only a few places. Logs of test borings in the vicinity of Hendricks quarry show a thickness of 145 feet of this formation, and possibly a greater thickness may be found. The thickness of this formation corresponds rather closely to that of the Mayville limestone in Wisconsin, where an aggregate thickness of 149 feet was penetrated in a boring on the floor of a quarry south of Mayville.<sup>2</sup>

About one-half mile north of Hendricks quarry the Fiborn limestone is exposed near the top of a bluff 90 feet high, but the underlying Hendricks dolomite is concealed by a heavy talus. From numerous limestone fragments in this vicinity moulds and casts of shells of *Virgiana barrandei* var. *mayvillensis* were collected, and the ledge from which they came is probably no great distance from this exposure. Three-fourths of a mile north of the Blaney quarry of the White Marble Lime Company, two and three-fourths miles north of Blaney Junction, the Hendricks dolomite is exposed over an area a

<sup>2</sup> Savage, T. E., Bull. Geol. Soc. Am., vol. xxvii, p. 308.

few hundred square yards in extent. The rock is here a coarse-grained, sandy, bluff dolomite which contains a few fossils among which were the following species:

*Favosites forbesi* var.

*Atrypa putilla* (Hall and Clarke)

*Camarotæchia?* *winiskensis* Whiteaves

*Homæospira subcircularis* ? Savage

*Spirifer* sp.

*Leperditia* cf. *hisingeri* var. *fabulina* Jones

From fragments of limestone in the drift on Garden Peninsula north of Van's Harbor, excellent moulds and casts of *Virgiana barrandei* var. *mayvillensis* were obtained. The glacial drift in this region is immediately underlain by rocks of Niagaran age, and the *Virgiana* zone was not found in place at this locality.

On the west side of Lime Island, in St. Marys River, casts and molds of shells of *Virgiana barrandei* var. *mayvillensis* are abundant in the upper part of a ledge of coarse-grained, cream-colored dolomite that corresponds to the Hendricks formation farther west, and is overlain by a bed of fine-grained limestone that resembles the Fiborn.

Through the kindness of Professor E. C. Case, the writers have examined specimens of *Virgiana barrandei* var. *mayvillensis* that were collected from Limestone Mountain in the southeast part of Houghton County, Michigan. There is no doubt that the zone of *Virgiana barrandei* var. *mayvillensis* in the northern peninsula of Michigan represents an eastward continuation of the horizon of the Mayville limestone in Wisconsin.

The senior writer has previously shown that the early Silurian rocks included between the top of the *Virgiana* zone and top of the underlying Maquoketa in Wisconsin correspond in age to the Edgewood formation of Illinois and Missouri. Consequently, the Hendricks dolomite and probably also the Fiborn limestone in northern Michigan, including all of the Silurian strata between the top of the zone containing *Virgiana barrandei* var. *mayvillensis* and the top of the Maquoketa, and which contain fossils consistent with the Edgewood, are considered the time equivalents of some part of the Edgewood formation, and are thus much older than the Niagaran.

A noteworthy fact in connection with the fauna of these rocks in northern Michigan is the presence of *Camarotochia? winiskensis* in all of the exposures of both the Hendricks dolomite and the Fiborn limestone that were examined. This species was described by Whiteaves from the lower strata of the Silurian system near the mouth of Winisk River, west of Hudson Bay; and has more recently been found by the senior writer in rocks near the base of the Silurian not only along that river, but also along the Ekwon and the Severn rivers in that region. In all of these localities it came from Silurian rocks which had been considered about the age of the Guelph, but which are thought by the writer to be probably pre-Niagaran in age. These occurrences suggest that during a part of Alexandrian (Edgewood) time there was an extension of the Arctic sea as far south as Michigan and Wisconsin, in which the early Silurian rocks of these states were laid down.

University of Illinois,  
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ART. IV.—*A Second Meteorite Find in Florida*;\* by  
GEORGE P. MERRILL, Head Curator of Geology, U. S.  
National Museum.

The stone described below was received from Mr. John W. Alger of Eustis, Florida, accompanied by the statement that it was found by his father when plowing some new land from which the trees had been recently cut. The soil was what is locally known as high, sandy pine-land and the stone lay but four inches below the surface. Although considerably discolored by oxidation, its meteoric nature was at once recognized. As received the stone was plainly a fragment from a larger mass fractured before reaching the earth. The primary incrustation was still evident over a considerable portion of the surface with thinner crusts on surfaces of more recent fracture. The weight of the entire mass was but 502 grams.

\* Published with permission of the Secretary of the Smithsonian Institution.



A polished surface is dense dark brown in color, abundantly besprinkled with small flecks of metal and with a chondritic structure very obscure owing to the similarity in color of chondrules and ground. In thin sections the stone is found to be so badly discolored and otherwise injured by oxidation of the ferruginous minerals as to make microscopic determinations somewhat difficult. Olivine, enstatite and twinned monoclinic pyroxenes together with nickel iron form the recognizable constituents. The structure is chondritic, the individual chondrules often fragmental but showing no uncommon variations. The ground is distinctly fragmental, a condition much exaggerated by oxidation. The iron sulphide still retains in part its original identity, but the staining by oxidation so obscures minor details that the presence or absence of other minerals than those noted cannot with certainty be made out. No chemical analysis has been deemed worth the while under the conditions mentioned.

Eustis is situated in Lake County, about Latitude  $28^{\circ} 20'$  north, Longitude  $81^{\circ} 40'$  west, 150 miles south of Jacksonville and about 130 miles northeast of Lake Okechobee. This last distance is given from the fact that the stone so closely resembles in structure, mineral composition and oxidized condition that recently described by the writer<sup>1</sup> as to at once suggest its being a part of the same fall. Nevertheless, the distance is so great that in view of the lack of confirmatory evidence, it seems best to distinguish it for the present by an independent name. Mr. Alger states that a family living about 2 miles from Eustis saw, about 25 years ago, a meteorite fall and made fruitless search for it, contenting themselves with a fragment of sandstone which they mistook for the object in question. The meteor as seen was traveling toward Eustis and it would seem probable at least that this was the one here described. The stone will be classified as a spherulitic chondrite and, pending further information, known as the Eustis stone, the second find of meteorites within the state limits of Florida.

<sup>1</sup> A Newly Found Meteoric Stone from Lake Okechobee, Florida, Proc. U. S. National Museum, vol. 51, pp. 525 and 526, 1916.

ART. V.—*On Mullanite, a new Member of the Jamesonite Group, from Two Localities*; by EARL V. SHANNON.

Quite recently the present writer published a short note on the occurrence of the rare sulphantimonite, epiboulangerite, at the Iron Mountain mine, near the town of Superior, in western Montana.<sup>1</sup> Very soon after this note was submitted for publication, there was obtained a mineral very similar in appearance and associations, from the Gold Hunter Mine, near the town of Mullan, in the Coeur d'Alene District, Idaho. Only a small amount of the Idaho material was available and the most striking fact brought out by the preliminary investigation was that the streak was distinctly brown, while that of epiboulangerite is dull grayish black. A request for more of the mineral was directed to the Gold Hunter Company, and Mr. C. L. Herrick, manager of the mine, responded by sending some excellent specimens. While awaiting the arrival of the Idaho material, the writer undertook to analyze more completely, a very fine specimen of the sulphantimonite from the Iron Mountain mine. The streak of this mineral was found to be brown like that of the Gold Hunter material, and analysis showed that it was not epiboulangerite but a mineral having the composition expressed by the formula  $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$ . The mineral from the Gold Hunter Mine, later received from Mr. Herrick, proved to have the same composition.

While the composition is essentially that of a silver-free diaphorite, that mineral as described contains silver to the amount of around 23%, the ratio of  $\text{Pb} : \text{Ag}_2$  being 4:3. That the compound is distinct, and not a variable mixture of the two end members,  $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$ , and  $5\text{Ag}_2\text{S} \cdot 2\text{Sb}_2\text{S}_3$ , is established by the fact that the compound  $5(\text{Pb}, \text{Ag}_2)\text{S} \cdot 2\text{Sb}_2\text{S}_3$  in its two forms, has been found from a number of widely separated localities, yet in all observed occurrences the silver and lead are present in the same ratio. The mineral described below can thus no more be regarded as a variety of the species diaphorite than chalcocite can be regarded as a variety of stromeyerite, or than calcite can be regarded as a variety of dolomite. The mineral here described is free from silver and hence seems to deserve a distinctive

<sup>1</sup> American Mineralogist, vol. 2, No. 11, 1917.

name. The name *mullanite* is after Capt. John Mullan, who in 1858 began construction on the military road connecting Fort Benton, Montana, with Fort Walla Walla, Wash. The Mullan Road furnished a means of access to the Coeur d'Alene region and resulted in the discovery of the important mineral deposits of the district. Both of the mines in which the new mineral has been

FIG. 1.

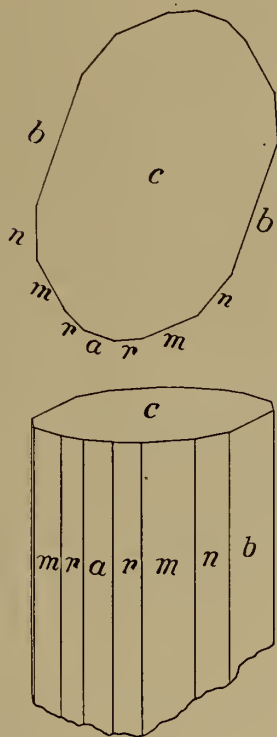
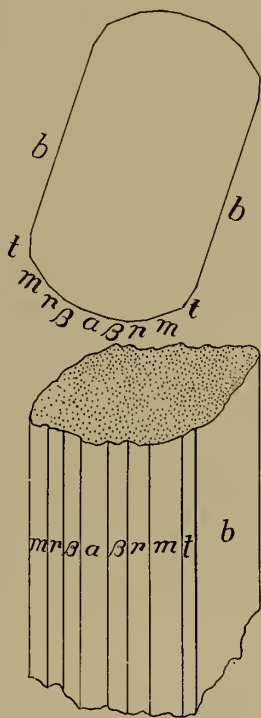


FIG. 2.



found are located near this old highway. Incidentally the name indicates one of the localities, Mullan, Idaho, also named after Capt. Mullan.

*Occurrence.*—The mode of occurrence of mullanite in the Iron Mountain Mine is the same as that described for epiboulangerite. No distinction was made between the two minerals in the field. The gray sulphantimonite occurs in grains and minute needles throughout the vein material and the granular sphalerite of the ore, constituting about 15% of the zinc ore as shipped. It also occurs as bunches and masses of fibers in snowy white quartz

which seems to cut the main mass of the vein. The mullanite and the epiboulangerite look exactly alike in the hand specimen, being distinguished from each other only by their streak and in what proportion they occur is not known. Of five specimens examined, only one consisted of epiboulangerite, which, therefore, is believed to be somewhat rarer than mullanite. There is no indication that the epiboulangerite is secondary or an alteration product of the mullanite.

In the Gold Hunter Mine, mullanite is a constant, though not abundant constituent of the ores. It has for years been thought to be stibnite. Ransome,<sup>2</sup> writing about 1905, gives the following: "Stibnite (=mullanite) has been found, in this district, only in the Gold Hunter Mine and in a neighboring prospect, the Enterprise. In the Gold Hunter the stibnite forms small needles or acicular clusters in quartz, or, more rarely, in siderite. In some of the quartz, the needles project into little vugs. The mineral occurs sporadically in the quartzose parts of the lode, usually near the hanging wall." This so-called stibnite seems to be the sulphantimonite, mullanite. Whether the mineral mentioned by Ransome from the Enterprise prospect is the same is not known. Material, indistinguishable from mullanite in appearance, from the Greenhill-Cleveland Mine contains only 36.4% lead and is probably jamesonite. A similar mineral from the Bunker Hill & Sullivan Mine contains lead in unknown proportion. The two mines in which mullanite occurs, although near 40 miles apart, are strikingly similar in many respects. The veins are inclosed in rocks of the same geologic formation.

*Description.*—The specimen from the Iron Mountain Mine consists of an aggregate of long, parallel, steel-gray fibers. In the lower end of the specimen, a rounded crystal of quartz is embedded. The fibers of mullanite curve around this quartz fragment which has somewhat the appearance of a water-worn pebble. Needles of mullanite occur also imbedded in the quartz. At the upper end of the specimen the needles project into an open cavity and are squarely truncated by a flat plane. The aggregate of fibers is friable and can be easily broken up with the fingers.

<sup>2</sup> Prof. Paper, U. S. Geol. Survey, No. 62, p. 92.

The Gold Hunter specimens occur in quartz and consist of fine matted, wool-like masses of dark gray fibers and compact, steel-gray fibrous material having somewhat the appearance of Astrakhan fur. The fine fibers in the cavities rest upon a base of small quartz crystals or of translucent buff crystals of siderite. The matted aggregates also contain scattered, minute, perfect crystals of quartz and siderite.

*Crystallography.*—The crystals of mullanite are prismatic needles, deeply striated and somewhat flattened parallel to the brachypinacoid. On the specimen from the Iron Mountain Mine, the free needles are truncated by a terminal face which is perpendicular to the prismatic direction and was taken as the basal pinacoid. The crystals are provisionally considered orthorhombic. The prism zones of the crystals from Iron Mountain do not yield reflections of the signal and only after trying a dozen or more, was a very minute needle found which gave reflections indicating the forms shown in fig. 1. All attempts to refer the observed faces to the axes of diaphorite and freieslebenite were unsuccessful. The prism  $m$  in the drawing was taken as the unit prism (110). Only a single crystal was found in the material from the Gold Hunter Mine, which gave even approximate values for the interfacial angles. This was a deeply striated prism, flattened parallel to (010), broken at both ends and having essentially the form shown in fig. 2. The value for the  $a$ -axis on the crystal shown in fig. 1 was 0.85, and on the crystal fig. 2 was 0.82. Provisionally the mean between these is taken to represent the length of the  $a$ -axis in terms of the  $b$ -axis, thus:

$$a : b : c = 1 : 0.835 : x$$

The forms observed on the two crystals measured are then:

$a(100)$	$m(110)$	$n(130)$
$b(010)$	$r(120)$	$t(140)$
$c(001)$	$\beta(510)$	

It should be remembered, however, that the measurements were based upon barely perceptible reflections of the signal, or in some cases, upon light reflected from the faces. The crystallographic data are certainly subject to revision should well-crystallized material be found. Some very minute fibers from a cavity in quartz in one of the Gold Hunter specimens, examined under the

microscope by means of a vertical illuminator, had chisel shaped terminations which suggested monoclinic symmetry, but none of these terminated crystals was large enough for measurement. It is not improbable that the compound  $5\text{PbS}\cdot 2\text{Sb}_2\text{S}_3$  is, like the similar compound,  $5(\text{Pb}, \text{Ag}_2)\text{S}\cdot 2\text{Sb}_2\text{S}_3$ , dimorphous, and both forms may be present in the Gold Hunter ores.

*Physical Properties.*—Specific gravity, 6.274 on coarse fibers from Iron Mountain, 6.407 on fine fibers from the Gold Hunter Mine. The last is probably the true value for the mineral as the former may have contained some included air. Color steel-gray, of free crystals somewhat darker due to tarnish; hardness 3.5; luster metallic to metallic-adamantine; opaque; streak, when rubbed upon unglazed porcelain, gives a somewhat shining brownish-black streak which when rubbed fine with a blunt end of a test tube or some other hard object, becomes first more metallic and then a distinct brown. This constitutes the only ready method of distinguishing this mineral from the associated epiboulangerite, the streak of which is dull grayish-black. Habit, prismatic-fibrous; cleavage,  $c(001)$  and  $b(010)$  distinct,  $a(100)$  and probably  $m(110)$ , imperfect. The thick fibers from Iron Mountain are brittle. The flexibility of the Gold Hunter needles depends directly upon their thickness, the thinner fibers being very flexible while the thickest ones are quite brittle.

*Composition.*—The composition of mullanite is shown in the following table:

	I	II	III	Ratios			IV	V
Sb	25.73	25.69	25.71	.2140	or 1.00	or 4	25.725	24.67
Pb	55.125	54.926	55.046	.2664	1.25	5	55.405	53.331
S	18.665	18.970	18.817	.5869	2.74	11	18.869	18.112
As	.249	.249	.....	.....	..	..	.....	.641
Cu	0.00	0.00	.....	.....	..	..	.....	0.00
Fe	trace	trace	.....	.....	..	..	.....	1.47
Total	99.77	99.835	98.563	....	...	..	99.999	98.224

I, II. Mullanite, Iron Mountain Mine, Superior, Mont.

III. Mullanite, average of I and II.

IV. Mullanite, values calculated for the formula  $5\text{PbS}\cdot 2\text{Sb}_2\text{S}_3$ .

V. Mullanite, Gold Hunter Mine, Mullan, Idaho. The iron represents siderite (3.04%) present as impurity. Pure needles of mullanite contain no iron.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *The Solubility of Bismuth Oxychloride in Hydrochloric Acid and its Relation to Complex Formation.*—ARTHUR A. NOYES, FRANK W. HALL and JAMES A. BEATTIE have made an investigation of this subject and have reached interesting conclusions in regard to the condition of the dissolved substance in the solution. In the first place, it was found that the electrical conductance of hydrochloric acid solutions was decreased by dissolving the bismuth oxychloride in them. This fact indicated that the bismuth chloride in solution could not be in an ionized condition, for with  $\text{Bi}^{+++}$  and  $3\text{Cl}^-$  or with  $\text{BiCl}^{++}$  and  $2\text{Cl}^-$  the conductance would be much increased. Moreover, if  $\text{BiCl}_3$  molecules were formed, without ionization, the conductance would be little changed, while if complex combinations with  $\text{HCl}$  were formed, resulting in  $\text{BiCl}_4^-$  or  $\text{BiCl}_5^-$  ions the conductance should decrease. The fact, therefore, that a pronounced decrease was observed shows that the complex anions are present in large proportion. Calculations made from the results of a series of determinations indicated that the substance formed in the solutions might be either  $\text{HBiCl}_4$  or  $\text{H}_2\text{BiCl}_5$ , and the latter seemed to be the more probable one in cases where a considerable excess of hydrogen chloride was present.

A further investigation of the matter was made by finding the solubility of the oxychloride in hydrochloric acid of various strengths. When these results were calculated from a mass-action standpoint they were found to be intermediate between  $\text{HBiCl}_4$  and  $\text{H}_2\text{BiCl}_5$ , thus confirming the results derived from the conductance. It is interesting to observe that alkali-metal salts of both these acids have been prepared.—*Journ. Amer. Chem. Soc.*, **39**, 2526.

H. L. W.

2. *A Revision of the Cobalti-Nitrite Method for the Determination of Potash.*—On account of the high price of platinum and the advantages of a volumetric method, the cobalti-nitric process has come into rather extensive use in the determination of potassium. C. R. HAFF and E. H. SCHWARTZ have described their application of the method in the examination of cement materials, including the flue-dust, and it appears that their method is satisfactory and convenient. The details need not be given here, but it is of interest to notice that they decompose clinker and raw materials by the well known "fusion" of J. Lawrence Smith, precipitate the triple salt,  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ , without separating calcium, and finally titrate by the use of an excess of permanganate, then, after acidifying with sulphuric acid, adding an excess of oxalic acid, and at last the proper

amount of permanganate. The reaction of permanganate with the cobalti-nitrite precipitate is represented by a rather complex equation where  $22\text{KMnO}_4$  are equivalent to  $10\text{K}_2\text{NaCo}(\text{NO}_2)_6$ . The authors derive their factor from the calcium oxide factor used in the titration of calcium oxalate with permanganate, but perhaps they would have made the matter clearer to chemists generally if they had stated that the normal quantity in the reaction is  $1/11$  of the formula weight of  $\text{K}_2\text{O}$ , or Fe factor  $\times 0.1532 = \text{K}_2\text{O}$  factor.—*Jour. Indust. Eng. Chem.*, **9**, 785.

H. L. W.

3. *The Estimation of Arsenic in Organic Compounds.*—A. J. EWINS has applied for this purpose a modification of the method of Norton and Koch, which was devised for the determination of arsenic in animal tissues. To apply the method to organic compounds, such as salvarsan, for example, a portion of from 0.1 to 0.2 g is weighed and washed into a long-necked Kjeldahl flask by means of a little water, 10 g of potassium sulphate, 0.2 to 0.3 g of starch and 20 cc of concentrated sulphuric acid are added, and the flask is heated as in the ordinary nitrogen determination until the liquid is colorless or nearly so. This usually requires about 4 hours. After cooling, the residue is taken up with water, transferred to a 350 cc flask, a solution of sodium hydroxide is then added from a burette until the liquid is just distinctly alkaline to litmus paper, a piece of which may be put into the solution. The contents of the flask are then cooled to about 30 or 40° and a few drops of concentrated sulphuric acid added until the liquid is again distinctly acid. A cold-saturated solution of hydrogen sodium carbonate is then added from a burette until an excess of 5 or 10 cc of the reagent is present. The arsenic is now titrated by means of  $N/20$  iodine solution in the presence of starch solution as an indicator. The test-analyses carried out by the author upon a large number of complex arsenic compounds show excellent results.—*J. Chem. Soc.*, **109**, 1355.

H. L. W.

4. *A Calorimeter for Measuring Heats of Dilution.*—D. A. MACINNES and J. M. BRAHAM have devised a calorimeter which seems to be worthy of special mention on account of its remarkable delicacy and accuracy. It is a modification of the adiabatic calorimeter of T. W. Richards. In the Richards instrument a bath surrounding the calorimeter is kept throughout the determination at the same temperature as that in the vessel in which the heat is being evolved. This arrangement eliminates the radiation and conduction of heat from the calorimeter, but a correction must be made for the heat effect due to stirring. In the new modification the outer bath is kept at a temperature slightly lower (about 0.15°) than that of the calorimeter. This difference of temperature is the one at which a thermometer inserted in the calorimeter remains constant indefinitely. This modification of the adiabatic method makes the use of platinum



resistance thermometers reading to 0.0001° practical and convenient. For further details reference must be made to the original article.—*Jour. Amer. Chem. Soc.*, **39**, 2110. H. L. W.

5. *The Detection of Carbon in Inorganic and Organic Substances.*—ERNST MUELLER has described a general method for the qualitative detection of carbon. A mixture of about 0.02 g of the substance to be tested is mixed with roughly 20 times its weight of potassium trinitride,  $\text{KN}_3$ , and the mixture is heated gently at first, then finally for two minutes at a red heat. Potassium cyanide is formed when carbon is present in any form and this may be detected in the usual way by conversion into Prussian blue. The test, which is rendered still more delicate by the addition of a little metallic potassium to the reaction mixture, can be applied not only to organic compounds but also to steel and carborundum.—*Jour. prakt. Chem.*, **95**, 53 (through C. A.).

H. L. W.

6. *The Extreme Ultra-Violet Spectra of Helium, Hydrogen, and Mercury.*—The region of the spectrum between the shortest wave-length (about 590 Å) obtained by Lyman and the longest X-ray wave-length (approx. 12.3 Å) given in Siegbahn's tables is a very important one, hence the recent investigation of one end of this gap by O. W. RICHARDSON and C. B. BAZZONI merits special attention. The most serious difficulties encountered by Lyman in his important work with the so-called vacuum spectrograph were (i) the absorption of the radiation in question by the two meter layer of gas between the luminous source and the photographic plate, (ii) the fogging of the plate by the fluorescence excited in the gas, and (iii) the introduction of traces of impurities in the gas. It is practically impossible to prevent contamination when the apparatus cannot be heated and when the discharge takes place in the gas itself. To avoid the limitations apparently inherent in the vacuum spectrograph, Richardson and Bazzoni designed and used a complicated quartz apparatus which could be kept at a red heat until all occluded gases had been pumped out prior to the introduction of the pure gas.

The most essential features of the quartz apparatus and the functions of its various parts may be briefly described or explained as follows. One cylindrical portion of the system contained a tungsten filament, a copper plate anode, and an auxiliary copper wire anode. The tungsten filament was used as a thermionic source of electrons for exciting the radiation in the gas. The cylinder just mentioned was connected to a larger quartz chamber by a tube of rectangular cross-section made of the same material. This tube contained a pair of condenser plates which prevented the passage of electrons and ions from the cylinder to the vessel beyond. The ultra-violet waves could, of course, pass unhindered between the plates. After entering the chamber the waves fell upon a copper target and liberated photo-electric electrons. At 90° and at 180° from the target

two copper diaphragms, each perforated with one slit, were so placed as to cause the long axes of the target and slits to lie in the (geometrical) surface of a right circular cylinder. This portion of the apparatus was supported inside by a double coil of the Helmholtz type. Accordingly, when the magnetic field was excited, the paths of the photo-electrons were bent around in circles or helices some of which would have just the right radii to pass through the two slits. After so doing, these electrons entered a copper cup and indicated their arrival by the deflection of the associated electrometer.

If  $r =$  radius of path and  $H =$  magnetic field strength, then the speed of the photo-electrons may be calculated at once from the relation

$$v = \frac{e}{m} r H.$$

The impinging frequency corresponding to any particular speed is determined by the equation

$$\frac{1}{2} m v^2 = e V = h(\nu - \nu_0).$$

In this formula  $\nu_0$  denotes the frequency at which photo-electric emission from copper begins. Using  $m = 0.898 \times 10^{-27}$ ,  $h = 6.55 \times 10^{-27}$ , and  $\nu_0 = 0.38 \times 10^{15}$  it follows that

$$\nu = 0.0686 v^2 + 0.38 \times 10^{15}.$$

Therefore, the maximum and minimum frequencies can be computed directly from the corresponding speeds.

The most important results obtained from this investigation may be summarized as follows: "The helium spectrum extends to a limit which is certainly between 470 and 420 and probably near to the latter value. The hydrogen spectrum terminates at a wave-length between 830 and 950 Angström units and probably close to 900. The mercury spectrum terminates at a wave-length between 1000 and 1200 Angström units.

So far as we are able to ascertain, the observed terminal frequencies are identical with the frequencies calculated from Bohr's theoretical values of the ionization potentials of the respective gases, and they exhibit no obvious relationship to the ionization potentials which have been determined experimentally by Franck and Hertz and others."

"The high frequency limits of the spectra referred to are independent of the applied potential up to about 800 volts, provided this potential exceeds a lower limit which has not been determined with any accuracy."—*Phil. Mag.*, **34**, 285, 1917.

H. S. U.

7. *Navigation*; by HAROLD JACOBY. Pp. xi, 330. New York, 1917 (The Macmillan Co.).—In his preface, the author sets forth very clearly the definite aims which he has endeavored to attain in preparing the text. These may be summarized as:

(i) the volume is complete in itself, so that it should enable the beginner to acquire all the information necessary for the navigation of a ship in any ocean not too close to the poles of the earth, (ii) it is assumed that the reader neither possesses nor desires to acquire formal mathematical and astronomical knowledge, (iii) the requirements of those who may study without a teacher have received constant and special attention, and (iv) no attempt has been made to include every method that can possibly be used to navigate a ship but, on the contrary, the volume has been limited to the methods at present considered the best by the most reliable modern authorities.

An idea of the scope of the text, and of the way in which the above mentioned problems have been attacked, may be gleaned from the titles of the chapters, which are: "The Fundamental Problem of Navigation, Dead Reckoning without Logarithms, Dead Reckoning with Logarithms, The Compass, Coastwise Navigation, The Sextant, The Nautical Almanac, Older Navigation Methods, Newer Navigation Methods, and A Navigator's Day at Sea."

The entire subject-matter is presented in a very readable, lucid style, the last chapter being especially interesting. The condensed, but complete, tables extend from page 154 to page 322. The only auxiliary book required by the novice is the nautical almanac for the year in which the voyage is to be made. The diagrams are clear-cut, and special care has been taken to reduce the number of typographical errors to a minimum. It is thus clear that the book seems very well adapted to attracting students to the fascinating and important subject of navigation.

H. S. U.

8. *Practical Pyrometry*; by ERVIN S. FERRY, GLENN A. SHOOK, and JACOB R. COLLINS. Pp. vii, 147, with 73 figures. New York, 1917 (John Wiley and Sons).—In preparing the text, the authors have kept in mind the needs of three distinct classes of readers, namely—college students, technically trained men who deal with processes involving high temperature determinations, and relatively untrained observers. For the benefit of the first two classes, the underlying principles and the theoretical consequences of the same are fully discussed. The requirements of the third class are met by descriptions of the various types of apparatus, by explanations of the manipulation of the instruments, and by directions for the performance of fourteen experiments on calibration, temperature determinations, etc.

The successive chapters deal respectively with: standard temperature scales, resistance pyrometry, thermoelectric pyrometry, radiation pyrometry, and optical pyrometry. The selection of material and the conciseness of presentation should make the book very useful. On the other hand, the text is somewhat marred by lack of sufficient care in proof-reading. Most of the slips are obvious, but a few of them tend to confusion of

ideas. For example, on page 5, the following sentence occurs: "It is found that the temperature of melting ice expressed in centigrade degrees on the thermodynamic scale is about  $273.7^{\circ}$  C. on the thermodynamic scale." H. S. U.

9. *The Mystery of Matter and Energy*; by ALBERT C. CREHORE. Pp. xii, 161. New York, 1917 (D. Van Nostrand Co.).—The avowed object of this little book is an attempt to state what the problem of the structure of matter really is, in the hope that the mere statement will arouse enthusiasm and prove to the reader the fundamental, all-embracing character of the problem, including in the final analysis all other physical problems. The text has been kept entirely free from mathematical symbols in order that it may be useful to the general reader as well as to the specially trained scientist. The subject-matter involves, among other topics, the discovery and properties of electrons, the electromagnetic theory of light, X-ray phenomena, the gravitational problem, the principle of relativity, and the scientific contributions of J. J. Thomson, Lorentz, Planck, Michelson, Millikan, etc.

After reading the book through the writer of this notice came to the following conclusions. The text is largely built up from the mathematical papers written by the author. In the absence of the mathematical analysis the reader is forced to accept the statements and deductions made, without being able to check the validity of the hypotheses involved or the steps in the analysis. The impression produced may be concisely expressed by saying that the text seems to be "dangerous" for the general reader. This adverse criticism applies particularly to the discussion of gravitation. Moreover, in a few instances the text is confusing. For example, on page 14 may be found: "The electron is always associated with a negative charge of electricity, . . ." On pages 18, 19, and 71, on the contrary, positive electrons are introduced either directly or by implication. H. S. U.

## II. GEOLOGY.

1. *The Structure of the Himalayas, and of the Gangetic Plain, as Elucidated by Geodetic Observations in India*; by R. D. OLDHAM. Pp. 153; figs. 13. *Memoirs Geol. Surv. India*, Vol. 43, pt. 2, 1917.—This is the most important memoir which has been published on the bearing of the geodetic evidence to the geologic structure of northern India and the Himalayan mountain system. The geodetic evidence of the existence of a condition of isostasy in the crust was first established in India, more than half a century ago, but has recently been elaborated by Major Crosthwaite. The Himalayas, the greatest mountain system of the globe, is also one of the youngest and perhaps the best adapted to show the relations of compressive and eleva-

tory forces in mountain growth. In front of the great range are foothills of folded and uplifted Pliocene strata. Beyond these to the south is the great Indo-Gangetic trough of alluvium.

Oldham has computed the effects of these several provinces on the deflections of the plumb-line under the hypothesis of isostasy and compared these with the actual deflections. He finds that under the central part of the range the complete isostatic flotation would require a somewhat greater elevation than now exists but that the foothill range, on the contrary, is over-elevated, perhaps to the extent of about 2,000 feet. The weight of this over-elevated zone is given as the cause for the depression of the Indo-Gangetic trough; the latter, from the defect of gravity, is concluded to be between 15,000 and 20,000 feet deep to the bottom of the alluvium, the deepest part lying near the mountains.

The results indicate a considerable strength of the crust, enabling a load in one place to be partly supported by the surrounding zone. The degree of isostasy found in the Himalayan system as a whole, however, Oldham takes as indicating that the vertical forces of uplift are more fundamental in producing the regional elevations than are the horizontal forces of compression. The arguments against various older hypotheses are also presented.

J. B.

2. *The Origin and Evolution of Life*; by HENRY FAIRFIELD OSBORN. Pp. xxxi + 322, 136 figs. New York, 1917 (Charles Scribner's Sons).—This comprehensive and abundantly embellished book seeks to synthesize all the interrelated sciences toward an explanation of the origin and evolution of life, on the theory of action, reaction and interaction of energy. In these Hale Lectures of the National Academy of Sciences the author takes "the initial steps toward an energy conception of Evolution and an energy conception of Heredity and away from the matter and form conceptions which have prevailed for over a century" (vii). The book is symbolic of the present trend toward a centralization and synthesis of related sciences. It is one of the first on this new road of intellectual endeavor and is a good model. That this road of evolution under the energy concept will be difficult and even dangerous for the pioneer travellers is a foregone conclusion. This Professor Osborn knows, and when on unfamiliar ground he introduces the specialist for the part and allows him to revise the compiler's statements so that all may be in order in the general setting of the book. The author does not "pretend to offer an explanation of the miracles of adaptation and of heredity," but he recites them "to show that the germ evolution is the most incomprehensible phenomenon which has yet been discovered in the universe" (vii). Further, that "the causes of the evolution of life are as mysterious as the law of evolution is certain" (ix).

The first chapter of the book deals with the "preparation of the earth for life" in a study of the composition of the lifeless

earth, air, and water. Then the "physicochemical origins of life" are considered, followed by a study of the "energy evolution" of plants and the "evolution of animal form." The four complexes of energy at the basis of life are (1) inorganic environment, (2) the organism, (3) the heredity germ, and (4) life environment.

If the reader is to put himself in accord with the book, he will first read the Preface, scan the succeeding pages, and take up for study Part II, following this with a study of Part I and the Introduction, and then end with a re-reading of the Preface. Of course this is a long road to the attaining of Professor Osborn's point of view, and yet the effort will be worth the reader's time. If the reader follows this course, he will be more than ever impressed with the extraordinary complexities involved in the evolution of life, and with the fact that the subject can not be understood without a general knowledge of the evolution of that matter out of which organic bodies and the manifestations of life are evolved. Though our search for causes of the evolution of living matter began with Buffon 150 years ago, our insight into them has only just begun. c. s.

3. *The Cretaceous Faunas of the North-eastern Part of the South Island of New Zealand*; by HENRY WOODS. New Zealand Geol. Survey, Pal. Bull. No. 4, 1917, 41 pp., 20 pls., 2 figs. (maps).—In this memoir are described by a specialist sixteen species of bivalves (six new) from the earlier Cretaceous (Albian) and fifty-one (twenty new) from the Senonian. About one third of the forms are unnamed specifically. It is interesting to note that the fossils of the southern hemisphere are being studied more and more by paleontologists from the northern one. It is in this way that we shall finally learn to know the actual differences between the life of any given time in the two hemispheres, and the reviewer sees no danger at all that the paleontologists of the north will see the fossils of the austral region too much in the light of their own environment. c. s.

4. *New and Little Known Gastropoda from the Upper Cretaceous of Tennessee*; by BRUCE WADE. Proc. Acad. Nat. Sci. Philadelphia, Sept., 1917, pp. 280-304, pls. 17-19.—This interesting paper describes eight new genera and seventeen new species of gastropods out of a total of 151 forms of this class of mollusks in a fauna of more than 350 species. c. s.

5. *The "Mark Stirrup" Collection of Fossil Insects from the Coal Measures of Commeny (Allier), Central France*; by HERBERT BOLTON. Mem. and Proc. Manchester Lit. and Phil. Soc., vol. 61, pt. 1, 1917. 23 pp., 5 pls.—In this good paper are described two new genera of late Paleozoic insects, along with eight species of which two had been made known heretofore. c. s.

6. *Fossil Plants from Bolivia and their Bearing upon the Age of Uplift of the Eastern Andes*; by EDWARD W. BERRY. Proc. U. S. Nat. Mus., vol. 54, 1917, pp. 103-164, pls. 15-18.—In

1915 Professors Singewald and Miller collected in the high Andes near Corocoro and Potosi in Bolivia the eighty-five species of fossil land plants here described. In close association with this flora were found many specimens of a new brachiopod, *Discinisca singewaldi*. These marine shells are now 13,500 feet above the sea and their presence here means "that the Andes in the region of Bolivia have been raised that much since Miocene or even Pliocene time." After a consideration of all the evidence, biologic and physiographic, the author concludes that

"The flora is Pliocene in age and the major elevation of the eastern Andes of Bolivia and the high plateau took place in the late Pliocene and throughout the Pleistocene, and the extensive mineralization of this region also took place during this same period" (114).

c. s.

7. *West Virginia Geological Survey*; I. C. WHITE, State Geologist.—A new edition of a geological map of the coal, oil, gas, limestone and iron deposits of West Virginia has recently been issued. This has been thoroughly revised and shows oil and gas pools, many anticlinal lines not heretofore shown, and also the names and post-office addresses of all the principal coal mining operators in West Virginia up to July 1st, 1917; the map is issued under date of October 1st, 1917; scale, 8 miles to the inch. Price, folded in strong envelope and delivered by mail, 50 cents.

The Survey has also issued a New Railroad Map of West Virginia on a scale of 8 miles to the inch, showing by numbers all the steam railways of the State up to July 1st, 1917, with their mileage and valuation for taxation. Price, 50 cents.

Detailed Report on Clay and Braxton Counties, by RAY V. HENNER, with notes on Conemaugh fossils, by WM. ARMSTRONG PRICE and E. C. CASE. Pp. xix, 893; with 29 halftone plates and 16 text figures and a case of topographic and geologic maps of each county. This large volume contains valuable detailed information on the coal, oil, gas and other minerals of the counties named; also geologic maps give the anticlinals and synclinals in accurate detail. Price, including case of maps, delivery charges included, \$2.50; extra copies of the geologic maps, 75 cents each, and of topographic maps, 50 cents each.

8. *United States Bureau of Mines, Year Book for 1916*: by VAN H. MANNING. Bulletin No. 141. Pp. ix, 174, with 17 plates and 8 figures.—The interest of this annual report by the superintendent of the Bureau of Mines is increased by the statements recently made by Secretary Lane as to the work being accomplished by the Bureau in connection with war. Some of the special investigations undertaken are: (1) the fixation of atmospheric nitrogen and the oxidation of ammonia to nitric acid for the purpose of obtaining the nitrates necessary in agriculture and explosives; (2) domestic sources of pyrite, sulphur and sulphuric acid; (3) the noxious gases used in warfare and the masks needed by those who must be protected from them; (4) the use of smoked screens on the ocean, and (5) the obtain-

ing of the necessary supplies of certain relatively rare mineral substances, notably manganese, nickel and potash.

The regular work of the Bureau for 1916 is detailed in this report and shows the large amount being accomplished in increasing the safety of mining, and in educating miners in this direction. This applies not only to the coal mines, but also to metal mines, as for example those at Joplin where pulmonary disease is common. Extensive investigations have been carried on also with reference to the efficiency in the use of fuel, a subject hardly less important in the country today than the conservation of food.

A special chapter is given to petroleum investigations in which the limitations in its supply and hence of gasoline are emphasized. Efforts are being made to improve the methods of producing gasoline and at the same time to increase the production of oil.

The publications of the Bureau, since the beginning, include some 100 bulletins, 150 technical papers and 20 miner's circulars. The titles of bulletins recently received are noted below (see earlier, vol. 43, 86, 1917):

No. 120. Extraction of gasoline from natural gas by absorption methods; by G. A. BURRELL, P. M. BIDDISON, and G. G. OBERFELL. Pp. 71; 2 pls., 17 figs.

No. 130. Blast furnace breakouts, explosions, and slips and methods of prevention; by F. H. WILLCOX. Pp. xii, 280; 2 pls., 37 figs.

No. 131. Approved electric lamps for miners; by H. H. CLARK and L. C. ILSLEY. Pp. 59; 17 pls., 7 figs.

No. 133. The wet Thiogen process for recovering sulphur from sulphur dioxide in smelter gases; by A. E. WELLS. Pp. 66; 2 pls., 3 figs.

No. 136. Deterioration in the heating value of coal during storage; by H. C. PORTER and F. K. OVITZ. Pp. 38; 7 pls.

No. 138. Coking of Illinois coals; by F. K. OVITZ. Pp. 71; 11 pls., 1 fig.

No. 141. Yearbook of the Bureau of Mines, 1916, as above.

No. 142. The mining industry in the Territory of Alaska during the calendar year 1915; by S. S. SMITH. Pp. 65; 1 pl.

No. 147. Abstracts of current decisions on mines and mining, reported from September to December, 1916; by J. W. THOMPSON. Pp. 84.

No. 152. Abstracts of current decisions on mines and mining, reported from January to April, 1917; by J. W. THOMPSON. Pp. viii, 77.

#### OBITUARY.

PROFESSOR EDWARD HULL, late Director of the Geological Survey of Ireland and Professor of Geology in the Royal College of Science, Dublin, died in London on October 18 at the age of eighty-eight years. He was born in Antrim, in 1829, and of his many contributions, one of the most important was the series of detailed geological maps of Ireland.



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*Entomology:* J-30. Supplies. J-125. Life Histories. J-128. Live Pupae.  
*Zology:* J-116. Material for Dissection. J-26. Comparative Osteology. J-94. Casts of Reptiles, etc.  
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# AMERICAN JOURNAL OF SCIENCE

[ F O U R T H S E R I E S . ]

ART. VI.—*The Coral-reef Problem and the Evidence of the Funafuti Borings*; by ERNEST W. SKEATS, Geological Department, University of Melbourne.

## *Introduction.*

INTEREST in the vexed problem of the origin of atolls and barrier reefs has been again stimulated during the last few years by the writings of the two Harvard geologists, Professors W. M. Davis and R. A. Daly. Davis\* has reinforced Darwin's view of the origin of atolls in a series of papers, by amplifying and elaborating the evidence, first recorded by Dana, in favor of the subsidence theory which is yielded by the presence of drowned valleys and embayed coasts in many of the central islands surrounded by barrier reefs.

Daly,† elaborating and adding to the earlier work of Belt‡ and Penck,§ among others has propounded the "glacial-control theory of coral reefs," claiming that the Pleistocene glaciation by means of Polar ice caps locked up so much water that a lowering of level of the tropical seas of 50–100 meters occurred. The lowering of temperature is pictured as killing most of the corals, while prolonged abrasion of oceanic islands during the period of lowered sea level led to the development of wave-cut "reef platforms" which served as the foundations on which the existing atolls were built up when sea temperatures and sea level subsequently rose. The phenomena of drowned

\* Davis, W. M., this Journal, xxxv, pp. 173–188, 1913; *ibid.*, xl, pp. 223–271, 1915; Bull. Am. Geogr. Soc., xlvi, pp. 561–739, 1914; Proc. Acad. Sci., Washington, pp. 146–152, March 1915.

† Daly, R. A., this Journal, xxx, pp. 297–308, 1910; Proc. Amer. Acad. Sci., li, pp. 157–251, Nov. 1915; this Journal, xli, pp. 153–186, 1916; Nat. Acad. Sci., pp. 664–670, Dec. 1916.

‡ Belt, Quart. Journ. Science, xi, p. 450, 1874.

§ Penck, Jahr. Geogr. Ges. München, vi, p. 76, 1881. Penck, Morphologie der Erdolurhäsehe, Stuttgart, ii, p. 660, 1894.

valleys and embayed coasts are by Daly attributed to rise of sea level and not to subsidence of the land.

Davis, in common with others, admits some change of sea level due to glaciation and subsequent melting of Polar ice caps, but doubts the quantitative significance which Daly attributes to it, and indeed, regards it as of minor importance. These indirect methods of enquiry have assumed much of their importance from the circumstance that the materials and constitution of normal atolls are not commonly available for direct examination except when subsequently elevated or explored by boring.

Some fifteen to eighteen years ago the writer, while a demonstrator under the late Professor J. W. Judd at the Royal College of Science, London, was concerned in the examination of coral limestones from upraised coral islands\* and also made a large number of the analyses of the materials of the cores from the borings into the atoll of Funafuti. For some years he was handling the sliced cores of the latter bore and has examined most of the rock sections so ably described by Professor Cullis in the mineralogical part of the Funafuti report.† The writer's familiarity with the bore cores from Funafuti and his experience with limestones from upraised coral islands constitute his justification for contributing to the present discussion. The significance of the evidence made available by the publication of the very detailed and exhaustive examination of the Funafuti bores appears to have escaped many workers on coral reef problems or to have been misunderstood. This no doubt is partly to be attributed to the circumstance that the committee responsible for the work consisted of adherents of diverse views on atoll formation, and decided that the experts to whom the material was submitted should publish descriptions of the material but should draw no conclusions from the facts as to the mode of formation of the atoll. The writer believes he is correct in stating that these experts were unanimous in their views that the published descriptions supported Darwin's subsidence theory, and in fact were fairly susceptible of no other known explanation.

In this paper it is not proposed to discuss in detail the big problems raised by Prof. Davis or by Prof. Daly with the exception of three points raised by the latter, namely, the submarine profile of Funafuti, Daly's and Von Lendenfeld's views and diagrams of the development of coral atolls and the mechanism of the filling of "lagoon moats."

The author is principally concerned that more serious consideration should be accorded to the positive evidence provided by the examination of the bore cores which is published in the

\* Skeats, Bull. Mus. Comp. Zool., Harvard, xlii, pp. 53-126, 1903.

† Funafuti report, Royal Society, London, 1904.

Funafuti report. In a succeeding paper he proposes to recall the attention of workers in this field to the support given to the subsidence theory of atoll formation by a consideration of the apparently unrelated problem of the origin and distribution of dolomite in coral and other limestones.

Some of these facts and the legitimate conclusions which follow from them were pointed out by Professor Sollas in 1905,\* but subsequent writers on the subject have not commented on them and apparently have not realized their significance.

*Von Lendenfeld's and Daly's Diagrams of Atoll Development.*

Darwin's and Dana's diagrams of atoll development show a centripetal displacement of the outcrop of the reef of an atoll as the result of growth during subsidence. Von Lendenfeld† and Daly‡ have published diagrams showing a centrifugal displacement of the outcrop of the atoll reef during subsidence. This latter view can only be tenable on the assumption that the debris broken from the seaward face of the reef accumulates as a submarine talus *within the limits of coral growth*, and that fresh coral reef material grows upwards on that talus.

On "a priori" grounds the writer would expect the following factors to determine in large measure the nature of the submarine profile of an atoll.

1. The relative rates of subsidence and of upward growth of corals.§
2. Rate of abrasion of the seaward face of the growing reef by wave attack.
3. Rate of lateral regrowth of corals on the seaward side of the abraded reef.

With regard to the first point, if the rates of subsidence and of upward growth are nearly equal a very steep outer wall to the reef will develop and might continue for many hundreds of feet. If this were the only factor involved a slight centripetal shift of the outcrop of the reef would be expected, for only submarine talus formed within the limits of coral growth can sustain growing corals and these will fail to reach the surface. If the rate of subsidence is less than that of upward growth of coral, the latter will be checked on reaching sea level and more material will be abraded from the seaward face, submarine talus will collect and if within the limits of coral growth upward growth of coral on the talus will commence. The

\* Sollas, *The Age of the Earth*, T. Fisher Unwin, London, pp. 121-132.

† R. Von Lendenfeld, *Gaea*, Jahrg. 26, 196, 1890; *Westermann's Monatshefte*, p. 505, Jan. 1896.

‡ *Op. cit.*, p. 247.

§ One may neglect the case where the rate of subsidence exceeds that of upward growth of coral, since the atoll would in that case be drowned.

accumulation of talus will be slow and whether or no corals can grow from such a talus and reach the surface will depend on the submarine slope of the island, on the relation between the rates of supply of talus material, of subsidence, and of upward growth of coral. Any considerable accumulation of submarine coral talus necessarily involves extensive abrasion of the growing reef by wave action and considered by itself will cause a centripetal shift of the position of the outer reef-face at the surface. But here the second and third factors mentioned above, which involve the relative rates of abrasion of the reef face and repair by regrowth of corals, become important. Von Lendenfeld's and Daly's diagrams can only express the facts in the case of a reef in which the rate of subsidence is much slower than that of upward growth of coral, lateral abrasion of the reef-face and its repair are rapid and a large quantity of submarine coral talus accumulates at depths less than 15 to 40 fathoms giving a foundation for the seaward and upward growth of coral. In the writer's view the combination of these factors in the history of an atoll is likely to be exceptional rather than normal and the alternative view seems more probable that usually during subsidence the upward growth of coral will occur on dead coral reef and only as the result of occasional long pauses in subsidence or prolonged periods of very slow subsidence will sufficient talus accumulate to provide a foundation for coral growth. If this latter picture of the development of an atoll is correct, on the whole a centripetal shift of the outcrop of the reef will take place.

Davis\* has discussed this question and defined the conditions under which centripetal or centrifugal shift of the reef may possibly take place. Let us turn from these "a priori" arguments to consider the facts so far as they may be disclosed by an examination of the submarine profile of Funafuti. The diagram shown in Daly's paper is not helpful in this connection for it is generalized and the vertical scale is exaggerated three times. In the Funafuti report several cross profiles are shown on the true scale and if we limit our attention to the part within 200 fathoms of the surface (slightly greater than the depth of the main bore) it will be noticed that the cross profiles show varying slopes. It may be noted here that the soundings showed that down to 400 fathoms from the surface round most of the island the average submarine slope is about  $40^\circ$ , a figure which must reach if it does not exceed the upper limit for the angle of rest of submarine talus. One profile, AA in the Funafuti drawings, between the surface and a depth of 200 fathoms shows the existence of 4 very steep walls with angles up to and exceeding  $70^\circ$  and one of these is over three hundred feet in height and slopes at  $78^\circ$ . Between

\* W. M. Davis, Proc. Nat. Acad. of Sci., ii, pp. 466-471, 1916.



these steep slopes are several which are at much lower angles. These steep walls most probably represent the outer parts of the growing reef at various stages of development while the methods of formation of the intervening flatter slopes may be more debatable. The important point to note is that in the development of the Funafuti atoll we have evidence in the submarine profiles that there has been a centripetal not a centrifugal shift of the outcrop of the reef since the more deeply buried submarine steep walls representing former positions of the outer reef-face are further from the center of the island than those of more recent origin and shallower depth. An appeal to the facts as shown in the submarine profile of Funafuti indicates, therefore, that the development of that atoll is in general accordance with the diagrams of atoll growth originally published by Darwin and by Dana while Von Lendenfeld's and Daly's views and diagrams are clearly inapplicable to that particular atoll.

*The Filling of the "Lagoon-moat".*

Daly\* attaches much importance to the mechanism of the filling of the "lagoon-moat" in atolls. He claims that, according to the subsidence theory of atoll formation, the fairly shallow and relatively flat lagoon floors which are commonly met with, imply advanced filling of the lagoon to depths of scores, hundreds or possibly thousands of meters. The filling mechanism according to Daly involves two factors, sediment and active transportation of that sediment. On this basis he claims that the lagoon floors should not be flat but should slope away from the sources of supply of sediment, i.e. the reef-face and the central island in the case of barrier reefs in course of development to atolls. Further he claims that the supply of sediment is quite insufficient unless in the case of all atolls a very prolonged pause has followed subsidence. He favors the view that the "lagoon moats" really represent wave-cut surfaces or rock platforms developed by the erosion of pre-existing islands while the sea level stood lower than it does at present. Davis† has criticised this theory of wave-cut platforms as the support for modern atolls from the point of view among others that enormous periods of time would be necessary to develop level rock platforms in the case of islands some of which must have been 20 to 30 miles in diameter. The writer is more particularly concerned with Daly's criticism of "moat" filling previously stated above. It will be noted that although Daly quotes Darwin's view that the "moat" is slowly filled through the accumulation of detritus and shells and skeletons of organisms inside the reef, in his discussion of the mechanism of

\* R. A. Daly, Proc. Nat. Acad. Sci., ii, pp. 664-670, 1916.

† W. M. Davis, Bull. Am. Geogr. Soc., xlii, p. 646, 1914.

“moat” filling he ignores the activity of organisms and develops his destructive criticism on the assumption that the moat is filled entirely by means of transported and deposited sediment. While it may be granted that Daly’s criticism would have some force if sediment were the only factor in moat filling, the argument is very seriously weakened if not completely vitiated by ignoring the part played by organisms. One of the best established facts in modern work on coral reefs is that any effects due to solution from lagoon waters, which was an important element in Murray’s picture of the development of lagoons, is negligible in amount and quite overbalanced by organic growth and the deposition of sediment. In fact measurements show that the lagoons of many atolls are becoming shallower owing to these causes. If it can be shown that the growth and deposition of organisms within the waters of the lagoon are quantitatively much more important than the deposition of sediment the weight of Daly’s destructive criticism would be removed and the relatively flat floors of many lagoons could be attributed to the deposition of organisms. To decide between the opposing hypotheses the appeal is to the facts so far as they are known. The Funafuti report\* again provides the most definite evidence of the nature of lagoon deposits. Two bores were put down from the waters of the lagoon and penetrated to depths of 113 and 144 feet respectively below the floor of the lagoon. The record of the deeper boring, L, shows that of the material from the first 70 feet between 80 and 95 per cent consists of loose uncemented fronds of the calcareous alga, *Halimeda*; below 70 feet the organisms are cemented by calcite into a white limestone and for about 20 feet consist of about one third of *Halimeda* and two thirds of foraminifera. In the lower 50 feet the rock is mainly composed of corals and foraminifera while *Halimeda* is scarce. It will be noted that for the first 60 feet the filling of the lagoon “moat” consists of loose fronds of *Halimeda* practically devoid of sediment; below this level the calcite cement, small in amount, may or may not represent recrystallized calcareous sediment. At Funafuti, therefore, it is clear that of the two factors, organisms and sediment, which have filled the lagoon “moat”, the organisms are of overwhelming importance. The deposits of *Halimeda* in the upper part of the lagoon bore must have been accumulated fairly rapidly since from the floor of the lagoon down to a depth of 35½ feet the fronds of *Halimeda* were still sufficiently preserved to show the peripheral cells on decalcification. We may therefore conclude, at any rate, so far as Funafuti is concerned, that Daly’s objections to the subsidence theory of atolls so far as they are based on difficulties connected with the filling of the lagoon “moat”, have no weight

\* The Atoll of Funafuti, London, 1904, pp. 310-315.

for the predominant factor, the activity of calcareous algæ, foraminifera, corals, etc., has been completely overlooked.

*The evidence of organisms from the main Funafuti bore.*—The careful, precise, and monumental work of Dr. Hinde on the materials from the borings at Funafuti provides a wealth of information on the organisms which built up that atoll. From his report, from Prof. Judd's general report on the materials, and from a personal communication from Mr. F. Chapman, now paleontologist to the National Museum, Melbourne, who sliced all the cores, and examined the foraminifera, the writer selects the following statements as bearing on the question of the origin of the atoll.

Dr. Hinde reported that in the upper 180 ft. of the boring, whose coral reef origin no one has questioned, about one-fifth of the organisms consisted of corals, the remainder consisting of calcareous algæ, foraminifera, and other organisms.\* In the lower third of the boring from 750 ft. to the bottom at 1114 feet the corals form a larger proportion of the whole rock, but, even here, are considerably exceeded by the foraminiferal and fragmentary rocks. Between 600 ft. and 748 ft. coral casts are more numerous and *Halimeda* is abundant. He further stated that 27 genera of corals were recognized in the main boring, all of which belong to well-known reef-building forms, most of which still exist on the reef, and in the lagoon at Funafuti 35 genera of foraminifera are recognized in the main boring, of which only 7 are of importance as rock-formers, and they are still flourishing on the present reef or in the lagoon.

Prof. Judd† states that the corals which occur are sometimes *upright and in the position of growth*, but very frequently broken and fragmentary, this being true of all parts of the core from the top to the bottom. So far as could be made out the corals are as often "in situ" in the lower as they were in the upper parts of the core.

Mr. Chapman,‡ whose opinion is of great weight, as he did all the slicing of the cores, as well as from his position as an expert in the study of foraminifera, states that "throughout the bore the corals were found in the position of growth. *Pocillopora* was found in the boring down to 750 feet. In the living state at Funafuti it occurs from 30–180 ft.

*Coeloria* occurs in the bore from 340–1114 ft. 6 in., and is found living at 4½ ft.

*Alveolina boscii* was found in the bore down to a depth of 700 ft. In soundings it is found commonly in shallow water down to 30 fathoms, below which it is rare.

The delicate megalospheric form of *Orbitolites complanata* in its reproductive stage was found in the lowest cores of the bore in the condition in which it lives in the shallow waters of

\* Funafuti Report, pp. 333–334.

† Op. cit., p. 173.

‡ Personal communication.

coral reefs. This material could not have tumbled down a talus bank and have been preserved loosely and intact. Moreover, it is associated in this lowest core of the boring with other evidence of shallow water conditions.

Halimeda, now living in the lagoon to the depth of about 200 ft., was found in the cores at 660 ft., proving a subsidence of nearly 400 feet."

Prof. Judd also stated that careful search was made to see if deeper water organisms mixed with those building up the reef could be detected in the cores.

If any part of the bore represented material fallen from above such an admixture of shallow and deep-water forms must have occurred. Not a trace of deep-water forms was found in the lower or any other parts of the Funafuti bore. Dr. Hinde's carefully drawn up lists show that from top to bottom the same organisms occur, sometimes plants, sometimes foraminifera, sometimes corals predominating, but in the whole depth bored the same genera and species of these various groups of organisms take their part in the building up of the mass.

Moreover, as Judd states, not a trace of *Orbitoides* or other Tertiary fossils such as occur and have been recorded, by the writer among others,\* at Christmas Island in the Indian Ocean, and at Mango and Namnka in the Fiji group in the Pacific Ocean, was found from top to bottom of the boring.

#### *Textural features of the boring.*

If any part of the boring had passed through a submarine coral talus, its coarse fragmentary condition and bedded character should have been recognizable. Prof. Judd† reports that "nowhere could a stratification, such as might be expected in a talus formation, be found, but only such irregular accumulation of detrital materials as takes place between and around the corals, and these appearances were presented at many points from the top to the bottom of the bore hole, whenever consolidated rock could be examined."

Dr. Cullis‡ in his valuable report draws attention to and figures remarkable stalagmitic coatings to cavities in the limestone of the bore, chiefly formed of fibrous calcite, sometimes of alternating layers of calcite and dolomite, and these are found at intervals, not only in the upper part of the bore in the case of the fibrous calcite, but also from a depth of 815 ft. down to the bottom. This material from its appearance and occurrence as a lining of cavities is strongly indicative of rapidly deposited carbonate under conditions of supersaturation such as occur under very shallow water conditions or even between

\* Skeats, Bull. Mus. Comp. Zool., Harvard, xlii, June 1903.

† Op. cit. pp. 174-175.

‡ Op. cit. pp. 392-420.

high and low tide level. Dr. Cullis also draws attention to the mineralogical change from aragonite to calcite in the materials of the upper part of the bore cores. In the top cores aragonite is freely represented in the corals, and certain other organisms, and as chemically deposited carbonate. With this occurs calcite in the form of organisms and as chemically deposited material. At about 100 ft. in depth it is noted that less aragonite and more calcite are represented due partly to the deposition of calcite instead of aragonite and partly to conversion of aragonite to calcite. Below 100 ft. this mineralogical change is more noticeable, and at 150 ft. practically all aragonite has gone, the lowest depth at which it has been recognised being 220 feet.

This mineralogical change involving a change in the appearance of the rock cores, it will be noted, is gradual and not abrupt, but it is probably responsible for certain erroneous conclusions to be mentioned below. Summarizing the evidence of the organisms and of the textural features of the main boring at Funafuti it may be stated that all the organisms belong to recent forms, most of the species are still living, nearly all are forms which only live in the shallow water of the reef and lagoon, many of the reef-forming corals in all parts of the bore, including the lowest cores, occur upright, in the position of growth, no deep-water types of organisms were found and no Tertiary forms.

No evidence of coral talus and no true sign of bedding was noticeable although carefully sought for. Stalagmitic linings to cavities in the coral limestone, such as might be expected to be deposited in very shallow or tidal waters, occurred at intervals down to the bottom cores, while the change from aragonite to calcite in the material of the core involving a change in the appearance of the rock occurred gradually between the depths of 100–150 ft., and was complete at a depth of 220 ft.

It will be noted that the above facts are completely at variance with the view expressed by Agassiz\* in his paper on the Coral Reefs of the Tropical Pacific. Therein he remarked as follows: "The boring at Funafuti reached 1114 ft. It passed at first through the modern reef rock material and below that must have, judging by analogy, penetrated either an underlying mass of Tertiary limestone or have passed through the mass of modern reef rock forming the outer talus of the atoll of Funafuti."

Prof. Daly † in his paper on the glacial control theory of Coral Reefs after discussing Von Lendenfeld's view of the development of an atoll by centrifugal displacement of the outerop as sinking progresses, states: "If Von Lendenfeld's

\* Mem. Mus. Comp. Zool., Harvard, xxviii, pp. 21, 22, 1903.

† Daly, Proc. Amer. Acad. Sci., li, p. 247, 1915.

view is correct, the massive reef of a large atoll must lie unconformably upon talus of indefinite depth. Hence the Funafuti borings could not, in any case, have penetrated massive reef material in situ to a depth greater than about 45 meters." Again, at p. 218, he states: "the boring at Funafuti showed massive coral to persist to a depth of about 46 meters. Below that depth the log of the boring suggests that it passed through talus material all the way to the bottom at a depth of 340 meters. This conclusion was reached by the writer after a careful study of the Funafuti report, issued by the Royal Society of London; a subsequent inspection of a duplicate set of the core material has tended to confirm the opinion." These statements of Agassiz and Daly require some comment. The underlying mass of Tertiary limestone beneath a shallow reef, pictured by Agassiz, and the reef platform required by Daly's hypothesis cannot be recognized in the Funafuti boring.

Prof. Daly's opinion, after an examination of the report and of a duplicate set of core material, that below 46 meters the bore continued in talus material to the bottom, appears to the writer to be in conflict with the published facts and with the views of the experts who examined the material. It would involve a sharp, unconformable break at 46 meters below the surface between the coral reef rock and the underlying talus. The evidence on the contrary shows similar organisms and texture above and below this depth, and the only change noticeable near this depth is a gradual mineralogical change from aragonite to calcite between 100–180 ft.

### *Conclusions*

The conclusion is reached, based on the examination of the organisms and textures from the bore and the submarine contours of the island of Funafuti, that the only hypothesis of origin capable of correlating and accounting for all these facts is the subsidence theory of Darwin. Supporting evidence of the shallow-water origin of all the material and therefore subsidence of the land will be brought forward in a succeeding paper dealing with the formation of dolomite and its distribution among coral and other limestones.

The conclusions to be drawn from this summarized statement of observations, both positive and negative, seem to the writer to be clear, namely, that the whole material of the atoll from the surface down to the bottom of the core at 1114 ft. 6 inches is essentially homogeneous in origin and organisms, and all of it was formed in shallow water. This necessarily involves either a subsidence of the land to the extent of 1114 ft. or possibly while the bulk of the material was formed during subsidence, a small portion may be due to growth during a post-glacial rise in sea level.

ART. VII.—*The Estimation of Phosphorous, Hypophosphoric and Phosphoric Acids in Mixture*; by R. G. VAN NAME and WILBERT J. HUFF.

(Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxvii.)

Since hypophosphoric acid solutions undergo a gradual hydrolytic decomposition with the formation of phosphorous and phosphoric acids, the possession of a dependable method for the quantitative analysis of the resulting mixture is of fundamental importance for any extended study of the properties of hypophosphoric acid. The standard methods for determining phosphorous acid, as ordinarily carried out, would be inapplicable in the presence of hypophosphoric acid, while both the iodometric method proposed by Rupp and Fink<sup>1</sup> and the essentially equivalent method of Rosenheim and Pinsker,<sup>2</sup> which the last named authors claim to be accurate in the presence of hypophosphoric acid, are unfortunately unsound. In both the phosphorous acid is oxidized by an excess of iodine in the presence of potassium bicarbonate, and the iodine remaining is titrated with thiosulphate in the bicarbonate solution. Since, however, it has been conclusively proved that the estimation of iodine by thiosulphate in the presence of an alkali bicarbonate gives wholly inaccurate results,<sup>3</sup> it is evident that these methods are of little value.

In connection with a study of the reducing properties of hypophosphorous and phosphorous acid, Sieverts<sup>4</sup> estimated phosphorous acid by a modification of the method of Rupp and Fink, in which the excess of iodine was determined by arsenic in the bicarbonate solution, thus avoiding the objection above mentioned. This method, though not used or recommended by Sieverts for such a purpose, would in fact be applicable in the presence of hypophosphoric acid, but, as will be shown later, there is an inherent source of error in the method which limits its accuracy. In anything but a very thorough search of the literature this method might easily be overlooked, since the description of it is merely incidental, in an article upon a wholly different subject.

<sup>1</sup> Ber. chem. Ges., 35, 3691, 1902.

<sup>2</sup> Zs. anorg. Chem., 64, 327, 1909, also Pinsker, Dissertation, Berlin, 1909.

<sup>3</sup> Topf, Zs. anal. Chem., 26, 183-188, 1887; Ruff and Jeroch, Ber. chem. Ges., 38, 409, 1905; Ashley, this Journal, 19, 237, 1905.

<sup>4</sup> Zs. anorg. Chem., 64, 29, 1909.

The methods of analysis to be described were developed to meet the need for accurate analytical processes for the special purposes of a research upon hypophosphoric acid, the results of which will be published in subsequent articles.

### I. *The Estimation of Phosphorous Acid in the Presence of Hypophosphoric Acid.*

A solution of phosphorous acid, slightly less than tenth normal in reducing power, was prepared by dissolving in water the crystallized acid (furnished by Baker and Adamson). This solution, which contained a little phosphoric acid as impurity, was standardized by three independent methods as follows:

(a) *As Magnesium Pyrophosphate.*—To estimate the phosphoric acid present, measured portions of the solution were treated with magnesium chloride mixture under the conditions recommended by Gooch and Austin.<sup>5</sup> The precipitate was dissolved in a little hydrochloric acid and reprecipitated by ammonia. Rupp and Fink<sup>6</sup> have shown that a double precipitation is necessary to free the precipitated ammonium magnesium phosphate from phosphite. The precipitates were ignited and weighed as magnesium pyrophosphate. Other measured portions of the original solution were treated with aqua regia and evaporated as far as possible over a water bath, thus oxidizing the phosphorous acid to phosphoric acid, which was then precipitated as above and weighed as magnesium pyrophosphate. From the difference in the results before and after oxidation the phosphorous acid content of the solution was calculated. Two determinations, using 45 cm<sup>3</sup> portions of the solution gave, respectively, 0.2524 — 0.0366 = 0.2188, and 0.2523 — 0.0366 = 0.2187 grm. Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, equivalent to 0.003583 and 0.003582 grm. H<sub>3</sub>PO<sub>3</sub> per cm<sup>3</sup>.

(b) *As Mercurous Chloride.*—Adherence to the directions for this method of estimating phosphorous acid, as given in the standard text-book of Treadwell-Hall<sup>7</sup> led to several failures from incomplete precipitation. Pro-

<sup>5</sup> This Journal, 7, 187, 1899.

<sup>6</sup> Ber. chem. Ges., 35, 3692, 1902.

<sup>7</sup> "Analytical Chemistry", 3rd English ed., pp. 374 and 372. The conditions recommended are the same for phosphorous as for hypophosphorous acid.



longed heating at a fairly high temperature is essential, acidity accelerating the reaction.<sup>8</sup> Success was finally attained by adding an excess of mercuric chloride, then concentrated hydrochloric acid in quantity sufficient to make up about two per cent of the total volume, and finally heating the liquid at 80°-85° for seven hours. The precipitates were collected on asbestos and dried at 100°-105°.

From two 45 cm<sup>3</sup> portions of the solution 0.9331 and 0.9302 grm. Hg<sub>2</sub>Cl<sub>2</sub> were obtained, equivalent to 0.003604 and 0.003593 grm. H<sub>3</sub>PO<sub>3</sub> per cm<sup>3</sup>.

(c) *Oxidation by Permanganate.*—The method employed was a modification of that of Kühling.<sup>9</sup> Portions of the phosphorous acid solution were measured into conical flasks, and to each was added 40 cm<sup>3</sup> of 10% solution of crystallized zinc sulphate, and an excess of a potassium permanganate solution containing about 3.16 grams of that salt per liter. The zinc sulphate serves to prevent the solution from becoming alkaline. The flasks were heated on the steam bath for 90 minutes, cooled and treated with an excess of acidified potassium iodide solution, and the iodine thus liberated was titrated with thiosulphate in the presence of starch. Kühling filtered off the manganese dioxide and estimated the latter by treatment with potassium iodide, but the modification described above is more rapid and convenient. We would also emphasize the importance of a precaution not mentioned by Kühling, that of determining the standard of the permanganate, or, rather, the ratio of the permanganate to the thiosulphate, by means of blank experiments carried out under precisely the same conditions as the determinations themselves. This procedure tends to cancel out a possible error resulting from decomposition of the permanganate during the heating. The results obtained by this method are recorded in full in Table I. Their average gives for the standard of the solution the value 0.003594 grm. H<sub>3</sub>PO<sub>3</sub> per liter, as compared with 0.003591 for the average of the results of (a) and (b).

Although the volumetric method is probably equally accurate, we shall give the benefit of the doubt to the older methods and accept the value 0.003591 as the

<sup>8</sup> Linhart, this Journal, 35, 353, 1913.

<sup>9</sup> Ber. chem. Ges., 33, 2914, 1900.

TABLE I.

Standardization of Phosphorous Acid Solution, Oxidation by Permanganate.  
Kühling's Method Modified.

Sodium Thiosulphate Solution, 1.008 N/10.				
H <sub>3</sub> PO <sub>3</sub> solution taken cm <sup>3</sup>	KMnO <sub>4</sub> solution taken cm <sup>3</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution required cm <sup>3</sup>	H <sub>3</sub> PO <sub>3</sub> found gram.	H <sub>3</sub> PO <sub>3</sub> found gram./cm <sup>3</sup>
0.00	50.00	47.22	.....	.....
10.00	50.00	38.50	0.03607	0.003607
15.00	50.00	34.20	0.05385	0.003590
20.00	50.00	29.82	0.07197	0.003599
25.00	50.00	25.57	0.08954	0.003582
27.00	150.00	79.15	0.2585	0.003591

standard of the solution. It should be noted that hypophosphates, though they are readily oxidized by hot permanganate, can not be estimated by this method. Low and irregular values are obtained, probably because of the insolubility of zinc hypophosphate under the conditions.

*Iodometric Estimation of Phosphorous Acid in the Presence of Potassium Bicarbonate.*—In Table II are the

TABLE II.

*Estimation of Phosphorous Acid—Method of Sieverts.*

Iodine solution 1.133 N/10.		Arsenite solution 0.9812 N/10.			
H <sub>3</sub> PO <sub>3</sub> taken cm <sup>3</sup>	gram.	Iodine solution taken cm <sup>3</sup>	Arsenite solution required gram.	H <sub>3</sub> PO <sub>3</sub> found gram.	Per cent of theory
5.00	0.01795	25.00	24.39	0.01804	100.50
10.00	0.03591	24.50	19.31	0.03617	100.72
15.00	0.05387	45.07	38.58	0.05420	100.61
20.00	0.07182	44.32	33.18	0.07247	100.91
20.00	0.07182	28.35	14.80	0.07219	100.52
30.00	0.1077	48.03	28.52	0.1085	100.74
50.00	0.1795	48.05	10.77	0.1800	100.28

results of a series of determinations obtained by the method of Sieverts,<sup>10</sup> already referred to. Measured volumes of the standard phosphorous acid solution were placed in glass-stoppered flasks, to each of which was added two grams of potassium bicarbonate and a known excess of standard iodine solution. The flasks were then

<sup>10</sup> Zs. anorg. Chem., 64, 29, 1909.

set aside in the dark for periods varying from 2 to 24 hours,<sup>11</sup> after which the iodine remaining was titrated with standard arsenite, using starch as indicator.

The results are fairly accurate but show, throughout, a small positive error. That this was chiefly due to an interaction between the iodine and bicarbonate is proved by Table III, which gives the results of a series of blank

TABLE III.

*Error due to Iodide and Iodate Formation.*

Iodine solution 0.9438 N/50.		Arsenite solution 1.000 N/50.			
KHCO <sub>3</sub> gram.	Iodine solution taken cm <sup>3</sup>	Time hours	As <sub>2</sub> O <sub>3</sub> solution to bleach cm <sup>3</sup>	Iodine total to color cm <sup>3</sup>	Volume N/50 Iodine absorbed cm <sup>3</sup>
2	49.05	2	45.35	49.15	1.04
1*	49.00	2	46.00	49.07	0.31
5	49.00	2	45.20	49.03	1.08
In solution† cm <sup>3</sup>					
5‡	49.00	2	46.18	49.07	0.13
100‡	49.00	2	44.00	49.10	2.34
5	49.00	2	44.88	49.10	1.46
10	49.00	2	45.90	50.10	1.39

\* One drop of dilute HCl added after the bicarbonate.

† The solution was prepared by dissolving 250 grams of potassium bicarbonate in a liter of water, and thoroughly saturating the liquid with carbon dioxide.

‡ This portion of the bicarbonate solution was further treated with a current of carbon dioxide gas for 20 minutes just before using.

experiments in which no phosphorous acid was present, but which in other respects were conducted like those of Table II. The solutions of iodine and of thiosulphate, however, were made fiftieth normal, so that small losses of iodine could be detected with greater certainty, and the influence of the hydroxyl-ion concentration of the solution was tested by employing varying quantities of bicarbonate (1 to 25 grams), and by saturating the solution in some cases with carbon dioxide before mixing with the iodine.

As the results show, there was in every case a marked loss of iodine. This is easily explained, for it is known that iodine on standing with potassium bicarbonate forms a little iodide and iodate with consequent loss of titrable iodine. Washburn mentions this reaction as a

<sup>11</sup> By heating in a pressure flask at 70°, Sieverts was able to complete the oxidation within 30 minutes.

possible source of error even in the direct titration of an arsenite by iodine in the presence of a bicarbonate, and states that for accuracy it is absolutely necessary that the solution be kept saturated with carbon dioxide.<sup>12</sup> It is obvious that the danger is far greater in a process in which an excess of iodine is left in prolonged contact with the bicarbonate, as in the present case.

Since all the iodine which enters into this reaction is set free again when the solution is acidified, it should be possible to improve upon Sievert's method by carrying out the final titration of the iodine in acid solution by means of thiosulphate. In practice, however, this is inconvenient because of the effervescence produced when the solution is acidified, and the special precautions necessary to prevent consequent loss of iodine.

For this reason we have adopted disodium hydrogen phosphate as a substitute for the bicarbonate. As solutions of this salt have a higher alkalinity than alkali bicarbonate solutions which are saturated with carbon dioxide, the amount of iodate formed during the first stage of the process may be much greater, but this does not affect the results because the solution is acidified before the final titration of the iodine. The absence of effervescence is a great advantage. The amount of the sodium phosphate used must, of course, be great enough to neutralize the hydriodic acid formed, and to keep the solution alkaline during the oxidation of the phosphorous acid. In an initially neutral solution, 11 grams of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  for every 100  $\text{cm}^3$  of N/10 iodine reduced, will just suffice to leave the solution neutral at the end.<sup>13</sup> This quantity represents the absolute minimum which must not be overstepped. In practice it is a safe rule to add twice as much, or at least 11 grams for each 50  $\text{cm}^3$  of N/10 iodine to be introduced. It is immaterial whether the amount used exceeds this or not, but it is desirable that the total be known as an aid in estimating the amount of acid needed for the acidification. A rough estimate is quite sufficient, for it is well known that the degree of acidity may vary over quite a wide range without affecting the accuracy of the thiosulphate titration.

That this procedure eliminates the iodate error is

<sup>12</sup> J. Am. Chem. Soc., 30, 43, 1908.

<sup>13</sup> Washburn, loc. cit., p. 44.

shown by the experiments of Table IV, in which the titration of a N/50 iodine solution with thiosulphate gave practically the same result whether the titration was performed in neutral solution in the ordinary way, or in acid solution, after the iodine had previously stood for 2½ hours with the amount of disodium phosphate recommended above.

The details of the procedure finally adopted for the estimation of phosphorous acid in the presence of hypo-

TABLE IV.

Iodine solution taken cm <sup>3</sup>	Iodine solution approximately N/50.			Thiosulphate solution required cm <sup>3</sup>
	Na <sub>2</sub> HPO <sub>4</sub> 110 grams per liter cm <sup>3</sup>	Time hours	H <sub>3</sub> PO <sub>4</sub> 85% solution cm <sup>3</sup>	
50.00	....	...	..	49.21
50.00	....	...	..	49.20
50.00	50.00	2½	5	49.16
50.00	50.00	2½	5	49.18

NOTE:—One gram of potassium iodide was added in the final titration to increase the sensitiveness of the starch reaction.

phosphoric acid are as follows: A suitable quantity of the solution to be analyzed is measured into a glass-stoppered conical flask of 300 cm<sup>3</sup> capacity. If strongly acid or strongly alkaline the solution is brought approximately to the neutral point toward litmus by cautious addition of sodium hydroxide or hydrochloric acid. This adjustment need only be very rough, but the litmus paper must be used very sparingly, and in such a way as to avoid the introduction of paper fiber, or of appreciable quantities of the indicator, into the solution. When phosphorous acid is the only acid present, this preliminary neutralization may be omitted if the quantity of disodium hydrogen phosphate employed is not less than that recommended above. This salt is now added, either as crystals or in solution, and an excess of a standard solution of iodine is measured into the flask,<sup>14</sup> which is then stoppered and set aside in the dark for at least two hours. Finally the solution is acidified by adding a measured quantity of phosphoric acid<sup>15</sup> (which must be

<sup>14</sup> If a number of determinations are to be made much time can be saved by adding the iodine solution with an accurately calibrated pipette. When this is done, it is best to use the same pipette in determining the ratio between the thiosulphate and iodine solutions.

<sup>15</sup> Though not tested, it is probable that hydrochloric or sulphuric acid could be used for this purpose.

free from impurities which reduce iodine), and the excess of iodine is at once titrated in the usual way with thio-sulphate, adding starch just before the end point is reached. If the iodine solution is more dilute than N/10 about a gram of potassium iodide should be added before or during the titration to increase the sharpness of the end point. The amount of acid taken for the acidification should be slightly more than twice the quantity, as determined by a rough preliminary test, which will just suffice to give an acid reaction toward litmus to a solution of disodium phosphate containing the same weight of that salt as has actually been added.

A number of test analyses of standard phosphorous acid solutions by this method are recorded in Table V and VI. For Table VI the solution used was the same as

TABLE V.

*Iodometric Estimation of Phosphorous Acid.*

Iodine solution 1.022 N/50. Thiosulphate solution 1.010 N/50.

H <sub>3</sub> PO <sub>3</sub> taken		Iodine solution cm <sup>3</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution required cm <sup>3</sup>	H <sub>3</sub> PO <sub>3</sub> found gram.	Found %
cm <sup>3</sup>	gram.				
15	0.01077	45.00	32.53	0.01078	100.09
20	0.01436	45.00	28.22	0.01435	99.93
25	0.01796	45.02	23.85	0.01799	100.17
30	0.02155	45.00	19.52	0.02156	100.05
35	0.02514	45.00	15.21	0.02513	99.96
40	0.02873	45.00	10.80	0.02879	100.21
0	0	45.00	45.52	.....	.....
0	0	45.00	45.58	.....	.....

*Reagents used in each determination.* 25 cm<sup>3</sup> of an 11% solution of Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O. 5 cm<sup>3</sup> of 42% H<sub>3</sub>PO<sub>4</sub> solution. 10 cm<sup>3</sup> of 10% KI solution.

in Table II, and a portion of the same solution, carefully diluted to five times its volume with the aid of a certified burette and a certified flask, was employed in the experiments of Table V. The results of Table V, obtained with N/50 solutions of iodine and of thiosulphate, show a very satisfactory accuracy. Those of Table VI, for which N/10 solutions were used, though remarkably concordant, all show a small positive error. Whether this is due in some way to the fact that in this series of experiments the solution was acidified with acetic instead of

TABLE VI.

*Iodometric Estimation of Phosphorous Acid.*

Iodine solution 1.049 N/10. Thiosulphate solution 1.008 N/10.

H <sub>3</sub> PO <sub>3</sub> taken cm <sup>3</sup>	grm.	Iodine solution cm <sup>3</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution required cm <sup>3</sup>	H <sub>3</sub> PO <sub>3</sub> found grm.	Found %
15	0.05387	45.00	33.75	0.05411	100.45
20	0.07182	45.00	29.37	0.07223	100.57
25	0.08978	45.00	25.03	0.09018	100.44
30	0.1077	45.00	20.68	0.1082	100.46
35	0.1257	45.00	16.35	0.1261	100.32
40	0.1436	45.00	11.93	0.1443	100.49

Reagents used in each determination. 11 grams of Na<sub>2</sub>HPO<sub>4</sub>.12H<sub>2</sub>O. 8 cm<sup>3</sup> of glacial acetic acid.

phosphoric acid, or is the result of an error in the standard of one of the N/10 solutions, we are unable to say. On account of lack of time this point was not further investigated.

Table VII is a study of the effect produced by the presence of a hypophosphate upon such analyses. The exact standard of the phosphorous acid solution was unknown. Its equivalent reducing power was approxi-

TABLE VII.

*Estimation of Phosphorous Acid in Presence of Hypophosphoric Acid.*

Phosphorous acid solution approximately N/50. Hypophosphate solution approximately N/20. Iodine 1.022 N/50. Thiosulphate 1.006 N/50.

H <sub>3</sub> PO <sub>3</sub> taken cm <sup>3</sup>	Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>6</sub> taken cm <sup>3</sup>	Iodine taken cm <sup>3</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> per 10 cm <sup>3</sup> of required hypophosphate cm <sup>3</sup> of I <sub>2</sub>	Error	H <sub>3</sub> PO <sub>3</sub> found grm.
25.00	....	45.00	21.38	...	0.02009
25.00	10.10	45.00	21.26	0.12	0.02019
30.00	....	45.00	16.58	...	0.02405
30.00	9.90	45.00	16.35	0.23	0.02424
35.00	....	45.00	11.61	...	0.02815
35.00	20.00	45.00	11.43	0.09	0.02831
....	....	45.00	45.70	...	.....
....	10.00	45.00	45.58	0.12	.....

Reagents used in each determination. 25 cm<sup>3</sup> of an 11% solution of Na<sub>2</sub>HPO<sub>4</sub>.12H<sub>2</sub>O. 5 cm<sup>3</sup> of 42% H<sub>3</sub>PO<sub>3</sub> solution. 10 cm<sup>3</sup> of 10% KI solution.

mately N/50, while that of the sodium acid hypophosphate solution, as determined by the permanganate method, was a little over N/20.

In this series a slight reduction of the iodine by the

hypophosphate solution is plainly evident, though the results are in other respects very concordant with one another. As the sample of acid sodium hypophosphate from which the solution was prepared had been recrystallized but once, it seems reasonable to conclude that the reduction of iodine was due to the presence of a little phosphite<sup>16</sup> in the hypophosphate, and not to oxidation of the hypophosphate itself.

This conclusion is supported by the following experiments: Salzer,<sup>17</sup> in 1886, stated that normal sodium hypophosphate,  $\text{Na}_4\text{P}_2\text{O}_6$ , is partly oxidized by iodine, though neither hypophosphoric acid nor the acid sodium hypophosphate are attacked. To test this point a solution prepared from a sample of the salt which had been recrystallized three times was treated with sodium hydroxide (free from carbonate) in quantity slightly greater than that calculated to be necessary to form the normal sodium salt. Two portions of this solution were each treated with a measured quantity of standard iodine more than sufficient to completely oxidize all the hypophosphate. After two hours' standing in the dark both of these solutions were colorless, but upon acidifying and titrating, the iodine found was practically equal to that taken, the deficiencies being only  $0.04 \text{ cm}^3$  and  $0.08 \text{ cm}^3$  of the iodine solution, respectively, though the hypophosphate present had a reducing power sufficient to call for about  $50 \text{ cm}^3$  of iodine. Losses as small as these might easily be due to experimental error, or to slight impurities in the reagents used, and certainly do not show that the hypophosphate has been attacked. It seems probable, therefore, that Salzer mistook the disappearance of iodine caused by iodide and iodate formation, which necessarily takes place in the rather strongly alkaline solution of the normal sodium hypophosphate, for an actual oxidation of the latter.

It is evident, in any case, that under the conditions recommended above for the determination of phosphorous acid, no appreciable oxidation of the hypophosphate is to be feared. We have used the method for many analyses in the course of a study of the hydrolysis of hypophosphoric acid,<sup>18</sup> and have found it entirely satisfactory.

<sup>16</sup> This impurity is always present in the crude hypophosphate as first prepared, and can only be eliminated by repeated crystallization.

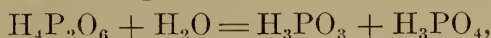
<sup>17</sup> *Ann. Chem.*, 232, 116, 1886.

<sup>18</sup> See the following article.



## II. The Estimation of Hypophosphoric Acid in the Presence of Phosphorous and Phosphoric Acids.

Since the hydrolysis of hypophosphoric acid gives an equimolecular mixture of phosphorous acid and phosphoric acid according to the equation:



it is obvious that the estimation of unknown quantities of hypophosphoric acid can be accomplished by first hydrolyzing completely and then estimating the phosphorous acid so formed by the method described in the foregoing section. Hypophosphates can be quantitatively hydrolyzed, as was first shown by Amat,<sup>19</sup> by

TABLE VIII.

### Estimation of Hypophosphoric Acid.

Iodine solution 1.029 N/50.		Thiosulphate solution 1.088 N/50.			
$\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ solution taken $\text{cm}^3$	Iodine solution taken $\text{cm}^3$	$\text{Na}_2\text{S}_2\text{O}_3$ solution required $\text{cm}^3$	$\text{H}_4\text{P}_2\text{O}_6$ found gram.	$\text{H}_4\text{P}_2\text{O}_6$ taken gram.	Found %
20.02	50.00	28.96	0.03233	0.03245	99.63
25.00	50.00	24.37	0.04042	0.04053	99.73
35.00	50.00	15.27	0.05648	0.05674	99.54
40.00	50.00	10.62	0.06467	0.06484	99.74
45.00	50.00	5.91	0.07298	0.07295	100.04

evaporating the solution to dryness with concentrated hydrochloric acid. Phosphorous acid is remarkably resistant toward atmospheric oxidation<sup>20</sup> and under these conditions undergoes no loss of reducing power.

Table VIII gives the results of a series of analyses, by this method, of measured portions of a hypophosphate solution, which was prepared of definite strength by weighing out the very stable, and beautifully crystalline, acid sodium hypophosphate,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ , using a sample of the salt which had been carefully purified by seven recrystallizations. In these experiments measured portions of the solution were evaporated nearly to dryness in small beakers over the steam bath. To each beaker 50  $\text{cm}^3$  of hydrochloric acid was then added, and the liquid again evaporated as before. To insure complete hydrolysis the treatment with hydrochloric acid

<sup>19</sup> Comptes rendus, 111, 676, 1890.

<sup>20</sup> Sieverts, Zs. anorg. Chem., 64, 32, 1909. Luther and Plotnikow, Zs. phys. Chem., 61, 513, 1908.

and subsequent evaporation was then repeated, after which the residue was taken up with water, transferred to a glass-stoppered flask, and the iodometric analysis carried out as already described.

If phosphorous acid is present at the outset, the iodometric analysis must be carried out upon separate portions of the solution before and after hydrolyzing with hypophosphoric acid, and the amount of the latter calculated from the difference. This presents no difficulty, and appears to be the most satisfactory method available for the estimation of hypophosphoric acid in the presence of phosphorous and phosphoric acids.<sup>21</sup>

### III. *Complete Analysis of a Mixture of the Three Acids.*

Three portions of the solution are measured out. In the first the phosphorous acid is determined as described in section I. In the second the hypophosphoric acid is hydrolyzed according to section II and the phosphorous acid then estimated as before, the gain as compared with the first portion giving the content of hypophosphoric acid. In the third portion the reducing acids are completely oxidized by treatment with hot aqua regia and evaporation nearly to dryness, and the total phosphoric acid then estimated by any one of the standard methods. The phosphoric acid originally present is calculated by difference.

#### *Summary.*

1. An iodometric method for the estimation of phosphorous acid is described, which is applicable in the presence of hypophosphoric and phosphoric acids.

2. Hypophosphoric acid can be estimated by first hydrolyzing completely and then following the method just mentioned.

3. A mixture of phosphorous, hypophosphoric, and phosphoric acids can be completely analyzed by the above processes, combined with the determination (after oxidizing the reducing acids) of the total phosphoric acid.

4. Incidentally, another volumetric process for the estimation of phosphorous acid is described. This process, which is a more rapid modification of Kühling's method, is applicable in the presence of phosphoric but not of hypophosphoric acid.

<sup>21</sup> For criticisms of the method proposed by Rosenheim and Pinsker, *Zs. anorg. Chem.*, 64, 333 ff., see the following article.

ART. VIII.—*The Rate of Hydrolysis and Electrical Conductivity of Hypophosphoric Acid Solutions*; by R. G. VAN NAME and WILBERT J. HUFF.

(Contributions from the Kent Chemical Laboratory of Yale Univ.—cexeviii.)

I.

*Rate of Hydrolysis.*

The stability of hypophosphoric acid in water solution is determined entirely by the rate at which the acid undergoes hydrolysis into phosphorous and phosphoric acids and for this reason a knowledge of the approximate rate of this reaction under various conditions is essential for a proper understanding of the chemical behavior of the acid. Though the nature of the reaction has long been known, no definite information about its rate has hitherto been available, investigation of this question having apparently been discouraged by the lack of methods of analysis suitable for the purpose.<sup>1</sup> The needs of the case, however, are fully met by the method for estimating phosphorous acid which we have described in the foregoing article, and it will be shown below that with its aid the velocity of this hydrolysis can be easily and accurately measured.

From a study of the literature of hypophosphoric acid the following inferences can be drawn concerning its hydrolysis: (a) The reaction yields an equimolecular mixture of phosphorous and phosphoric acid. (b) It is non-reversible. (c) It is accelerated by acids. (d) Solutions of acid sodium hypophosphate are stable at room temperature for long periods. This shows that in solutions whose hydrogen ion concentration is below the turning point of methyl orange,  $(H^+) = 10^{-4}$ , the hydrolysis at moderate temperatures is negligible. Distinctly alkaline solutions appear to be still more stable.

Our experience supports the correctness of these inferences: The measurement of the rate of hydrolysis

<sup>1</sup>Salzer, *Ann. Chem.*, **211**, 1, 1882, cites a single experiment in which 20 cm<sup>3</sup> of a solution of pure hypophosphoric acid, containing 1.154 grams of P<sub>2</sub>O<sub>4</sub>, were allowed to stand in a desiccator for four weeks, after which the volume of the solution was 1.3 cm<sup>3</sup> and only 0.150 gram of P<sub>2</sub>O<sub>4</sub> remained unhydrolyzed. The method of analysis here used was of very doubtful accuracy. Salzer also states that in a 5% solution of hypophosphoric acid which had been allowed to stand for three years, no trace of that acid could be detected.

is simplified by the fact that the reaction can be stopped at will, whatever the temperature of experiment, by neutralizing with an alkali. Although in measuring the rate of this hydrolysis we have employed a method of analysis which calls for a brief period of low acidity, the further hydrolysis which occurs during this interval is so slight that the error thus introduced is insignificant.

*Procedure.*—For the experiments at 25° the reaction

TABLE I.

*Rate of Hydrolysis of Hypophosphoric Acid at 25°.*Hypophosphate solution approx. N/20  $H_2Na_2P_2O_6$ .

1. Reaction mixture: Equal vols. hypophosphate sol. and HCl of sp. grav. 1.173.			2. Equal vols. hypophosphate sol. and HCl sp. grav. 1.185.		
Elapsed time min.	Thiosulphate $cm^3$	K	Elapsed time min.	Thiosulphate $cm^3$	K
0	48.18		0	46.15	
90.0	46.68	0.00105	87.3	43.70	0.00126
225.3	44.77	0.00102	232.7	40.28	0.00124
357.3	43.10	0.00102	353.6	37.81	0.00124
708.0	39.52	0.00104	484.2	35.55	0.00124
1293	35.98	0.00103	588.1	33.95	0.00125
$\infty$	{31.52		743.6	31.96	0.00125
	{31.57		1385	26.95	0.00124
			$\infty$	{22.70	
				{22.73	
3. Equal vols. hypophosphate sol. and HCl of sp. grav. 1.185.			4. One vol. HCl, sp. grav. 1.185 made up to 4 vols. with hypophosphate sol.		
Elapsed time min.	Thiosulphate $cm^3$	K	Elapsed time min.	Thiosulphate $cm^3$	K
0	46.06		0	42.85	
59.8	44.37	0.00125	877.1	37.90	0.000187
197.6	40.93	0.00125	2135	32.18	0.000185
318.0	38.37	0.00125	2821	29.55	0.000186
449.7	36.04	0.00124	3558	27.00	0.000187
707.7	32.23	0.00126	4335	24.92	0.000184
1339	27.06	0.00124	5759	21.53	0.000184
1630	25.68	0.00125	7176	18.67	0.000188
$\infty$	22.65		9245	15.89	0.000189
			$\infty$	10.20*	

\* Calculated from standards of solutions used.

mixture was prepared by mixing a solution of acid sodium hypophosphate (approximately N/20 in reducing power) with concentrated hydrochloric acid in definite proportions by volume. This solution was kept at a constant temperature in a thermostat, and from time to time samples for analysis were taken with a pipette and run into glass-stoppered flasks which contained the requisite amount of disodium hydrogen phosphate, together with enough sodium hydroxide to exactly neutralize the hydrochloric acid present. Each sample was then treated with the same amount of iodine solution (an excess), and after standing was finally acidified and titrated with thiosulphate.<sup>2</sup>

To obtain the final titration (for the completed reaction) a sample was run from the pipette into a stout

TABLE II.

Rate of Hydrolysis of Hypophosphoric Acid at 60°.

Hypophosphate solution approx. N/20  $H_2Na_2P_2O_6$ .

5. Reaction mixture: One vol. HCl of sp. grav. 1.185 made up to 4 vols. with hypophosphate sol.			6. One vol. of 1.062 normal HCl and three vols. of hypophosphate sol.		
Elapsed time min.	Thiosulphate $cm^3$	K	Elapsed time min.	Thiosulphate $cm^3$	K
0	44.63		0	46.48	
36.75	37.51	0.00630	1434	42.75	0.0000783
65.50	32.95	0.00632	3603	38.01	0.0000766
93.92	29.06	0.00640	6485	32.73	0.0000766
122.8	26.19	0.00624	9359	28.43	0.0000772
152.3	23.45	0.00626	13697	23.82	0.0000759
184.5	20.70	0.00643	16577	21.49	0.0000751
222.6	18.67	0.00629	19445	19.58	0.0000749
284.3	16.11	0.00620	$\infty$	11.41*	
$\infty$	10.20				

\* Calculated from standards of solutions used.

glass-stoppered bottle, the stopper clamped in place, and the bottle immersed in boiling water for eight hours, after which the sodium hydroxide and phosphate were added and the analysis completed as before.

Owing to the long duration of some of the experiments, and the consequent possibility of error from gradual change in standard of the thiosulphate or iodine solutions, the samples were usually not titrated when taken, but set aside after the neutralization until the series was

<sup>2</sup> For details of the procedure, see the preceding article.

complete. All were then treated with iodine at the same time.

In the experiments at 60° the procedure was slightly altered to avoid the difficulties involved in taking the reaction samples at this temperature with a pipette. The reaction mixture was prepared at room temperature, and like volumes were carefully measured out into a series of glass tubes, which were then sealed and placed in special weighted holders. When all were ready they were inserted at the same time in the thermostat at 60°. For the analyses heavy, wide-mouth, glass-stoppered bottles were used instead of flasks, and the proper quantities of sodium hydroxide and phosphate placed in each. To make an analysis a tube was removed from the thermostat and quickly shattered against the bottom of the bottle, noting the time. After the fragments of the tube had been broken up into small pieces with a heavy glass rod, the analysis was carried out in the way already described.

The values of the velocity constant  $K$ , as given in the following tables, were calculated from the equation for a monomolecular reaction, which here takes the form

$$K = \frac{2.3}{t} (\log_{10} (T_0 - T_\infty) - \log_{10} (T_t - T_\infty)); \quad T_0, \quad T_\infty, \quad \text{and}$$

$T_t$  representing cubic centimeters of thiosulphate required at the corresponding times.

This equation assumes that the rate of hydrolysis is proportional to the total concentration of the hypophosphoric acid molecules, ionized and non-ionized, thus ignoring the possible differences in behavior between the molecules and the different anions. In every experiment with the exception of No. 6, where the conditions were the least favorable for accuracy on account of the excessively slow rate, the constancy of  $K$  is very satisfactory, thus proving that the above equation is closely obeyed. Whether this indicates a like rate of hydrolysis for the molecules and the different anions of hypophosphoric acid, or shows, rather, that the reaction is almost wholly confined to some particular kind of molecule or ion whose concentration is closely proportional to the total concentration of hypophosphoric acid, is a question upon which these experiments throw no light.

At constant temperature,  $K$  increases rapidly with the concentration of the hydrogen ion, and much more rapidly than the latter, being apparently roughly proportional to its square. The exact relation can hardly be determined from our values on account of the high concentration of the hydrochloric acid in most experiments. Any considerable change in the hydrogen-ion concentration during the course of the experiment would produce a marked variation in  $K$ . That no such effect is visible is due to the fact that the change in the hydrogen-ion concentration resulting from the hydrolysis is in any case rather small, and here, where hydrochloric acid is present in large excess, the relative change is too small to affect the results appreciably.

*Temperature Coefficient.*—From the mean values of  $K$  in experiments 4 and 5, 0.000186 for  $25^\circ$  and 0.00631 for  $60^\circ$ , the temperature coefficient of the reaction for a  $10^\circ$  temperature rise may be calculated by means of the relation

$$\log_{10} K_2 - \log_{10} K_1 = A (t_2 - t_1), \text{ whence } \log_{10} \frac{K_{t+10^\circ}}{K_t} = 10A.$$

The value of  $\frac{K_{t+10^\circ}}{K_t}$  so found is 2.7.

*Practical Applications.*—The above results show that in dealing with free hypophosphoric acid the hydrolytic decomposition can seldom be ignored, though this may occasionally be permissible in cases where one or more of the factors, temperature, acidity, concentration, or time, have exceptionally low values. It is plain that acid solutions of hypophosphates can not be boiled without loss, nor can they safely be concentrated by heat, and even at room temperature there will be serious danger of loss (a) in solutions containing a large excess of other mineral acids, and (b) when the hypophosphate itself is present in high concentration, as is the case, for example, in strong solutions of pure hypophosphoric acid.

An objection might be made to the method of analysis which we have used in the measurement of the reaction velocity on the ground that the solution is made acid before the final titration of the iodine. Any hydrolysis of the hypophosphoric acid during this period of acidity would increase the original amount of phosphorous acid

and tend to give high results. We have already stated that the error so produced is negligible, but we are now in a position to support the statement with figures. Let us assume that the hydrogen-ion concentration produced by acidifying is equal to that in Experiment 6. It need be no greater and will usually be less. Assume further that the titration requires ten minutes, and that the temperature is 25° (the temperature will usually be less). Then, if the concentration of hypophosphoric acid is  $C$ ,  $dC/dt = 0.0000023C$ ,<sup>3</sup> and when  $dt$  is ten minutes  $dC/C$  is 0.000023, that is, 1/400 of one per cent of the hypophosphoric acid is decomposed. This would be wholly negligible except where the concentration of the hypophosphoric acid was many times greater than that of the phosphorous acid, and in such cases it would be easy, by employing lower temperature and acidity, to restrict the decomposition to a small fraction of that calculated above. Moreover, the oxidation of phosphorous acid by iodine is so slow in acid solution that only a partial oxidation would take place under the conditions of the titration, so that the actual error would be smaller than that estimated from the amount of hydrolysis. It is evident, therefore, that if this method is used with proper attention to the conditions of analysis, the hydrolysis error will be insignificant.

This, however, is very far from being true for the iodometric method proposed by Rosenheim and Pinsker<sup>4</sup> for the estimation of phosphorous and hypophosphorous acids in the presence of hypophosphoric acid, which is based on the assumption that the hypophosphoric acid is not appreciably hydrolyzed when the solution, made acid by the addition of "5-10 cm<sup>3</sup> of 10 per cent hydrochloric acid," is heated for several hours in a container immersed in boiling water. In support of this assumption the authors quote two blank experiments in which only a trifling loss of iodine was shown on heating with hypophosphoric and hydrochloric acid under the above conditions. Since, however, the iodine was titrated with thiosulphate in the presence of bicarbonate, a thoroughly discredited procedure known to give erroneous results,<sup>5</sup>

<sup>3</sup> Comparison of Exps. 4 and 5 shows that the reaction is about 34 times more rapid at 60° than at 25°. Hence if  $K_{60^{\circ}} = 0.000076$ ,  $K_{25^{\circ}} = 0.0000023$ .

<sup>4</sup> *Zs. anorg. Chem.*, 64, 333 ff., 1909.

<sup>5</sup> See the preceding article, p. 91, third foot note.



this evidence is of little value. Unfortunately the degree of acidity recommended and used by Rosenheim and Pinsker for this process is in doubt, as their statements are somewhat ambiguous, but in these two blank experiments the hydrochloric acid appears to have been about N/4 (certainly not below N/8). That such a degree of acidity (or even one a good deal lower), would produce a very considerable hydrolysis under the conditions named by Rosenheim and Pinsker is at once evident from the reaction velocity observed in Experiment 6 above, if due allowance be made for the difference in temperature.

This is confirmed by the experiment recorded in Table III, in which the composition of the reaction mixture was

TABLE III.  
*Hydrolysis of Hypophosphoric Acid.*

Temperature 87°-95°.

Iodine and thiosulphate solutions approximately N/50.

Time heated min.	Iodine solution added cm <sup>3</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution required cm <sup>3</sup>	Per cent of hypophosphate hydrolyzed
0	50.00	44.63	
60	50.00	41.07	10
90	50.00	39.54	14.5
120	50.00	38.39	17.3
∞	50.00	(9.52)*	

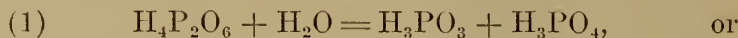
\* Calculated from standards of solutions used.

the same as in Experiment 6, but the bath in which the sealed tubes were immersed had an initial temperature of 87°, which rose steadily to about 95° during the course of the experiment. Although the concentration of the hydrochloric acid was only about N/4, seventeen per cent of the hypophosphoric acid had been hydrolyzed at the end of two hours.

*The Molecular Formula of Hypophosphoric Acid.*— Though the weight of evidence favors the view that the molecular formula of hypophosphoric acid is H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> rather than H<sub>2</sub>PO<sub>3</sub>, the question is still under debate, Rosenheim and co-workers<sup>6</sup> supporting the simpler formula. The fact, established by our reaction velocity measurements, that the hydrolysis is a monomolecular

<sup>6</sup> Rosenheim, Stadler and Jacobsohn, Ber. chem. Ges., 39, 2837, 1906; Rosenheim and Pritze, *ibid.*, 41, 2708, 1908; Rosenheim and Pinsker, *ibid.*, 43, 2003, 1910.

reaction, furnishes an important argument in favor of the double molecule. According to the formula assumed this reaction may be written either



the former requiring that the reaction velocity in dilute solution shall be proportional to the concentration of the hypophosphoric acid, as we have found to be the case, while the latter requires that the rate shall be proportional to the square of that concentration.

While it is true that any molecular formula represented by an integral multiple of  $\text{H}_4\text{P}_2\text{O}_6$  would also account for the monomolecular reaction, the results of molecular weight determinations by the freezing point method<sup>7</sup> show that molecules containing four or six phosphorus atoms can hardly be present in any considerable quantity, if at all. We are thus led to the conclusion that the normal molecule of hypophosphoric acid in water solution is that corresponding to the formula  $\text{H}_4\text{P}_2\text{O}_6$ . This conclusion can not be avoided by assuming that these molecules, though present only in small amount, are the more reactive, since in that case their concentration would be proportional to the square of the concentration of the predominating  $\text{H}_2\text{PO}_3$  molecules, and the reaction would appear to be bimolecular. It would, of course, be possible to explain the facts by assuming that the reaction was bimolecular but confined to one type of molecule or anion whose concentration was proportional to the square root of the total concentration, but this hypothesis is arbitrary, and seems to be without rational foundation.

## II.

### *Conductivity.*

Measurements of the conductivity of hypophosphoric acid have been made by Parravano and Marini,<sup>8</sup> using a solution prepared by the action of hydrogen sulphide upon lead hypophosphate suspended in water, and by Rosenheim and Pinsker,<sup>9</sup> who worked with a solution

<sup>7</sup> Cornec, *Comptes rendus*, **150**, 108, 1910; Rosenheim and Pinsker, *Ber. chem. Ges.*, **43**, 2010, 1910.

<sup>8</sup> *Atti Accad. Lincei* (5), **15**, II, 203, 305, 1906.

<sup>9</sup> *Ber. chem. Ges.*, **43**, 2003, 1910.

prepared by dissolving the crystalline hydrate of hypophosphoric acid. Both of these methods of preparation have disadvantages. In the former, impurities may be introduced by failure to wash the lead hypophosphate until free from adhering salts, or by incomplete removal of the hydrogen sulphide or its possible oxidation products. In the latter, the high solubility and deliquescence of the hydrate make it very difficult to free the crystals from traces of the syrupy mother liquor, the presence of which not only contaminates the preparation but induces hydrolysis of the crystals at such a rapid rate that solutions prepared from them almost inevitably contain more or less phosphorous and phosphoric acid. The conductivities found by Parravano and Marini at 25° are on the average about 15% higher than those of Rosenheim and Pinsker, measured at 25.6°.

Knowing from practical experience the difficulty in preparing a pure solution of hypophosphoric acid by way of the hydrate, we have preferred to adopt the principle used by Parravano and Marini. Two solutions, A and B, have been employed in our conductivity measurements, the former prepared by the action of hydrogen sulphide on lead hypophosphate, the latter in a similar manner from copper hypophosphate.

In preparing solution A, acid sodium hypophosphate, four times recrystallized, was treated in hot solution (80°-90°) with an excess of lead acetate, and the mixture heated on the steam bath for several hours to bring the precipitate into a dense and easily washable condition. The precipitate was then collected on a suction filter, transferred to a porcelain dish, and digested for some hours with distilled water over a steam bath, again filtered, and the alternate digestion and filtering continued until the filtrate gave no test for lead salt, and a portion evaporated in platinum showed no residue.

To decompose the lead hypophosphate it was placed, together with enough conductivity water to make the resulting solution of  $H_4P_2O_6$  about 0.08 molar, in a large bottle surrounded by a cooling bath of ice and water, and closed by a stopper carrying a rotary glass stirrer, as well as the inlet and outlet tubes for the gas. With the stirrer in operation, driven by an electric motor, hydrogen sulphide was passed in until tests of the liquid showed that the decomposition was complete and the hydrogen sulphide permanently in excess.

The lead sulphide was then filtered off, and the residual hydrogen sulphide was removed by a current of purified air. During this process, which required several hours, and thereafter until the conductivity measurements were made, the receptacle containing the solution was kept in a bath of ice and water. The solution of hypophosphoric acid so obtained gave no test for hydrogen sulphide when treated with acidified silver nitrate, and tests, by the usual methods, for sulphuric acid, lead, and sodium were negative.

A sample of this solution was at once titrated with sodium hydroxide, using Congo Red as indicator, and with the result of this titration as a guide, was diluted so as to be approximately  $N/32$  with respect to  $H_4P_2O_6$ . Immediately after the completion of the conductivity measurements described below, this solution was analyzed iodometrically, both for hypophosphoric and phosphorous acids, by the method given in the preceding paper, making each determination upon duplicate samples of the solution. The quantity of phosphorous acid present was taken as a measure of the extent to which hydrolysis had occurred. The amounts of hypophosphoric acid found in duplicate, 20 cm<sup>3</sup> samples were 0.05243 and 0.05257 gm., and of phosphorous acid in samples of the same volume, 0.00050 and 0.00060 gm., showing that the concentration of the  $H_4P_2O_6$ , including the small fraction hydrolyzed, was 0.03197 molar, and that 98.96% of this amount was unhydrolyzed.

The conductivity of this solution was measured as soon as possible after its preparation, using a carefully calibrated three-meter bridge and an accurate Leeds and Northrup resistance box, and diluting the solution in the conductivity cell in the usual way with the aid of accurately paired pipettes. The cell constant was twice determined with solutions prepared from samples of specially purified potassium chloride from different sources, both determinations giving exactly the same value. The whole series of dilutions was then repeated with a second sample of the same solution, using a different pair of pipettes, the duplicate results agreeing closely. The conductivities recorded in the following tables are in every case the mean of two such duplicate determinations.

A 100 cm<sup>3</sup> portion of solution A was then hydrolyzed completely by evaporating in a platinum dish over a

water bath and continuing the heating in the same manner for five or six hours. The residue was then carefully diluted to the original volume. An iodometric analysis by the method previously used, showed that the hydrolysis of the hypophosphoric acid had been complete. The conductivity of this solution was then measured in the same way as before.

Solution B was prepared from a sample of acid sodium hypophosphate which had been recrystallized eight times. This was converted into the copper salt by treatment with pure copper sulphate, and the copper hypophosphate washed and finally decomposed with hydrogen sulphide by the same method and with the same precautions used in preparing Solution A. The use of the copper salt has the advantage that the sulphate radical can readily be tested for and its elimination insured. After diluting the solution it was analyzed in the same manner as Solution A. Duplicate samples gave 0.05499 and 0.05490 gm. of hypophosphoric acid per 20 cm<sup>3</sup>, and in samples of the same volume 0.00015 and 0.00007 gm. of phosphorous acid, thus showing the solution to be 0.03347 molar H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> of which 99.80% was unhydrolyzed, a higher degree of purity than that of Solution A. The same conductivity measurements were then made with Solution B, both before and after hydrolysis, as had previously been made with Solution A. The results for both solutions are recorded in Table IV.

TABLE IV.

*Molecular Conductivity of Hypophosphoric Acid, H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> at 25°.*

Solution A. (98.96% unhydrolyzed)			Solution B. (99.80% unhydrolyzed)		
Molec. concentration	$\mu$ Molec. cond. Sol. A ohm <sup>-1</sup>	$\mu$ , after complete hydrolysis ohm <sup>-1</sup>	Molec. concentration	$\mu$ Molec. cond. Sol. B ohm <sup>-1</sup>	$\mu$ , after complete hydrolysis ohm <sup>-1</sup>
0.03197	381.2	345.6	0.03347	384.0	341.0
0.01599	415.4	412.8	0.01674	416.2	407.2
0.007993	456.6	483.8	0.008369	456.0	478.0
0.003997	506.2	555.0	0.004184	505.0	551.2
0.001998	565.8	614.6	0.002092	564.8	614.8
0.0009992	624.2	666.2	0.001046	626.4	678.6

To facilitate comparison with similar data recorded in the literature we have recalculated our results to round

dilutions of 32, 64, 128, etc. liters, upon the assumption (sufficiently accurate for the short intervals involved), that the conductivity is a linear function of the logarithm of the dilution. The results are given in Table V, and

TABLE V.

*Molecular Conductivity of Hypophosphoric Acid at 25°.*  
*Referred to Formula H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>.*

Dilution lit./mol.	$\mu$ Sol. A ohm <sup>-1</sup>	$\mu$ Sol. B ohm <sup>-1</sup>	$\mu$ Mean ohm <sup>-1</sup>	After complete hydrolysis.		
				$\mu$ Sol. A ohm <sup>-1</sup>	$\mu$ Sol. B ohm <sup>-1</sup>	$\mu$ Mean ohm <sup>-1</sup>
32	382.3	387.2	384.7	347.2	347.6	347.4
64	416.8	421.2	419.0	415.2	414.3	414.7
128	453.2	460.9	459.5	486.2	485.3	485.8
256	508.2	511.0	509.6	557.0	557.6	557.3
512	567.7	571.0	569.3	616.4	621.2	618.8
1024	626.1	632.6	629.3	668.0	685.0	676.5

*Referred to Formula H<sub>2</sub>PO<sub>3</sub>.*

Dilution lit./mol.	$\mu$ Sol. A ohm <sup>-1</sup>	$\mu$ Sol. B ohm <sup>-1</sup>	$\mu$ Mean ohm <sup>-1</sup>	After complete hydrolysis.		
				$\mu$ Sol. A ohm <sup>-1</sup>	$\mu$ Sol. B ohm <sup>-1</sup>	$\mu$ Mean ohm <sup>-1</sup>
16	191.1	193.6	192.3	173.6	173.8	173.7
32	208.4	210.6	209.5	207.6	207.1	207.4
64	229.1	230.4	229.7	243.1	242.6	242.9
128	254.1	255.5	254.8	278.5	278.8	278.6
256	283.8	285.5	284.6	308.2	310.6	309.4
512	313.0	316.3	314.6	334.0	342.5	338.2

for convenience are expressed also in terms of the simpler molecular formula, H<sub>2</sub>PO<sub>3</sub>.

The relation between the conductivities of the acid before and after hydrolysis is interesting. At the lower dilutions the conductivity of the pure hypophosphoric acid is larger than that of the equimolecular mixture of phosphorous and phosphoric acids which is formed by its hydrolysis, while at the higher dilutions this relation is reversed. At a dilution slightly above 64 liters (referred to H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>) the conductivity would not change as the hydrolysis progressed, at higher dilutions it would increase and at lower dilutions it would decrease. Except in proximity to this special dilution it should therefore be possible to determine the rate of hydrolysis

by conductivity measurements, but we have not attempted to do this.

Table VI shows the molecular conductivities of  $H_4P_2O_6$

TABLE VI.

<i>Results of Other Investigators.</i>								
v	31.6	63.2	126.4	252.8	505.6	1111.2	2222.4	Rosenheim
$\mu$	367.4	399.0	443.4	491.4	549.8	608.8	739.2	and Pinsker
$\mu$	420.4	496.8	522.1	581.1	646.2	716.6		Parravano
v	32	64	128	256	512	1024		and Marini

as measured by Rosenheim and Pinsker at 25.6°, and the results of Parravano and Marini for 25°. Our results lie between the two series but nearer to those of Rosenheim and Pinsker. The high values obtained by Parravano and Marini are probably due to failure to free their lead salt from adhering impurities, or to oxidation of the hydrogen sulphide. The discrepancy between our values and those of Rosenheim and Pinsker is hard to explain. It is unlikely that our solutions contained any considerable amount of impurities other than the products of hydrolysis. This conclusion is supported both by the qualitative tests above mentioned, and by the approximate agreement between the observed conductivities of the two solutions, prepared independently, and by somewhat different methods. Finally, the comparative purity of our solutions is shown by the fact that their molecular conductivities after complete hydrolysis, referred to the formula  $H_2PO_3$ , coincide very closely with the mean of the molecular conductivities of phosphorous and phosphoric acids, as will be evident on comparing our results with the following figures for these acids at 25°, as given by Kohlrausch and Holborn:<sup>10</sup>

TABLE VII.

<i>Molecular Conductivities at 25°.</i>								
	v	=	16	32	64	128	256	512
$H_3PO_3$	$\mu$	=	222	257	292	318	337	351
$H_3PO_4$	$\mu$	=	124	156	195	240	279	317
Mean	$\mu$	=	173	206.5	243.5	279	308	334

It therefore seems probable that the results of Rosenheim and Pinsker are somewhat too low.

<sup>10</sup> Leitvermögen der Electrolyte, p. 167, from measurements by Ostwald. These values for phosphoric acid are in good agreement with the more recent results of Noyes and Eastman, Carnegie Inst. Pub. No. 63, p. 262, 1907. For phosphorous acid Ostwald's values seem to be the only ones which have been published.

*Molecular Conductivity and Molecular Formula.*—In support of the smaller molecular formula for hypophosphoric acid, Rosenheim and Pinsker emphasize the fact that the molecular conductivity referred to the formula  $H_2PO_3$  (see Table V, lower section, column 4) is of the same order of magnitude as the molecular conductivities of  $H_3PO_3$  and  $H_3PO_4$  (Table VII) and seems to tend with dilution toward the same limit. This tendency would be expected, as they point out, if the normal molecule were  $H_2PO_3$ , since the anions  $HPO_3'$ ,  $H_2PO_3'$ , and  $H_2PO_4'$ , on account of their similarity in composition would probably have nearly the same velocities.

This argument is not a strong one, for the facts can be equally well explained upon the other hypothesis. Owing to the high velocity of the hydrogen ion the conductivity of  $\frac{1}{2}(H^+ + H^+ + H_2P_2O_6'')$  would be nearly the same as that of  $(H^+ + HPO_3')$  which would account for the tendency above mentioned. That two and only two of the equivalents of hydrogen in the molecule  $H_4P_2O_6$  are extensively ionized is indicated by the fact that two of these equivalents of hydrogen, but not the third, can be titrated in the presence of methyl orange.

It is interesting to note that ionization relations of this kind have been proved to exist in the case of pyrophosphoric acid by Abbott and Bray,<sup>11</sup> who determined the ionization constant for each of its four equivalents of hydrogen. This is important, because, if the formula of hypophosphoric acid is  $H_4P_2O_6$ , we should expect a rather close analogy with pyrophosphoric acid  $H_4P_2O_7$ , both in conductivity and in other properties. Such an analogy unquestionably exists. If we calculate the conductivity of pyrophosphoric acid at 25° from the results of Abbott and Bray for 18°, allowing for a temperature coefficient of 1% per degree in round numbers, we find that within the range of dilution covered by their experiments (20 to 800 liters) the molecular conductivities of  $H_4P_2O_6$  and  $H_4P_2O_7$  show a maximum difference of less than 10%, and approach one another at higher dilutions. Abbott and Bray have also showed that with reference to the ionization of the first equivalent of hydrogen, pyrophosphoric acid is not far below the strongest acids in strength; with reference to the second equivalent, it

<sup>11</sup> J. Am. Chem. Soc., 31, 729, 1909.



is a fairly strong acid having an ionization constant close to that of the primary ionization orthophosphoric acid; and with reference to the third it is a weak acid, approximating in strength to the secondary ionization of orthophosphoric acid. This relation is further shown by the behavior of these two acids toward indicators. With pyrophosphoric acid as with hypophosphoric acid, two equivalents of hydrogen are titrable in the presence of methyl orange, with orthophosphoric acid only one.

Finally, the close analogy between pyrophosphoric and hypophosphoric acid is conspicuous in many other ways. Of the six oxy-acids of phosphorus, ortho-, pyro-, and meta-phosphoric acid, hypophosphoric acid, phosphorous acid, and hypophosphorous acid, no two show as close a mutual resemblance in general chemical behavior as do pyro- and hypophosphoric acid, at least when in the form of salts. In general appearance, as well as in relative solubility in various reagents, there is a most striking resemblance between those hypophosphates which can be obtained as precipitates, and the corresponding pyrophosphates, a similarity which is the cause of much difficulty in qualitative analyses which involve these two acids. In fact, in most cases, the most certain way of distinguishing them is to dissolve and hydrolyze the hypophosphate precipitate, best by heating with strong hydrochloric acid, and to test the product for phosphorous acid. Pyrophosphoric acid, similarly treated, yields only orthophosphoric acid.<sup>12</sup> Thus it is only by actually decomposing the hypophosphate and pyrophosphate molecules that radical differences are revealed. Even the hydration of pyrophosphoric acid bears a formal resemblance to the hydrolysis of hypophosphoric acid, since it involves the division of the molecule into two smaller ones, and therefore might also be called a hydrolysis in the broadest sense of the term. This reaction, as Abbott<sup>13</sup> has shown, is monomolecular and is catalyzed by hydrogen ions, though the effect of these ions is proportional to a lower power of their concentration than is the case with hypophosphoric acid.

It is evident that these various points of resemblance

<sup>12</sup> We are at present engaged in a study of the qualitative separation and identification of the different oxy-acids of phosphorus and hope soon to publish our results.

<sup>13</sup> *J. Am. Chem. Soc.*, **31**, 763, 1909.

between pyrophosphoric and hypophosphoric acid can be much more easily and logically explained if we accept the larger formula for the latter acid.

*Summary.*

1. The rate of hydrolysis of hypophosphoric acid in the presence of hydrochloric acid as catalyzer has been measured at 25° and at 60°.

2. In dilute solutions whose hydrogen-ion concentration is approximately constant, the reaction is monomolecular.

3. This fact supports the view that the normal molecular formula for hypophosphoric acid in water solution is  $H_4P_2O_6$  rather than  $H_2PO_3$ .

4. The conductivity of hypophosphoric acid has been determined at 25° in dilutions from 32 to 1024 liters and also the conductivity of the same series of solutions after complete hydrolysis.

5. At a dilution slightly above 64 liters the hydrolysis does not alter the conductivity. At lower dilutions it lowers the conductivity, and at higher dilutions raises it.

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ART. IX.—*On the Occurrence of Ilvaite in the South Mountain Mining District, Owyhee County, Idaho;*  
by EARL V. SHANNON.

In 1913, Mr. Oscar H. Hershey, following a trip of inspection to the South Mountain District in southwestern Idaho, presented the writer with a specimen of ilvaite from that district. During last year, through correspondence with Mr. H. I. Ellis, then in charge of the development at one of the mines, three additional specimens were obtained. The writer's thanks are due Mr. Ellis and Mr. Hershey for the specimens which form the basis for the following notes. These have been placed in the Brush Collection of the Sheffield Scientific School of Yale University.

Ilvaite is coming to have considerable interest for students of economic geology inasmuch as it is supposed to be an important diagnostic mineral; the tendency of at least one prominent teacher being to regard its presence as unquestionable evidence that the deposit in which it

occurs is of contact-metamorphic origin.<sup>1</sup> The data on the South Mountain occurrence are incomplete but in the opinion of at least two competent observers, the minerals of the ore in which the ilvaite occurs are of contact-metamorphic origin. If this is true, this must be one of the few known deposits, of true contact origin, which contain lead as the predominant metal. The amount of silver present is also unusually high for a contact deposit.

If the diagnostic value of the mineral is to be conclusively proven, it is important that the occurrences of the mineral be fully described. Most of the localities, thus far discovered, have been described in languages other than English and it is possible that some of the papers already published prove the mineral to have originated by other processes. Ilvaite is of interest to the mineralogist especially because each of several authorities who have worked upon the crystallography of the mineral has given a different axial ratio. The specimens described below are interesting because of the large size of the crystals, these being perhaps the largest ever found in the United States. The results of the crystallographic work have not been such as to settle any of the doubtful points regarding the mineral. It is possible, however, that, were a special search made with a view of obtaining smaller crystals, more suitable for crystallographic investigation, this locality might furnish material on which the crystallographic constants of the mineral could be accurately determined.

The ilvaite from South Mountain was first identified by Dr. W. F. Hillebrand and Prof. F. W. Clarke in specimens of ore from the Golconda Claim, collected by Dr. Waldemar Lindgren. The ilvaite is mentioned by Lindgren in the brief description of the deposit in which it occurs.<sup>2</sup> Later an analysis of the mineral was published by Hillebrand.<sup>3</sup> Aside from these incomplete references, the only mention of the occurrence is to be found in the report of Bell, for 1906.<sup>4</sup> The locality is not mentioned in any of the standard works on mineralogy.

*Location and geology of South Mountain.*—South Mountain is located some 20 miles southwest of Silver

<sup>1</sup> Irving, John Duer, *Economic Geology*, Lecture Course, S. S. S., Yale University, 1916.

<sup>2</sup> Lindgren, W., *Gold and Silver Veins of Idaho*, 20th Ann. U. S. G. S., Pt. III, 1900.

<sup>3</sup> *Anal. of Rocks and Minerals*, U. S. G. S. Bull. 591, p. 318.

<sup>4</sup> Bell, Robert M., 8th Ann. Rept. Mining Industry of Ida., Boise, 1906.

City, in Owyhee Co., which occupies the extreme southwestern corner of the state. The mines are reached by a wagon road from Jordan Valley, Oregon. According to Bell,<sup>4</sup> South Mountain is an isolated uplift or offset from the Owyhee Range and is entirely surrounded by a broken lava plateau. It rises to an extreme elevation of 8000 feet and is probably 10 miles long by 5 miles broad. It represents an anticlinal arch of eruptive granodiorite, a medium-grained, gray, granitic rock which carries an excess of hornblende over biotite. This uplift has evidently been broken by a fault along its axis, which has been eroded into a deep gulch, now forming the bed of William Creek, which practically traverses the center of the uplift in a northwesterly direction. Parallel to the bed of William Creek, and climbing over the highest crest of the mountain near its source, there is a belt or zone of white marbleized limestone, showing a blocky structure, with black lines of silica and impurities. Its general strike is northwest and southeast, turning sharply to the east where it crosses under the highest crest of the mountain near the head of the creek. It is from 100 to 300 feet wide and makes a distinct white line readily traceable for ten miles. It has a dip to the southwest of about sixty degrees and is underlain by one thousand feet of schist, succeeded by a like width of gneiss, which is in turn succeeded by a wide belt of granodiorite. The same succession, partly capped by basalt, recurs on the opposite side of the marble band.

*Character of the Ores.*—According to Lindgren, the ore minerals consist of argentiferous galena with some zinc-blende and copper minerals in a gangue of quartz, calcite, actinolite and ilvaite. The ores contain from 20 to 60 per cent. lead and from 40 to 100 ounces of silver per ton. "The deposits are supposed to be veins but the mineral association appears to be one clearly indicating contact deposits."

Hershey,<sup>5</sup> more recently, gives the following notes:—The ilvaite occurs in a contact-metamorphic deposit. A large area of rather fine-grained granite, or granodiorite, adjoins an area of highly metamorphosed sedimentary rocks now largely schists, quartzites, and marble. In a broad band of marble near the granite, there is a series of masses of contact-metamorphic minerals including

<sup>5</sup> Hershey, Oscar H., personal letter, 1916.

actinolite, garnet, epidote, and ilvaite, carrying in places pyrrhotite, chalcopyrite, sphalerite, and galena. "I did not pay any attention to the paragenesis of the minerals, but, if my memory serves me well, I should say they are all distributed in the irregular manner characteristic of contact deposits. The ilvaite is in bunches scattered through the masses."

*Description of Ilvaite.*—The specimen received from Mr. Hershey consists of a large aggregate of imperfect black prisms of ilvaite associated with white calcite and granular aggregates composed of small dodecahedral crystals of brownish-red garnet. The ilvaite only approximates prismatic form and no good faces occur. The specimens received from Mr. Ellis show far better crystals. The first of these consists of a mass of translucent, glassy, white quartz, completely filled with grains and crystals of ilvaite. These are commonly prismatic and deformed by mutual interference, but some of them, when removed from the enclosing quartz, are suitable for measurement on the reflecting goniometer. Only the prismatic zone is represented, these embedded crystals never, so far as observed, being terminated. The most common habit is like the prism zones of figs. 1 to 4, although all of the forms observed in this zone on the terminated crystals were found on the embedded crystals. The crystals are often deeply striated and rounded, apparently by oscillation between the prisms  $m(110)$  and  $s(120)$ . They greatly resemble embedded black tourmaline and a casual observer would probably mistake them for that mineral. The forms observed on one of the best of these crystals were identified as:  $a(100)$ ,  $b(010)$ ,  $m(110)$ ,  $h(210)$ ,  $s(120)$ ,  $d(140)$ .

The measurements obtained on one of these embedded crystals are compared with the angles given by Dana, as follows:

	Observed.		Calculated ( $a = 0.6665, D$ ).	
$m : m''$	66°38'	67°46'	Av. 67°12'	67°22'
$h : h''$	37°28'	38°00'	37°44'	36°52'
$s : s'$	72°42'	73°10'	72°56'	73°45'

This agreement with the calculated angles is as close as was obtained upon any of the crystals measured. That there should be a discrepancy is not at all surpris-

ing in view of the fact that in very few cases did the faces of the crystals give single distinct signals. Much more frequently a face is represented by a continuous band of signals, a degree or more wide. Usually there is one signal in the band which stands out more clearly than the others and, in such cases, this more distinct signal was the one measured. In other cases it was necessary to take the mean between the two ends of a series of signals. Vicinal faces seem to be a constant characteristic of ilvaite and in measuring a prism zone of this mineral, one seldom fails to note some faint but distinct signals of this kind. If one were dealing with a single crystal, it might be considered justifiable to record these forms and calculate indices for them, but the examination of a number of crystals leads to such a confusion of unsubstantiated forms with improbable indices that the attempt can not but be abandoned. The following vicinal forms have been recorded on ilvaite from Herbornseelbach by Bauer:<sup>6</sup> (13.17.0), (7.11.0), (4.11.0).

The best specimens of Idaho ilvaite consist of well-terminated prisms. The smallest specimen is a large prismatic crystal about two and one-half inches long and averaging perhaps one-half inch in diameter, with some small crystals attached to the larger prism. The other specimen is an aggregate of such large prismatic crystals in parallel position. Attached to or projecting from the larger crystals were a number of smaller terminated prisms and it is on these that most of the measurements were made. When received, these specimens were covered with a thin film of ochreous limonite and looked as though they had been embedded in a soft gossan of oxidized material. Scrubbing with a stiff brush removed all of this limonite and left the crystals clean and lustrous. Some very thin drusy coatings of calcite were also easily removed, leaving no scar on the ilvaite. The crystals are fragile and liable to crumble away if roughly handled, owing to the presence of minute, irregular cracks which thoroughly traverse the mineral, somewhat after the fashion of glass which has been heated and plunged into cold water. This breaking of the crystals is probably traceable to strains incident upon volume changes in the associated and enclosing minerals during surficial oxida-

<sup>6</sup> Bauer, *Jb. Min.*, 1, 31, 1890.

tion and hydration. Frequently a crystal seems to have been split longitudinally and the two halves slightly displaced, this discrepancy in one case reaching five degrees. The fracture was parallel to *b*, the most prom-

FIG. 1.

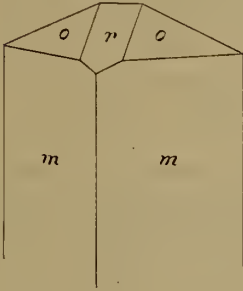


FIG. 2.

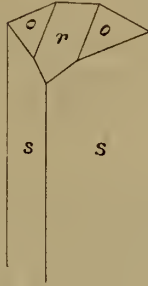


FIG. 3.

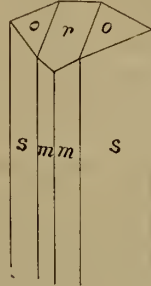


FIG. 4.

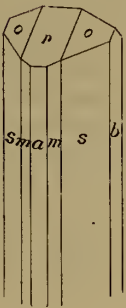


FIG. 5.

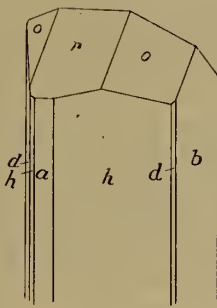
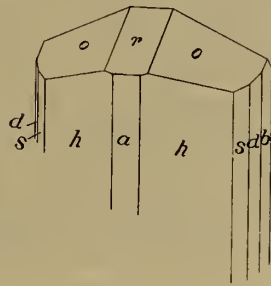


FIG. 6.



inent cleavage, and was not visible on the crystal, being located on a deeply striated face. Its location was clearly shown when the angles measured on the crystal were plotted on a Penfield stereographic circle.

The terminated crystals show exactly the same forms in the prism zone as were observed on the embedded crystals. On the whole, the faces in this zone on the terminated crystals are not as good as they are on some of the embedded crystals. The crystals are frequently unsymmetrical as shown in fig. 5, where a form may be present as a broad face on one side of the crystal, and be absent or represented by a very narrow line on the

opposite side. The results obtained in measuring the terminal faces were quite disappointing. Only one value was obtained for the angle  $rr'$  (over  $c$ ),  $67^{\circ}2'$ , which is  $9'$  short of the angle given by Dana. The values obtained for the angle  $oo'''$  form the most puzzling feature of the crystals. The angle given by Dana is  $40^{\circ}29'$ . The values read on the Idaho mineral range from  $36^{\circ}34'$  to  $42^{\circ}45'$ . Two values,  $36^{\circ}34'$  and  $39^{\circ}14'$ , fall below  $40^{\circ}$ ; seven fall between  $40^{\circ}9'$  and  $40^{\circ}52'$ ; three fall at  $41^{\circ}2'$ ,  $41^{\circ}21'$ , and  $41^{\circ}24'$ , respectively, and six fall between  $42^{\circ}1'$  and  $42^{\circ}45'$ . On the whole there is little difference in the relative quality of the faces upon which these angles were obtained. Assuming that all those values between  $40^{\circ}0'$  and  $41^{\circ}0'$  represent this angle, (the average for six of these values is  $40^{\circ}28'$  as compared with  $40^{\circ}29'$  calculated), we have still the group of six values between  $42^{\circ}0'$  and  $42^{\circ}45'$ , the average for the group being  $42^{\circ}27'$ . This doubtless is another form in the zone  $bob'$  having the value  $pyr. \wedge pyr''' = 42^{\circ}27' \pm 5'$ . It is possible that the other abnormal values obtained are due to the tendency of the crystals to split in half through the center of the crystal parallel to 010. Such rifts might easily be concealed in the deep striations of the 101 face and might easily separate the crystal sufficiently to change the angle between the faces of the pyramid.

*Composition.*—Since a complete analysis was available, the mineral was not reanalyzed. The analysis of Idaho ilvaite by Hillebrand is compared below with analyses of ilvaite from a number of other localities.

	I	II	III	IV	V	VI
SiO <sub>2</sub>	29.16	28.09	29.81	29.30	29.93	29.3
Al <sub>2</sub> O <sub>3</sub>	.52	.32	.16	....	....	....
Fe <sub>2</sub> O <sub>3</sub>	20.40	20.80	18.89	20.30	20.16	19.6
FeO	29.14	29.93	32.50	33.50	31.83	35.2
MnO	5.51	3.24	2.22	1.97	3.02	....
CaO	13.02	15.89	13.82	13.71	13.71	13.7
MgO	.15	.18	.30	....	....	....
Na <sub>2</sub> O	.08	Cr <sub>2</sub> O <sub>3</sub> 0.13	....	....	....	....
H <sub>2</sub> O—	.15	....	....	....	....	....
H <sub>2</sub> O+	2.64	1.62	1.62	1.90	0.42	2.2
Total	100.41%	100.20	99.32	100.68	99.07	100.00
Sp. Gr.	4.059	....	3.85	4.05	....	....



- I. Ilvaite, Goleonda Mine, South Mountain, Idaho. Anal. by W. F. Hillebrand, U. S. G. S. Bull. **591**, p. 318.
- II. Ilvaite, Potter Cr., near Baird, Shasta Co., Cal. Anal. by W. R. Moss, this Journal, **26**, 14, 1908.
- III. Ilvaite, Barclay Sound, Vancouver Id., B. C. Anal. by Hoffman, this Journal, **42**, 432, 1891.
- IV. Ilvaite, Greenland. Anal. by Lorenzen, Min. Mag., **5**, 63, 1882.
- V. Ilvaite, Elba. Anal. by Early, Proc. Irish Ac., **3**, 52, 1877.
- VI. Ilvaite, required by formula,  $H_2O.2CaO.4FeO.Fe_2O_3.-4SiO_2$ .

*Other Properties.*—In the ilvaite from Idaho, traces of cleavage are occasionally observed parallel to 010. This is very indistinct and no other cleavage was observed. The fracture is uneven; H. 5.75; G. 4.059 (Hillebrand); luster vitreous, and not sub-metallic as described from other localities; color black; streak black with very faint inclination toward brown. The mineral is rather difficultly fusible before the blowpipe. Intumesces slightly and yields a black magnetic bead. Readily soluble in hydrochloric acid giving an amber solution which gelatinizes upon cooling.

Several unsuccessful attempts were made to cut oriented sections of the crystals. The material is too opaque to transmit sufficient light to show the optical properties in the thinnest sections which could be ground. In rock or ore sections of the ordinary thickness ( $\pm 0.03$  mm.) this mineral would be perfectly opaque and anhedral grains might easily be mistaken for magnetite. It is therefore suggested that ilvaite may be present in fine-grained aggregates of contact-metamorphic minerals and have a much wider distribution than has hitherto been suspected.

West Haven, Conn.

ART. X.—*The Silurian Arisaig Series of Arisaig, Nova Scotia*,\* by F. H. McLEARN.*Introduction.*

The Silurian section of Arisaig has more than one claim to importance and is responsible for the reputation of this place in geological literature. As the most continuous and longest ranging of its age in eastern Canada it serves well as a type exposure, by comparison with which the more fragmentary occurrences of less favoured localities may be integrated and assigned to their true position in the stratigraphic column. It is interesting because of the resemblance of its faunas to those of Great Britain and for the light it sheds on the paleogeographic relations of the North Atlantic to the interior seas of America. The unusual faunal associations, and in particular the rich development of bivalves, also attract attention.

*Previous studies.*—The section possesses considerable historic interest and has been studied by the geologists and paleontologists of three generations. Among them may be mentioned Abraham Gesner, J. William Dawson, James Hall, Rev. David Honeyman, E. Billings, Hugh Fletcher, Henry M. Ami, Charles Schuchert, W. H. Twenhofel, and M. Y. Williams. Briefly the work already done at Arisaig may be stated as follows: The general geological problems, igneous, structural and physiographic, and the correlation of the Ordovician have been treated at length by M. Y. Williams (1914)<sup>1</sup>. In Silurian stratigraphy, the section has been finally divided into five formations whose delimitations and thicknesses have been determined by Twenhofel (1909). These have been correlated with interior North America and Kristiania, Norway, by Schuchert and Twenhofel (1909) and with Anticosti by Twenhofel (1913). The important and necessary direct comparison with the British succession has been almost entirely neglected. There has also been no correlation with the neighboring section of Eastport, Maine. The identifications and zonal

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<sup>1</sup> Since a complete bibliography will be given in the final monograph, only the year of publication of the works cited is thought necessary here.

range of the species as given by Schuchert and Twenhofel were only intended to be preliminary and deal chiefly with well-known American forms. The peculiar faunal content and its relation to the muddy seas of Arisaig has been briefly noted by Schuchert and Twenhofel (1909, 1913), but the details of response to the silt factor and the evidence for its operation have not been considered. In paleogeography the transatlantic affinities of the fauna have been recognized since the time of Honeyman (1859). The overlying Knoydart formation has been referred to the Lower Devonian by Ami (1901).

*Scope of present investigation.*—The present investigation differs from that of all previous workers by dealing primarily with the purely paleontological problems of the Silurian. In spite of all that has been done at Arisaig, the whole fauna is now assembled and systematically studied for the first time. That this is necessary is shown by the fact that eight new genera, forty-nine new species and twenty-seven new varieties have been erected, and many species not previously recognized in this fauna have been identified. With the taxonomic work as a basis, the problem is expanded to include the zonal range of all the species, the evolution of the fauna, the biological associations and their causes, correlation with Great Britain and Maine, and finally the paleogeographic relations. While the age of the overlying Knoydart formation and its relation to the Arisaig series are not solved, the whole problem is restated and a Silurian age suggested.

The entire work, including the description and illustration of all the species, and the bibliography, is to be published by the Geological Survey of Canada. For this reason, only a summary of the main results, together with a preliminary description of the new genera and a few new species, is given below. The complete taxonomic treatment of the fauna, its evolution and zonal arrangement, full faunal lists, etc., are reserved for the final report.

*Acknowledgments.*—The whole investigation has been carried out under the constant supervision of Professor Charles Schuchert of Yale University and has thus benefited by the long experience of that research worker in Paleozoic stratigraphy. The author is under obligations to other members of the Department of Geological

Sciences at Yale University, and in particular to Professors Joseph Barrell and R. S. Lull. He is also indebted in many ways to the officials of the Geological Survey of Canada. More detailed acknowledgment will be made in the final publication.

*Location.*—The Silurian rocks of Arisaig occupy a small area in northern Antigonish County, Nova Scotia, on the shore of Northumberland Strait. The best sections are in the sea cliffs along the shore, and an almost continuous exposure of the whole Arisaig series extends from the small fishing village of Arisaig westward to the vicinity of McAra's Brook.

### *Stratigraphy.*

*Arisaig series.*—The name of Arisaig series has been given by M. Y. Williams to the entire marine Silurian column as developed at Arisaig. It has a total thickness of about 3800 feet. The sediments are prevailingly argillaceous and consist of shales, sandstones and impure limestone bands. Limestone, properly speaking, is entirely absent. It has been divided by the cumulative efforts of previous workers into five formations. In ascending order, these are Beechhill, Ross Brook, McAdam, Moydart and Stonehouse. Locally it is underlain by a flow of aporhyolite of Ordovician age, but Williams (1914) and others have shown that the relation to the sediments of the Ordovician is that of an angular unconformity. The Arisaig series is followed by the subaërial strata of the Knoydart formation.

*Beechhill formation.*—The Beechhill, the basal member of the Arisaig series, has a thickness of about 200 feet and is made up of sandstone and arenaceous shale with a few local lenses of arenaceous limestone. The fauna is a poorly developed one and only fourteen species are recognized. The guide fossils are: *Heliophrentis bilateralis* var. *beecehillensis*, n. var., *Rhipidomella arisaigensis*, n. sp., *Camarotæchia bimesiornata*, n. sp., *Whitfieldella?* *crassa* var. *beecehillensis*, n. var., and *Cyclonema parvimedium*, n. sp.

*Ross Brook formation.*—The Ross Brook consists of about 830 feet of black, gray and greenish gray shales and gray, somewhat lenticular, finely cross-bedded sandstones. The fauna consists of forty-three species of

which twenty-three are confined to this formation. Among the guide fossils are: *Retiolites geinitzianus* mut. *venosus* (Hall), *Monograptus clintonensis* (Hall), *Camarotachia llandoveriana* var. *rossbrookensis*, n. var., *C. (Pectorhyncha) humiliplicata*, n. sp., *Plagiorhyncha decemplicata* (Sowerby), *P. glassii* (Davidson), *P. plastica*, n. sp., *Calospira hemispherica* (Sowerby) and *Dalmanites weaveri* (Salter). *Chonetes tenuistriatus* Hall appears here for the first time.

*McAdam formation.*—The McAdam is made up of 1120 feet of gray and black shales and sandstones with a little argillaceous limestone. Near the base is a three-foot bed of iron-ore. The fauna totals forty-seven species, of which twenty are restricted. The bivalves, for which this locality is so noteworthy, now appear in abundance for the first time and make up sixteen species of the fauna. The guide fossils are: *Dalmanella abdidimacula*, n. sp., *D. elegantula* var. *transversomedia*, n. var., *Camarotachia (Pectorhyncha) obtusiplicata* (Hall), *Delthyris crispa* (Hisinger), *Honeymania planimarginata*, n. sp., and its variety *elongimarginata*, n. var., *Arisaigia postornata*, n. sp., *Orthonota arisaigensis*, n. sp., *O. pressiorinata*, n. sp., and *Modiolopsis postunisulcata*, n. sp. *Chonetes tenuistriatus* Hall makes its last appearance here.

*Moydart formation.*—This formation has a total thickness of 380 feet. Impure limestone now becomes common and the lithology consists of thin-bedded, flaggy and ripple-marked greenish shales and arenaceous and argillaceous limestones. The fauna numbers thirty-four species of which nine are restricted. The principal guide fossils are: *Eatonioides lamellornatus*, n. sp., *Wilsonia wilsoni* var. *saffordi* (Hall), *Delthyris crispa* mut. *moydartensis*, n. mut., *Seelya moydartensis*, n. sp. The following are among those forms that appear here for the first time and continue into the Stonehouse: *Orbiculoidea novascotica* Ami, *Chonetes novascoticus* Hall, *Goniosstrophia aciculata* (Hall), *Calymene intermedia* var. *antigonishensis*, n. var., and *Dalmanitina logani* var. *conservatrix*, n. var.

The top 32 feet consist of massive red shale, without fossils, and are thought to indicate a subaërial stage of unknown duration.

*Stonehouse formation.*—This, the terminal member of the Arisaig series, has a thickness of 1275 feet and consists of gray, green and red thin-bedded, ripple-marked shales, sandstones and impure limestones. Two hundred feet of strata on Stonehouse Brook are now recognized for the first time and added to the top of the section. The fauna numbers ninety-four species, of which fifty-six are restricted. The principal guide fossils are: *Lingula minima* (Sowerby), *Dalmanella lunata* (Sowerby), *Brachyprion gilpini* (Dawson), *Camarotachia glomerosa*, n. sp., *Delthyris rugicosta* (Hall), *D. rugicosta* var. *subsulcata* (Hall), *Grammysia triangulata* (Salter), *G. obliqua* (McCoy), *Palæoneilo attenuata* (Hall), *Nuculites concentricus* var. *subequilatus*, n. var., *Arisaigia placida* Billings, *A. placida* var. *socialis* (Billings), *Tropinuculites carinatus* (Hall), *Pterinea honeymani* (Hall), *Palæopecten danbyi* (McCoy), *Goniophora* (*Cosmogoniophora*) *bellula* (Billings), *Modiolopsis exilis* Billings, *M. rhomboidea* (Hall), *Orthonota angulifera* (McCoy), *O. incerta* Billings, *Orthoceras antigonischene*, n. sp., *Dawsonoceras elegantulum* (Dawson), *Homalonotus dawsoni* Hall, *Dalmanitina logani* (Hall), and *Leperditia sinuata* Hall. Other common forms, but not restricted to this formation, are: *Chonetes novascoticus* Hall, *Calymene intermedia* var. *antigonishensis*, n. var., *Nuculites concentricus* (Hall), *N. concentricus* var. *subovatus* (Hall), *N. caudori* (Sowerby), *N. caudori* var. *elongatus* (Hall), *N. caudori* var. *erectus* (Hall) and *Kionoceras angulatum* (Wahlenberg).

#### *Physical conditions.*

Two dominant bottom conditions are recorded by the lithology. One is a mud habitat, the life of which is now enclosed in shale. The other is a shelly bottom, mixed with mud or sand and now recorded by the impure shelly limestone layers. The absence of pure limestone shows that clear waters never existed for any length of time. The series was probably laid down in a shallow marginal, but normally marine, sea, into which flowed silt-laden rivers from an elevated landmass.

#### *Biological associations.*

The faunal associations are somewhat unusual and merit consideration. One notes the absence of many

familiar groups of Silurian life. The almost entire absence of corals claims first attention, while the lack of Stromatoporidæ and the impoverishment in Crinoidea and Bryozoa do not escape notice. The Brachiopoda, outside of some common species of *Dalmanella*, *Chonetes* and *Camarotoæchia* and a few other genera, are poorly represented. Many ubiquitous species and with few exceptions all the higher and more specialized families, in particular the Pentameridæ and the spire-bearers, are missing. As if to atone for this, the bivalve families Grammysiidæ, Nuculacea and Modiolopsidæ have a rich development and make a strong impress on the total assemblage of the fauna. The Aviculidæ have about the normal development, but the bivalve Cardiolidæ, Conocardiidæ and Megalomidæ are conspicuously absent. The remaining phyla, the Gastropoda, Pteropoda, Cephalopoda, Trilobita and Ostracoda, make a very modest showing. Compared with the majority of Silurian faunas, the differences lie chiefly in a falling off in many groups and the only new and unfamiliar elements introduced are to be found among certain families of bivalves.

While it is natural to turn to the prevailing muddy bottoms as the cause of this faunal association, it must be remembered that there are other factors of marine environment. These must be considered and the evidence for the control of the mud factor must be examined. Curiously enough, some of these other factors tend to produce somewhat similar biological associations. A reduction in salinity would early be marked by an elimination of corals and then by a falling off within the other phyla, including the bivalves. Finally, it would result in a bivalve fauna largely, with some gastropods and crustaceans, including contributions from the fresh-water realm. But the molluscs would be poor in variety of development and in species. It would by no means explain the rich bivalve development of this fauna, for such diversification is only possible in the normal marine realm. Moreover, water bodies of decreased salinity are evanescent in geological time, as recently pointed out by Miss O'Connell (1916), whereas the factor or factors that controlled the biological associations of this fauna endured without relaxation throughout nearly a whole period. Reduced temperature also would finally result in the elimination of corals and in a depreciation in all

groups of organisms, since the variety of life declines in the cold waters. But this factor would not bring about the profound modification of this fauna and certainly would not result in a diversity of bivalves. Moreover, the climates of the Silurian seem to have been uniformly distributed. They were warm rather than cold, and in the earlier Silurian, reef corals flourished not far away in the Anticosti sea. No ecological factor related to depth could be called upon to explain this faunal association and the geological test of constancy throughout a whole period could not be met.

Among the known and larger factors, this leaves, by elimination, the control of the mud bottoms and turbid waters. The proof of their potency, however, need not be left to rest on negative evidence alone, for there is much of a positive kind in their favor. Criteria of a positive nature may be sought in the local distribution of the fauna. This may be called the internal evidence. It is found that the bivalves which are, in particular, characteristic of this locality, are confined to the shale beds, i. e., they were mud-dwellers and avoided the harder shelly bottoms. It is not a far step, therefore, to seek in the prevalence of mud bottoms the cause of this rich bivalve development. That the depauperation in other groups is related to the muddy conditions is suggested by their better, although still restricted, development in the impure limestone lenses as compared with shale. This can be well tested in the Stonehouse, the fauna of which embraces two distinct animal communities, one a mud faunule chiefly of bivalves, and the other a shell-bottom faunule, with few bivalves and richer in all other forms of life.

We can also examine the external evidence. It may be recalled that there is no true limestone in the Arisaig series. It is found that the forms of Silurian life absent from Arisaig are elsewhere most common in limestone or calcareous shale with pure limestone layers. This means that the absent forms are inhabitants of clear waters and suggests that it was the muddy bottoms and silt-laden waters of the Arisaig sea that prevented their entrance there.

Therefore, both the internal and external evidence support the conclusion that it was the silt factor that controlled the biological associations of this fauna, while a



study of the salinity, temperature and depth factors indicates that they cannot even be considered as contributory. It is well to note in passing that all shales do not record the same environmental conditions. Thus many calcareous shales must have accumulated quite slowly, for at times it was possible for thin layers of pure limestone to form within them. Such shales have faunal associations more closely related to those of pure limestone. Biological associations similar to those of Arisaig are found in the late Silurian (Upper Ludlow) of Great Britain, where similar groups of bivalves are related to similar mud bottoms, i. e., to those of marginal but normally marine seas receiving the silt-laden waters of inflowing rivers from a high landmass. The adaptation may not be to mud alone, but also to food supply associated with the incoming silt.

So the Arisaig fauna becomes an index of response to such a marine environment and the faunal associations described on a preceding page record the relative adaptability of various groups of organisms to it. The degree of adaptation varies considerably, some forms being restricted to one or another environment while others are more "indifferent." With the exception of a few species scattered through various phyla, it is only within the bivalve families Grammysiidae, Nuculacea and Modiolopsidae that a preference is prevailingly shown for the mud-bottom environment. Within them many of the genera and a preponderance of the species of the remaining genera are restricted to the shale beds. These then are primarily *the mud-dwellers of the Silurian seas*. The representation in this environment of all other families and phyla seems to depend on the resistance of some hardy forms to these, for them, unfavorable conditions. These include the "indifferent" organisms which have a wide environmental range and also the few species actually adapted and restricted to this mud habitat.

#### *Correlation.*

Owing to the peculiar biological associations of this fauna, it has fewer species than usual in common with other faunas. This makes the correlation difficult.

*Great Britain.*—The best comparisons can be made with the British Silurian. These are very important, for

it was in western England and in Wales that the Silurian was first studied and the Silurian system was established. The Beechhill is correlated with the Lower Llandovery of Wales, the Haverford stage of Haverfordwest in southwest Wales and the Mulloch Hill and Saugh Hill groups of Girvan in south Scotland. This is based in part on negative evidence, in the absence of such characteristic Upper Llandovery species as *Plagiorhyncha decemplicata* (Sowerby), *Calospira hemispherica* (Sowerby), and *Dalmanites weaveri* (Salter). More positive evidence is found in the presence of a variety of the typical Lower Llandovery, *Whitfieldella?* *crassa* (Sowerby). Accumulative evidence is sought in the presence of a single specimen of *W.?* *angustifrons* (McCoy) and the close resemblance of the Beechhill *Rhipidomella* (*Schizophorella*) *arisaigensis*, n. sp., to the Mulloch Hill *R. (S.) mullochensis* (Davidson). The resemblance of the Mulloch Hill *Calospira scotica* to *C. planoconvexa* (Hall), of which at best it is likely not more than a variety, suggests that the British equivalent of the American Cataract is to be found in the Mulloch Hill and probably also the Saugh Hill group of Girvan.

The Ross Brook correlates with the remainder of the Valentian, i. e., the Upper Llandovery and Tarannon of Wales and also the Mullin and Rosemarket stages of Haverfordwest and the Camregan and Penkill groups of Girvan. This is based chiefly on the highly diagnostic species: *Plagiorhyncha decemplicata* (Sowerby), *Calospira hemispherica* (Sowerby), and *Dalmanites weaveri* (Salter). For the first time the Tarannon is recognized in intercontinental correlation and indeed in any correlation founded on fossils other than graptolites. This is based on the writer's interpretation of the recent work of F. R. C. Reed (1917). The Tarannon has heretofore been recognized only by its characteristic graptolite faunas, other phyla being too poorly represented to have any significance. In the Penkill group of Girvan both graptolite and brachiopod phases are closely associated and the former establishes its Tarannon age. Reed's list of brachiopods includes such characteristic Llandovery species as *C. hemispherica*, *Clorinda undata* and *Pentamerus oblongus*, the first of which does not range below the Upper Llandovery. When correlating with brachiopods, therefore, the Tarannon is best combined

with the Upper Llandovery to form a single correlative unit. This unit, then, compares not only with the Arisaig Ross Brook, but also with the American Clinton (not including the Irondequoit).

The McAdam and Moydart are together correlated with the Salopian without regard at present to its component divisions. The Stonehouse compares very well with the marine zones of the Downtonian, i. e., with the Aymestry, Upper Ludlow and also the lower part of the Downton sandstone. This is based on the following: *Lingula minima* Sowerby, *Dalmanella lunata* (Sowerby), *Brachyprion gilpini* (Dawson) cf. *B. ornatella* (Salter), *Grammysia triangulata* (Salter), *G. obliqua* (McCoy) and *Orthonota angulifera* (McCoy).

*Eastport, Maine.*—Comparison with Eastport, Maine, indicates that the Edmunds fauna is intermediate in development between the Arisaig Moydart and Stonehouse faunas. Its duration may in large part be equivalent to the time represented at Arisaig by the "red bed" sub-aërial stage. The Eastport Pembroke formation correlates with the Stonehouse while the earlier Quoddy and Dennys compare with parts at least of the McAdam and Moydart.

*Interior America, etc.*—Comparisons with interior North America, Anticosti, and Kristiania, Norway, practically follow those of Schuchert and Twenhofel (1909). The same difficulty is met with in correlating with the later Silurian of interior North America, but this is shown to be the result of the paleogeographic relations that prevailed in post-McAdam-Rochester time.

*The Knoydart problem.*—The age of the Knoydart and its relation to the Arisaig series will be discussed in detail in the final report. It may be said that the faunal evidence is non-committal and the structural evidence obscure. The topographic conditions of the late Silurian, however, were more favourable for the building out of deltas into the sea than were those of the Lower Devonian. The evidence of the geologic setting, therefore, favors a Silurian age.

#### *Paleogeographic relations.*

While the affinities of this fauna are chiefly trans-Atlantic and with Great Britain, it also shows relation-

ship with interior North America in the early Silurian. Since the Beechhill fauna is not definitely correlated with the American succession, its paleogeographical relations can not be discussed with certainty. Its affinities are chiefly with Great Britain. It shows some relation to the Cataract sea, but the evidence is not conclusive.

*Ross Brook-McAdam time.*—In both Ross Brook and McAdam time, relationship is shown not only with Great Britain, but also with eastern and western New York and southward in the Cumberland trough. No relation, however, is exhibited with the Mississippi sea of Indiana, Ohio, etc. This is based in part on a number of forms which are confined to Arisaig and northwest Europe, of which *Dalmanites weaveri* (Salter) and the short-headed *Homalonotus*, *H. knightii* Koenig, are examples. Other forms are known only from Arisaig and southward in New York, etc., of which *Camarotoechia* (*Pectorhyncha*) *obtusiplicata* (Hall) and *Monograptus clintonensis* (Hall) are examples. Others are common to northwest Europe, Arisaig and southward in New York and the Cumberland trough. Among these are: *Plagiorhyncha decemplicata* (Sowerby) and *Camarotoechia* of the *C. llandoveriana* (Davidson) type.

*Moydart-Stonehouse time.*—At the end of McAdam-Rochester time important paleogeographic changes took place on the North American continent (1910). The seas were withdrawn from the Cumberland trough and a great invasion from the north spread down over the interior. At this time all further communication of the Arisaig sea with interior America was broken off and thereafter relationship with northwest Europe only is exhibited. This endured to the end of the Silurian and the seas which again appeared in the Cumberland trough in the late Silurian no longer display Arisaig or North Atlantic affinity. Outside of a few ubiquitous species there is nothing in common between the Arisaig and interior seas. This is based on brachiopod, gastropod, cephalopod and trilobite evidence alone. The bivalves indicate open seaways to northwest Europe but can not be used as evidence of paleogeographic relation with interior America of this time. For here the ecological factor also enters. The prevailing clear waters and hard shelly bottoms of the interior seas would prevent their development there anyway. Restriction of

the interpretation to evidence based on the other groups is for the purpose of eliminating, as far as possible, this ecological factor.

*New genera and subgenera.*

It is proposed below to present a brief description of the new genera and subgenera. Where the genotypes are new species, they are also described. The final report will include the taxonomy of the entire fauna of 169 species and varieties.

Class Brachiopoda Duméril.

Family Rhynchonellidæ Gray.

Genus *Camarotæchia* Hall and Clarke.

*Pectorhyncha*, new subgenus.

(Πηκτός, fixed.)

Obtusely plicated *Camarotæchia* in which the teeth are not supported freely by dental plates extending into the valves, but are cemented to the lateral walls of the ventral valve. Resembles *Plethorhyncha* Hall and Clarke in the prominently elevated and posteriorly thickened dorsal median septum and the thickened hinge-plate and crura. Lacks the fine median sulcus on the anterior part of the plications which is present in *Wilsonia*, *Plethorhyncha* and *Uncinulus*. Divided hinge-plate and crural cavity as in *Camarotæchia*.

*Genotype: Atrypa obtusiplicata* Hall.

Genus *Eatonia* Hall.

*Pareatonia*, new subgenus.

1857 *Eatonia* Hall (partim), 10th Rept. N. Y. State Cab. Nat. Hist., p. 90.

This subgenus is erected to embrace the plicate *Eatonia* stock of *E. medialis* (Vanuxem), *E. sinuata* Hall, etc. *Eatonia* is restricted to those forms which are finely striate but not plicate. They may be crenulate at the margins, however, "as if by the extremities of the rounded plications" (Hall and Clarke 1894, p. 206).

*Genotype: Eatonia medialis* (Vanuxem).

*Eatonioides*, new genus.

(*Eatonia* + εἶδος, form.)

The exterior of these forms is similar to that of the plicate or *Pareatonia* species of *Eatonia*. The broad,

rounded, flabellate and excavated ventral muscle scar and the short dorsal median septum are similar to *Eatonia*. But certain *Eatonia* characters are not developed. These are the radiating fine striæ, the cardinal process of crural origin and the ventral median septum. Probably ancestral to the *Pareatonia* forms of *Eatonia* at least, but the later of the two Arisaig species referred to this genus has developed concentric lamellæ and hence is off the main ancestral line.

*Genotype: Eatonioides lamellornatus*, n. sp.

*Eatonioides lamellornatus*, new species.

The form of this species closely resembles that of *Eatonia* (*Pareatonia*) *medialis* (Vanuxem). The dorsal valve is more convex and the surface is ornamented, not by radiating striæ, but by concentric lamellæ. The generic characters have already been described.

Width 25 mm., length 22 mm.

*Horizon and locality:* Common in the Moydart formation, coast section, Arisaig, N. S.

*Plagiorhyncha*, new genus.

(Πλάγιο lateral, referring to position of plate bearing the teeth.)

Dorsal interior as in *Camarotoechia* Hall and Clarke, but the teeth are not supported by a dental plate produced forward from the walls of the rostral cavity, but are borne on a short plate arising from the lateral walls of the ventral valve. Outline plicated biconvex, out of which arise independently nearly smooth and also striated species with shallow and marginally deflected ventral valve. The following are referred to the new genus: *Rhynchonella glassii* Davidson, *Plagiorhyncha plastica*, n. sp., and *Terebratula decemplicata* Sowerby.

*Genotype: Rhynchonella glassii* Davidson = *Atrypa depressa* Sowerby.

Class Pelecypoda Goldfuss.

Superfamily Nuculacea.

*Honeymania*, new genus.

The flattened post-cardinal border resembles some of the Limopsidæ Dall and also some of the Lunulicardiidæ

Fischer. The size is much smaller than the latter and there is no radial sculpture. The dentition consists of two transverse teeth posterior to the beak and two rows of numerous and much smaller transverse teeth anterior to it. The hinge below the beak is not known. The contrast in the dentition anterior and posterior to the beak recalls the Triassic to Recent Limopsidæ. But there does not appear to be any amphidetic area of the Arcacea type. This genus is named after Rev. David Honeyman, whose name will always be associated with this locality.

*Genotype: Honeymania planimarginata*, n. sp.

*Honeymania planimarginata*, new species.

Outline somewhat mytiliform, with the post-cardinal slope abruptly deflected and descending to a flattened and straight post-cardinal border. The margin is also slightly flattened anterior to the beak. Both adductors well impressed, equal in size, and small. Pallial line not preserved. A longer expression of this form is named var. *elongimarginata*, n. var.

Length 10 mm., height 12 mm.

*Horizon and locality:* Rare in the McAdam formation, McAdam Brook and coast sections, Arisaig, N. S.

*Arisaigia*, new genus.

Nuculacea with the dentition of *Nuculites* Conrad and the clavicle variably developed. Differs in particular from that genus by having radiating striæ on the post-umbonal slope. Escutcheon, better defined in later forms, also present. In later Silurian develops scarp or carina, extending from the umbo to the postero-basal angle. The following species are referred to the new genus: *Arisaigia postornata*, n. sp., *Nucula sinuosa* Simpson, and *Cytherodon? placida* Billings.

*Genotype: Arisaigia postornata*, n. sp.

*Arisaigia postornata*, new species.

This species differs chiefly from *Arisaigia sinuosa* (Simpson) in form. It is longer and only slightly convergent posteriorly, the post-cardinal margin being almost parallel to the basal margin. The Arisaig form

has a second low fold and often a second shallow sinus on the post-umbonal slope.

Length 20-37 mm., width 9.5-17 mm.

*Horizon and locality:* Common in the McAdam formation, coast section, Arisaig, N. S.

*Tropinuculites*, new genus.

(*Τρόπις*, carina or keel + *Nuculites*.)

Nuculacea with the dentition and clavicle of *Nuculites* Conrad, but differing from that genus in the presence of a carina from the umbo to the postero-basal angle. In the single species referred to this genus the surface in front of the carina is covered by concentric prominent ornamental striæ, while posterior to it are fine growth-lines only.

*Genotype:* *Nuculites (Orthonota) carinata* Hall.

• Family Modiolopsidæ Fischer.

Genus *Goniophora* Phillips.

*Cosmogoniophora*, new subgenus.

(*Κόσμος*, ornament.)

This subgenus is erected to include those forms of *Goniophora* Phillips with radiating striæ. They are very common in the Devonian, but in the Silurian are confined to the Arisaig Stonehouse fauna.

*Genotype:* *Goniophora bellula* Billings.

## SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. *Complex Atoms.*—As long ago as 1816, in the early days of modern chemical philosophy, the theory was advanced by Prout, an English physician, that hydrogen was the primordial element, and that the atoms of all the other elements were composed of multiples of the hydrogen atom, so that, consequently the atomic weights were all exact multiples of that of hydrogen. As our knowledge of atomic weights became more exact in later times it became evident that there were many cases where Prout's hypothesis in regard to the atomic weights was at least not far from the truth. The question as to the real truth of this hypothesis has been one of the incentives to the work of determining the atomic weights with great care by many investiga-



tors, and in recent times it has been generally admitted that Prout's hypothesis does not hold true, but it is recognized that there are a number of atomic weights that are curiously near to whole numbers on the basis of hydrogen as unity, and especially on the basis of oxygen as exactly 16. Recently WILLIAM D. HARKINS of the University of Chicago has brought forward again this frequently revived idea and holds the view that the elements are very probably inter-atomic compounds of hydrogen. He believes that hydrogen first forms helium ( $\text{He} = 4$ ) and that this becomes a secondary unit of fundamental importance in the formation of the higher atomic weights. He finds that the elements taken in their serial order have atomic weights that are multiples of helium in the even numbers of the series, while they are multiples of helium plus three hydrogens in the odd numbers. Thus, beginning with helium, the second element:  $\text{He} = 4$ ,  $\text{Li} = 4 + 3$ ,  $\text{Be}$  (exception),  $\text{B} = 8 + 3$ ,  $\text{C} = 12$ ,  $\text{N}$  (exception),  $\text{O} = 16$ ,  $\text{F} = 16 + 3$ ,  $\text{Ne} = 20$ ,  $\text{Na} = 20 + 3$ ,  $\text{Mg} = 24$ ,  $\text{Al} = 24 + 3$ ,  $\text{Si} = 28$ ,  $\text{P} = 28 + 3$ ,  $\text{S} = 32$ ,  $\text{Cl} = 32 + 3$ ,  $\text{A} = 40$ ,  $\text{K} = 36 + 3$ ,  $\text{Ca} = 40$ ,  $\text{Sc}$  (exception),  $\text{Ti} = 48$ ,  $\text{V} = 48 + 3$ ,  $\text{Cr} = 52$ ,  $\text{Mn} = 52 + 3$ ,  $\text{Fe} = 56$ ,  $\text{Co} = 56 + 3$ . The three exceptions noticed are that  $\text{Be}$  is accepted as 9.1 instead of 8,  $\text{N}$  as 14.01 instead of 15, while  $\text{Sc}$  is given in our tables as 44 instead of 43. Although other variations from the exact whole numbers occur,  $\text{Li} = 6.94$ ,  $\text{Mg} = 24.32$ ,  $\text{Al} = 27.1$ ,  $\text{Si} = 28.3$ ,  $\text{P} = 31.02$ ,  $\text{S} = 32.07$ ,  $\text{Cl} = 35.46$ ,  $\text{K} = 39.10$ ,  $\text{Cu} = 40.07$ ,  $\text{Ti} = 48.1$ ,  $\text{Mn} = 54.93$ ,  $\text{Fe} = 55.84$ , and  $\text{Co} = 58.97$ , there is a striking nearness to whole numbers and to the proposed rule in many cases. However, it must be emphasized that these differences, especially in the cases of chlorine, magnesium, silicon, iron and sulphur, where the atomic weights have been determined with great accuracy, and have thus overthrown Prout's hypothesis, without considering the other exceptions and without considering the fact that the rule gives many more exceptions and wider variations when it is applied to the higher atomic weights, are sufficient to overthrow the practically identical hypothesis under consideration.

In his last article on this subject the author has shown that the elements of even numbers in the series, those that he supposes to have atoms made up of multiples of helium, appear to be much more abundant than the " $n\text{He} + 3\text{H}$ " elements. There is evidence of this in a general way from a consideration of the composition of the earth's crust, but it is much better shown from the average composition of meteorites, and the author believes that the latter probably represents matter in general more accurately than the segregated material on the surface of the earth. This generalization appears to have too many exceptions to be worthy of very serious consideration. For example, the very rare element beryllium between lithium and boron, and the very rare element neon between fluorine and sodium should

be much more common than their companions according to the theory.—*Journ. Amer. Chem. Soc.*, **39**, 856. H. L. W.

2. *Disodium Nitrite*.—It has been found by E. B. MAXTED that when a solution of sodium nitrite in perfectly anhydrous liquid ammonia is subjected to electrolysis with electrodes of platinum a bright yellow substance was deposited on the cathode. This substance dissolved in water with violent evolution of hydrogen, thus resembling sodium, but it did not dissolve in an excess of anhydrous ammonia, although sodium does this with the production of a blue solution.

It was found further that the same compound could be obtained by the reaction of metallic sodium and sodium nitrite in anhydrous ammonia solution. A quantitative experiment showed that the blue color of a solution of sodium in liquid ammonia was discharged by the addition of exactly one molecule of powdered sodium nitrate, and that the weight of the yellow product after evaporating off the ammonia was the same as the sum of the weights of the sodium and sodium nitrite employed. It was thus found that the formula of the compound was  $\text{Na}_2\text{NO}_2$ , and that it contained no ammonia.

The substance was found to react explosively with moist air. After it had been decomposed by the action of moist nitrogen there was no evidence of the formation of hyponitrous acid or of hydroxylamine, but it was shown that sodium nitrite remained. No further theoretical discussion of the nature of the compound has been made, but it is proposed to study it further in the future.—*Journ. Chem. Soc.*, **111**, 1016. H. L. W.

3. *Recovery of Potash from Greensand*.—It is stated by W. H. CHARLTON that a process which was originally developed for the treatment of feldspar for the extraction of potash has been found to apply more advantageously to greensand or glauconite which occurs in great abundance in the eastern states, particularly in New Jersey. The process consists in heating the finely ground mineral under pressure with water and lime in autoclaves. Steam at a pressure of about 225 lbs. is led directly into the digester and this is maintained for a period of 2 to 4 hours. Although glauconite contains less potash than feldspar, it has been found that it is decomposed more readily than the latter, and that it yields potassium hydroxide that is nearly pure. It is proposed to utilize the waste material obtained by filtration from the potash solution for making bricks, tiles and similar articles, as it has been found that when mixed with sand, pressed, and steam hardened it makes durable products.—*Journ. Indust. and Eng. Chem.*, **10**, 6. H. L. W.

4. *A Method for the Determination of Rubidium and Cesium in Plant Ash*.—For this purpose W. O. ROBINSON advises preparing the ash of the plant, using 20 g. or more, at a temperature not exceeding  $525^\circ \text{C}$ . in a muffle. After obtaining the

alkaline chlorides by the usual methods, with the precaution of driving off ammonium chloride at a low temperature in a muffle, he treats their solution in water with about 0.05 g. of platinic chloride, evaporates to a paste, treats with a small amount of hot water, filters on an asbestos filter contained in a glass tube, washes with 80% alcohol, reduces in the tube by heating in hydrogen, dissolves the resulting chlorides in water, evaporates to a paste, takes up in four drops of concentrated hydrochloric acid, filters on a tiny filter, into a flask of 2 or 3 cc. capacity, washing several times with four drops of hydrochloric acid. He then applies the spectroscopic method of Gooch and Phinney which appeared in this Journal in 1892. He states that it is desirable for the operator to remain in the dark for at least an hour before making the observations. It is his opinion that an accuracy within from 5 to 10 per cent is easily obtained.—*Jour. Indust. and Eng. Chem.*, 10, 50. H. L. W.

5. *Absorption Bands of Ozone*.—When taken under favorable conditions, photographs of the ultra-violet spectra of many stars,—such as Capella, Regulus, Sirius, and Vega,—show a series of fairly narrow absorption bands near the short wavelength limit set by the earth's atmosphere. Since the wavelengths of these bands as given by Huggins and Sampson do not agree with the corresponding data for ozone published by Ladenburg and Lehmann, and since telluric ozone seemed to be the most probable cause of the occurrence of the bands in stellar spectrograms, A. FOWLER and R. J. STRUTT have recently subjected the matter to experimental investigation.

The first part of the work consisted in making a new and careful study of gaseous ozone artificially prepared. The ozone was generated in the ordinary way by means of a Siemens ozonizer. The absorption vessels were of various kinds. For great thicknesses glass tubes were used, closed by quartz plates cemented on with sodium silicate. The length of these tubes varied from 46 cms to 244 cms. For small thicknesses the ozone stream was delivered by displacement into silica flasks or test-tubes placed in front of the slit of the spectrograph. This instrument was furnished, of course, with a prism and lenses of crystalline quartz, and it gave a dispersion of 58 Å per mm. at  $\lambda$  3200. The best source of continuous radiation in the ultra-violet was found to be burning magnesium ribbon. The authors record the wave-lengths of 34 distinct bands due to ozone. These bands appear on the less refrangible side of the great ozone band that limits the solar spectrum, and their wave-lengths extend from 3089.5 Å to 3432.2 Å.

These data agree very well with the wave-lengths derived from the stellar spectrograms. The most convincing evidence, however, in favor of the belief that the bands in the spectra of the stars are due to ozone, is obtained by direct comparison of the

spectrograms of the stars with those obtained from the artificially prepared gas. When taken with the same linear dispersion, the bands on the juxtaposed spectrograms agree perfectly in position, intensity and character. The photographs of the solar spectrum corresponding to altitudes of  $55^\circ$ ,  $30^\circ$ ,  $10^\circ$ ,  $4^\circ$ , and  $1^\circ$  show a series of narrow ultra-violet absorption bands that increase in number and intensity as the altitude of the sun decreases. These bands also coincide with the ones obtained with laboratory ozone. It should also be added that the bands recorded on stellar photographs are independent of the spectral type of the stars. Consequently, Fowler and Strutt have proved conclusively that the bands in the stellar spectrograms owe their origin to telluric ozone. The full-page plate at the end of the paper is an excellent reproduction, and it merits the attention of those who are interested in the subject.—*Proc. Roy. Soc.*, **93**, 577, 1917. H. S. U.

6. *Mathematics for Agriculture and General Science*; by ALFRED MONROE KENYON and WILLIAM VERNON LOVITT. Pp. vii, 357, with 135 figures. New York, 1917 (The Macmillan Co.).—This book is designed as a text in freshman mathematics for students specializing in agriculture, biology, chemistry, and physics, in colleges and in technical schools. It is intended for a course of three hours a week for one year, but it can be used for a half-year course.

The scope of the text may be inferred from the following list of subjects: review of equations, graphic representation, logarithms, trigonometry, land surveying, statics, small errors, conic sections, variation, empirical equations, the progressions, annuities, averages, permutations and combinations, the binomial expansion—laws of heredity, the compound interest law, probability, correlation, and maxima and minima.

The exercises for solution by the reader constitute one of the most prominent features of the book. They include many data taken from agricultural and other experiments, carefully selected to stimulate independent thinking and to show the application of general principles to problems which actually arise in everyday life, and in the solution of which progressive men and women are vitally interested. The number of exercises is unusually large (1257, often with subdivisions), and they contain a wealth of material. The volume closes with tables of logarithms, of trigonometric functions, and of other useful constants. The typographical work, composition, text-tables, and diagrams are excellent, and the book seems very well adapted to the needs of those to whom it is addressed. H. S. U.

7. *The Radioactivity of Meteorites*; by T. T. QUIRKE and LEO FINKELSTEIN.—The following corrections should be made in this article in the September number, 1917, vol. 44, pp. 237-242:

Page 237, date of footnote should be 1906.

Page 241, radioactivity of Coahuila meteorite should be  $7.69 \times 10^{-14}$ .

## II. GEOLOGY.

1. *Geology of the Navajo Country—a Reconnaissance of Parts of Arizona, New Mexico, and Utah*; by HERBERT E. GREGORY. United States Geological Survey, Professional Paper 93. Pp. 161, pls. 34, figs. 3. Washington, 1907.—This publication is a welcome contribution on one of the little known parts of the United States. It is of interest to geologist and geographer, and deals with subjects of economic as well as scientific interest. The work might be termed missionary geology, for it was done chiefly for the benefit of the Navajo Indians. The report contains the usual wealth of detail, but the character which gives it unusual value is the straightforward manner in which debatable questions are discussed. Whether the author is right or not there is no doubt as to what he thinks.

Light is shed on several questions of unusual interest connected with the wonderland of Grand Canyon and the Plateau Country. Especially important are the contributions to the physiography of the Triassic and Jurassic periods. The oldest Triassic formation of the region, the Shinarump conglomerate, is described as a stream-laid deposit of sand and gravel spread out over a graded plain of great extent. The younger Triassic rocks containing the petrified forests were eroded to some extent and covered in Jurassic time with vast deposits of sand. The Wingate and Navajo sandstones are regarded as equivalent to the Vermilion Cliff (Triassic of former writers) and White Cliff sandstones of the plateau region, which have been famous since they were first described for a peculiar type of crossbedding and for marvelous landscape architecture. These sandstones possess characteristics supposed to indicate desert conditions. The question of origin of the sand which in Utah reaches thicknesses of about 3,000 feet was raised nearly half a century ago. It is now known that the sandstone occupies large parts of four States and that its general character is the same in all places. Thus the interesting possibility is presented of a great Sahara in western America in mid-Mesozoic time.

In the Navajo country the Wingate and Navajo sandstones are separated by thin beds of shaly limestone and correlated with the similarly constituted La Plata group. The correlation with La Plata on the one hand and with the Vermilion-White Cliff group on the other raises again a much debated question in correlation.

Many splendidly developed physical features are described and illustrated, such as the intrenched meanders in San Juan Canyon, remarkable natural bridges, and natural monuments of unusual expression. A commendable departure is an attempt to establish the correct spelling and origin of unusual names, such as Moen-

kopi in place of Moenkapi or Moeneopie. The pronunciation of uncommon Indian names might profitably have been added.

W. T. LEE.

2. *On Cyclical Variations in Eruption at Kilauea*; by H. O. Wood. Pp. 59, 10 pl. and 2 charts. Second Report, Hawaiian Volcano Observatory of the Mass. Institute of Technology, 1917.—The molten surfaces nearly always visible in Halemau-man at Kilauea, on Hawaii, rise and fall through a considerable vertical range, standing high near times of solstices and low near equinoxes. Also, from fortnight to fortnight a similar movement of smaller range is noticed frequently, and a movement, probably of greater vertical range, appears to go on over an interval of several years.

To explain such cyclical behavior a crude hypothesis is offered; a refined development of it would be very difficult. An effect of the varying declination of the sun is a nutation of the earth's axis produced by fields of gravitational attraction acting obliquely to the earth's equatorial protuberance, and its rotation. This action conflicts with the earth's gyrostatic tendency. Hence, very minute earth-strain, or earth-distortion, is considered to accompany it. This effect ranges from a maximum at solstice and after (*lag*) to nothing at equinox. A similar effect, but with period of only a fortnight, is produced by changing declination of the moon. Further, a minute change in the configuration of the earth is believed to accompany variation of latitude.

These minute changes in earth configuration are considered to produce minute changes in the shape and volume of the deep magma reservoir, which are integrated into visible, or pronounced, changes in the relatively very small passages which lead up into the crater-pit where the free surfaces rise and fall. These tendencies sometimes reinforce and sometimes oppose each other, and many other complications enter. This hypothesis is developed in considerable detail and an almanac is computed from which a hypothetical strain-curve is drawn, for the interval 1911-1915.

All observations bearing on the volcanic variations are presented in three categories: very sparse early records, 1823-1865, listed chronologically; more frequent sporadic records, 1865-1911, shown from month to month, year by year, on large charts; and routine observations and measurements, 1911-1915, shown diagrammatically.

The reader is asked to compare the assembled observations critically. Nevertheless, the hypothesis is considered to shed much light on a confusing aggregate of circumstances, and it appears to find strong support in the development of the study.

3. *The Geology of Part of the Transkei*; by A. L. DU TOIT. Introduction by A. W. ROGERS. Geol. Survey Union of South Africa, Dept. Mines and Industries, Cape Sheet 27, 1917. Pp. 32; 1 fig.; large, separate map.—A geological map with descrip-

tive text, a combination which serves the purpose of the folios of the U. S. Geological Survey, has been published for 5,460 square miles of the Transkei Country. This region possesses exceptional interest on account of the almost complete succession of the Karroo system embracing the Ecca, Beaufort, and Stormberg series. Strata assigned to the Permian include 2,000 to 2,500 feet of shale overlying the Dwyka glacial beds, 4,500 to 5,000 feet of feldspathic sandstone, and 700 to 800 feet of variegated calcareous sandstones from which *Lystrosaurus* and a new reptile, *Prolystrosaurus*, have been obtained. To the Triassic are assigned 1,500 to 2,000 feet of bright-colored, friable rocks, blue and greenish flagstones and shales, and feldspathic sandstones. Above these lie 1,400 to 1,800 feet of coarse pebbly feldspathic sandstones with plant remains, 1,200 feet of "Red Beds" from which *Thecodontosaurus minor* (Haughton) was obtained. The Rhaetic (?) is represented by volcanic deposits and 800 feet of Cave sandstone. There is a remarkable development of volcanic necks, dikes, and sheets dating from the Jurassic (?). H. E. G.

4. *The Geology of the Moonta and Wallaroo Mining District*: by R. LOCKHART JACK. Geol. Survey South Australia, Dept. Mines, Bull. 6, 1917. Pp. 135, 27 pls., 3 photos.—The mines of Moonta and Wallaroo, discovered in 1860, continue to hold first rank among the producers of South Australia. Their output of copper exceeds in value the total mineral production from other parts of the state. Mr. Jack has prepared a history of these interesting mines with a detailed account of the origin, nature, and treatment of the ores, supplemented by petrographic descriptions and chemical analyses. The geological column in this region is as follows: 1. Pre-Cambrian highly altered sediments with basic and felstitic igneous rocks, intruded by granite and pegmatite and containing the ore deposits; 2. peneplain; 3. Cambrian quartzite, conglomerate, limestone, and clay-slate slightly disturbed and without intrusions; 4. peneplain; 5. marine Tertiary limestone; 6. peneplain, which in many places is continuous with the pre-Cambrian erosion surface. A sheet of "travertine," the "caliche" of arid North America, lies at or near the surface. An unusual feature of the Cambrian rocks is the association of quartzite with unaltered fine-grained sediments, probably the result of metamorphism of the coarser beds by vadose waters. The veins are formed of an unusual assemblage of minerals. At Moonta the vein type is a copper-bearing schorlaceous pegmatite in which bornite and chalcopyrite are original constituents. At Wallaroo "the gangue minerals consist of quartz, coarse plates of biotite, . . . a little feldspar, schorl, apatite, fluorite, amphibole, pyroxene, siderite, calcite, dolomite, rhodocrosite, and mizzonite. Chlorite, muscovite, and sericite are also present in small amount. Metallic minerals are chalcopyrite, pyrite, pyrrhotite, and small amounts of galena, blende, ferberite, scheelite, molybdenite, and gold. Smaltite

also occurs in the Kurilla Lode, and is doubtless present in the Main Lode . . . The calcite and dolomite appear to have crystallized later than, and enwrap, chalcopyrite, and are, in turn, surrounded by galena. Both the galena and the blende appear to be among the latest metallic minerals deposited."

H. E. G.

5. *The Geology and Mineral Resources of the Reefton Sub-division (Westport and North Westland Divisions)*: by J. HENDERSON. New Zealand Geol. Survey, Bull. 18, 1917. Pp. viii, 232, 11 pls., 22 maps and plans.—Bulletin No. 18 of the New Zealand Survey deals with 1,046 square miles of typical "West Coast" country of the South Island, including mountain, plateau, and seacoast, glacial cirques, vigorous rivers, and flood plains. The region is in process of emergence and exhibits a remarkable series of wave-formed terraces and ancient coastal belts which have been correlated with inland terraces standing, respectively, at 10 feet, 80 feet, 200 feet, 320 to 360 feet, and 500 feet. The adjustment of drainage incident to these uplifts constitutes an attractive physiographic problem. Faulting on an extensive scale at four periods within Tertiary time has left its mark in horsts, graben, plateaus, and mineral-bearing fissures. The base of the stratigraphic column is a series of greatly disturbed greywackes and argillites assigned to the Silurian. The Devonian is represented by quartzites, shales, and fossiliferous limestones. Overlying the Paleozoic strata are Tertiary beds—Eocene, Miocene, and Pliocene. The igneous rocks, of which 19 analyses are given, include granite, lamprophyre, camptonite, pyroxenite, and diabase. Gold in quartz veins, most of them deposited from magmatic waters, and coal in the Tertiary strata are responsible for the economic importance of the Reefton area. The chapters on geography and the discussion of scenery in relation to structure are welcome, for publications relating to the geography of New Zealand are inadequate in number and scope.

H. E. G.

6. *The Vegetation and Flora of Lord Howe Island*; by W. R. B. OLIVER. Trans. New Zealand Inst., vol. xlix, 1916. Pp. 94-161, pls. 10-16.—Lord Howe Island, a remnant mass of lava and limestone, 3,220 acres in area, occupies an isolated position within a tract of ocean which bounds three biological regions of the globe. Among the 209 species of indigenous plants described by Mr. Oliver are a number which present interesting features of climatic and soil adaptation. The percentage of endemic forms in the whole flora is 33. The history of the flora shows that the island formerly had direct connection with New Caledonia and has witnessed the breaking down of the bridges which connected it with now distant land masses. "The plants of Lord Howe Island indicate former land connections with both New Zealand and New Caledonia. The greater degree of peculiarity in the



New Zealand elements points to the earlier severance of that connection. No closer connection with temperate Australia need be postulated to explain the affinities of the flora of Lord Howe Island and the continent. The last land connection being with New Caledonia, Lord Howe Island ought properly to be considered an outlier of that region." H. E. G.

7. *Block Mountains in New Zealand*; by C. A. COTTON.—Dr. Cotton desires to make the following corrections in his article which appeared under the above title in this Journal in October, 1917, vol. 44, pp. 249-293:

Page 272, legend of fig. 13, line 2; for Maniototo read Manuherikia.

Pages 277, 287, figs. 17 and 24, the blocks for these figures are transposed.

Page 278, fig. 18. For legend substitute: The Hawkdun fault scarp as seen from the northern part of Ida Valley. The scarp rises to between 3,000 feet and 4,000 feet above the neighboring portion of the lowland.

8. *The Origin of Chert in the Burlington Limestone*; by W. S. TARR. ERRATUM.—On page 447 of the December number, the *not* in the third line from the bottom should be omitted. The sentence then reads: "Evidently chert does occur in the beds below the surface . . ."

### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Report of the Secretary of the Smithsonian Institution*, CHARLES D. WALCOTT, for the year ending June 30, 1917. Pp. 110, pls. 2.—The general conditions which affect all the departments in Washington have materially influenced the work of the Smithsonian also during the past year. This is conspicuously true in regard to aviation, a subject with which the name of the Institution will always be connected. When Professor Langley, against many obstacles, worked out the mathematical theory of flight and demonstrated its practical possibility, nearly thirty years ago, he had little idea of the extent to which the subject would be developed at the present time. The work now being done by the Smithsonian is along a number of different lines and must contribute largely to the success of this branch of the service. The National Research Council, organized by the National Academy, is also spoken of in this report and the part taken by it in the general Council of National Defence. In one particular only are the war conditions severely limiting the activities of the Institution and that is in the International Exchange Service.

The various lines of special research and exploration are being carried forward as heretofore, including the geological work in

the Canadian Rockies by the Secretary, and other related investigations. The examination by Dr. Hrdlicka of ancient human remains in Florida is discussed and his conclusion given that the Vero deposits are probably not of great antiquity. A similar conclusion is reached with respect to human bones found on the small island off Fort Myers, called Demere Key. Natural history explorations have been carried on in the Hawaiian Islands, China, Santo Domingo and elsewhere.

The condition of the National Museum is discussed at length in the Appendix by Dr. Rathbun. Numerous additions to the collections have been made, but the most important point spoken of is the actual beginning of the building for the Charles L. Freer Collections in American and Oriental Art. This building is made possible by the gift from Mr. Freer of \$1,000,000, which is spoken of as "the most valued donation which any individual has ever made to the Government."

In regard to the work of the Astrophysical Observatory, Dr. Abbot gives an account of the station for measurements of solar radiation located temporarily at Hump Mountain, N. C., since its permanent location in South America, as planned, is at present impracticable. Mr. Fowle has carried forward the researches on the absorption of terrestrial radiation by the atmosphere, and Dr. Clayton has shown that it may be possible to forecast changes of temperature from solar observations. Other stations in addition to those in California and North Carolina are to be desired in accomplishing this end.

It is interesting to note that the permanent fund of the Smithsonian Institution now amounts to \$1,000,000, the limit authorized by Congress.

2. *Report of the Librarian of Congress*, HERBERT PUTNAM. Pp. 223, 6 pls.—The librarian of Congress remarks upon the remarkable growth in the Music Division under the auspices of Mr. Sonneck, the chief, who, however, was compelled (September, 1917) to give up this position. A collection of 250,000 musical compositions has been increased some three times and the works on the literature have gained even more. Among the gifts of the year, the most important noted is that of Whistleriana by Mr. and Mrs. Joseph Pennell. This includes all books by and about the artist as well as many in which he and his art are discussed; the collection is now stored in London. Numerous important historical manuscripts pertaining to the American Revolution have been added, and by purchase some 6600 volumes dealing with China, Japan and other countries of the far east. It is noted that the rapid growth of this Oriental collection is being accompanied by an increased use by the Government Bureaus and Chinese investigators.

3. *Audubon the Naturalist: A History of his Life and Time*; by FRANCIS HOBART HERRICK. Two volumes; vol. I, pp. xl, 451,

with 34 plates; vol. II, pp. xiii, 494, with 24 plates. New York and London, 1917 (D. Appleton and Co.).—Many readers will doubtless learn with surprise that the origin of the gifted bird and quadruped painter, John Jacques Fougère Audubon, or, as he is usually known, John James Audubon, has been hitherto veiled in mystery. Audubon, himself, in writing his autobiography throws but little light on his earliest years. Careful search for further information has been unsuccessful until by the merest chance the writer of these interesting volumes learned of the existence of documents in the hands of a retired notary in France which reveal the history of Audubon's father and his family. These documents consist of several hundred papers, including letters, deeds, and certificates of birth, baptisms, adoptions, and deaths. From these documents, supplemented by the writings of Audubon himself and of his contemporaries, as well as by later biographers, Professor Herrick has elaborated a graphic account of the famous naturalist's origin, life and environment.

The long-standing controversy as to when and where Audubon was born is now settled conclusively by the publication of a photograph of the bill rendered by the physician who attended "Mlle. Rabin" at Audubon's birth in Haiti in 1785. The author follows the young naturalist through his boyhood days in France to his settlement near Philadelphia at the age of eighteen, when he begins his studies of American birds. We learn of his wanderings through the sparsely settled portions of the country as far west as the upper Missouri seeking new birds for his study. We follow his struggles for a livelihood in unsympathetic communities, his failures in business ventures and his final triumph as artist and naturalist. The writer depicts the life and customs of the times as revealed by Audubon's experiences, thereby giving the reader an intimate history of the country during the first half of the 19th century. The illustrations include places and people familiar to the naturalist and many of his authentic likenesses, as well as several of his famous plates in colors; also a number of his other drawings, here published for the first time.

Appendices contain copies of important documents, including the certificate of Audubon's adoption by his father and foster-mother, of his baptism, etc., together with bills, letters, lists of drawings and an excellent annotated bibliography.

The painstaking collection of these data and their incorporation into so readable a narrative will prove a lasting service alike to history, literature, and science.

W. R. C.

4. *Mammalian Anatomy; with special reference to the cat*; by ALVIN DAVISON. Third edition revised by Frank A. Stromsten. Pp. xi, 243, with 115 illustrations. Philadelphia, 1917 (P. Blakiston's Son & Co.).—The book is designed to accompany

the laboratory work in courses in vertebrate anatomy in which the cat is used as an object for dissection. The earlier editions proved highly satisfactory for this purpose, and the present revision, containing such changes as have been suggested by practical experience and as are necessary to bring the work into harmony with more recent views, will be equally useful.

W. R. C.

5. *The Anatomy of Woody Plants*; by EDWARD CHARLES JEFFREY. Pp. x, 478, with frontispiece and 306 text figures. Chicago, 1917 (The University of Chicago Press).—The study of plant anatomy, in its historical and experimental aspects, has been pursued with unusual success by Professor Jeffrey and his students. In the present volume, which incorporates many of the results of this work, the general subject is reviewed, and the principles upon which its progress has been based are clearly outlined. The most important of these principles are embodied in the canons of recapitulation, conservative organs, and reversion; but in the application of these canons the greatest caution is advised, in order to avoid unwarranted conclusions. The importance of paleobotanical evidence is likewise emphasized, and the attempt is everywhere made to support the conclusions drawn from the study of living plants by observations on fossils.

In the early chapters, after a general account of the cell and of the tissue systems in the vascular plants, the individual tissues and their disposition in the various plant organs are taken up in detail. Later chapters interpret the affinities of the main groups of the vascular plants, on the basis of anatomical evidence, and discuss the influence of climatic changes on the evolution of anatomical structures. The concluding chapter deals with anatomical technique.

The book is so full of important observations and deductions that it is impossible to give an adequate idea of its contents in a brief notice. Attention may be called, however, to certain topics of more than usual interest, such as the derivation of the various elements of wood (parenchyma, vessels, fibers, etc.) from tracheids; the evolution of the wood ray from the primitive linear condition, through the aggregate type, to the diffuse and compound (parenchymatous) rays of the more advanced angiosperms; the retention of transfusion tissue in the sporangial walls of the higher spermatophytes; and the derivation of herbaceous dicotyledons from woody ancestors, through the specialization of compound rays and the loss of secondary growth. In the discussion of these and other topics of almost equal importance the conclusions reached are usually based on evidence drawn from several distinct sources, especially where the views advanced are at variance with those commonly held.

A. W. E.

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THE

# AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XI.—*An Example of the Possible Intricacy of Glacial Modification of Drainage within a Narrow Area;*<sup>1</sup> by LEON AUGUSTUS HAUSMAN.

The purpose of this paper is to point out that great complexity of modification, and even complete rearrangement of drainage courses, may result from a combination of the effects of glacial erosion and glacial deposition within a very restricted area, and in this way to emphasize the possibility of similarly notable changes elsewhere, and to suggest, therefore, the necessity for careful study before an attempt is made to interpret the broader relations of the preglacial drainage in any region occupied by the continental ice sheets.

### *Region Under Discussion.*

The region discussed in this paper lies in central New York state, in Tompkins County, latitude 42° 30' N., longitude 76° 20' W., southeast of Lake Cayuga and about ten miles from the city of Ithaca. Abutting on the south of the area lies the village of Slaterville Springs, to which further reference will later be made. The region comprises essentially the headwater drainage area of Sixmile Creek, and includes about twenty-five square miles of territory. (See sketch map, fig. 1.)

The probable physiographic history of this general central New York area, a portion of the Appalachian Plateau, is in brief as follows: Essentially horizontally bedded sediments, following a notable uplift, had been

<sup>1</sup> In the interpretation of the phenomena in the field, and in the preparation of the manuscript, the author wishes to acknowledge his indebtedness to Dr. O. D. vonEngeln of the Dept. of Geology, Cornell University.

penneplaned, then reuplifted and dissected by the rejuvenated streams to a stage of early maturity, when the country was covered by the first advance of the ice of the Pleistocene glaciation. The main preglacial drainage lines of the area seem to have been toward the north, and the advancing ice impounded this north-flowing water in proglacial lakes which rose in level until they overflowed at the lowest points in the east-west divide between north-flowing and south-flowing streams. The

FIG. 1.



FIG. 1. Portion of a sketch map of New York State to show location of the area under discussion (in black).

ice continuing in its advance, moved with the maximum freedom, in the fastest and deepest currents, and hence with the greatest erosive effectiveness, in the north-south valleys, and, overriding the lower divides between them and the south-flowing drainage, considerably reduced the elevations of these divides or cut them down entirely. Later, during the periods of recession of the ice fronts in the various valleys, moraines, together with the vast deposits of glacial streams, filled in the troughs of the glacially eroded valleys, often to great depths, and fashioned the present relief of their bottoms and sides. Many of these north-south valleys were, moreover, so

greatly deepened by the ice scour that tributary valleys, having an east-west axis, were left hanging high above the new valley bottoms. These tributary streams flowing down the newly steepened rock slopes and encountering horizontally bedded strata of varying degrees of resistance to water erosion, developed falls. The recession of these falls created gorges at the lower ends of the hanging tributaries.

There is evidence for postulating a second advance of the ice, known in this region as the late Wisconsin advance. While such an advance may have accentuated the phenomena resulting from the earlier ice occupation, it is now considered to have been of meager erosive effectiveness in this area. However, during the retreat of this second sheet the valleys were graded up with drift, outwash deposits, and lacustrine sediments, and there is no doubt that these deposits are chiefly responsible for the present relatively flat-bottomed topography of the through valleys common in the Finger Lake District.

Since the time of the several glacial occupations the tributaries of the overdeepened north-south valleys have, in places, been engaged in cutting gorges at their lower ends, as indicated above, and also along their upper courses where diversion from the axes of the preglacial valley bottoms results from the irregular dumping of glacial deposits. At some points, both in the case of the gorges at the lower ends of the valleys and of those along the upper courses, these gorges have developed on the sites of earlier interglacial cuttings; at other places they represent wholly post-glacial rock cuts.

#### *Previous Investigations.*

The first detailed examination of Sixmile Creek as a whole was made by Lockhead (3)<sup>2</sup> who, in 1895, pointed out that its early mature valley, with a hanging termination where it enters the Cayuga Valley, is occupied in its lower course by a stream that is now apparently flowing in a post-glacial gorge, and that, previous to the Wisconsin advance of the ice, had earlier occupied another gorge in the mature valley bottom. In 1898 Tarr (6) wrote: "In the case of Sixmile Creek . . . the post-glacial stream occupies the preglacial valley throughout its distance, but, because of the drift filling it is not now flowing at all places along the lowest part of the old val-

<sup>2</sup> See bibliography at end of article.

ley. So . . . this creek has, in places, cut through the drift to find itself superimposed upon the rock wall of part of the old valley. Where this is the case we have a rock walled gorge, often with falls and rapids, while the other parts of the valley are broad and drift walled . . .” More recent are the studies which Filmer (1) and Rich and Filmer (5) have made, developing further the relationships of the present stream course to the interglacial valleys.

The first, and only mention, however, of the glacial diversion of the course of *upper* Sixmile Creek is made by Tarr (2) who, in the Watkins Glen-Catatonk Folio, p. 25, observes: “Gorges of a second type, with associated waterfalls, are found where drift deposits have turned the stream to one side of the preglacial valley and forced it to flow across one side of the valley. This condition is illustrated at Brookton, about three miles to the west of Slaterville Springs, where a great delta deposit has pushed the stream over to the south side of the valley, forming a fall that is utilized for power, and north of Slaterville Springs (see fig. 2), where the creek is pushed over against its east wall by a massive drift deposit, associated in origin with a stand of the ice in this vicinity. Here a deep gorge has been cut.” This reference is, however, to East Sixmile Creek (C, fig. 2). No writer has, heretofore, noted the diversion of West Sixmile Creek (H, fig. 2) and the gorge which has resulted therefrom.

#### *Drainage of the Area Under Discussion.*

In the following description the reader is referred to the topographic key map, fig. 2, on which all streams and other localities mentioned in the text have been labelled, and also to the glacial deposits map, fig. 3.

Upper Sixmile Creek has been limited, for convenience, to that portion of the stream above its bend to the north-east just east of the village of Slaterville Springs (A, fig. 2). From thence the creek continues for two miles north-east, then divides. The western branch is called West Sixmile (D, fig. 2) and the Eastern branch, East Sixmile (C, fig. 2). Both branches are roughly five miles in length.

West Sixmile takes its origin in a small upland marsh, trends southeast, and after receiving the waters of four tributaries is turned abruptly, when about three miles

from its source, by a large stadal moraine (I, fig. 2) and enters a diminutive gorge (H, fig. 2) about forty feet at

FIG. 2.

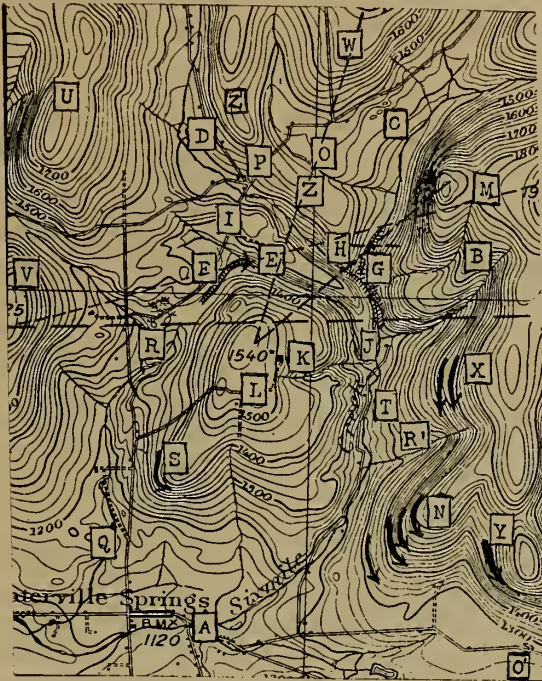


FIG. 2. Key map to all localities mentioned in text.

- |  |                                   |
|--|-----------------------------------|
| A, Beginning of Upper Sixmile Creek.         | O, Spur Creek.                    |
| B, Berry Creek.                              | O', Owego Creek Valley.           |
| C, East Sixmile Creek.                       | P, Van Pelt's.                    |
| D, West Sixmile Creek.                       | Q, Gravel Creek.                  |
| E, Moss Creek.                               | R, Swamp.                         |
| F, Moss Creek Outflow Channel.               | R', Reed Creek.                   |
| G, Gorge of East Sixmile Creek.              | S, Marginal Channel.              |
| H, Gorge of West Sixmile Creek.              | T, Buried Gorge of Upper Sixmile. |
| I, Moss Creek Terminal Moraine.              | U, Gilbert Hill.                  |
| J, Lower end of Moss Creek Terminal Moraine. | V, Hunter Hill.                   |
| K, Spring Creek.                             | W, Cole Hill.                     |
| L, Rowe Hill.                                | X, Marginal Channels.             |
| M, Davies Hill and Diedrich Creek.           | Y, Marginal Channels.             |
| N, Marginal Channels.                        | Z, Spur Creek Moraine.            |
|  | Z', Spur Hill.                    |

its deepest portion. Through this gorge it cascades for a distance of about 150 feet to its confluence with East Sixmile.

The three very small streams that comprise the farthest headwaters of East Sixmile rise at an elevation of about 1770 feet and, after an independent flow of a quarter of a mile or so, coalesce to form the more easterly of the two larger branches that join to form the main Sixmile Creek. From this point of junction of the three headwater streams, East Sixmile pursues a southward course, and its volume is further augmented by six other tributary streams before the point of its union with West Sixmile is reached. Just above this point of union the stream flows through a gorge from 50 to 75 feet in depth (G, fig. 2). The merging of East and West Sixmile develops a relatively large stream, and this increase in volume has resulted in the deepening of the gorge below the point of the confluence already alluded to. From the lower end of this gorge to within half a mile of Slaterville Springs the main Sixmile Creek takes a meandering course through the bottom of a drift-filled valley along the eastern side of which a gorge wall obscured by glacial drift can occasionally be detected (T, fig. 2). In this lower course the creek receives additions from the combined Moss and Spring Creeks (E, K, fig. 2) and from several other less important tributaries.

About one-half mile west of Slaterville Springs a small creek, here termed Gravel Creek (Q, fig. 2), joins Sixmile, and pushes its headwaters up a moraine-filled valley for a distance of three miles. This creek is now in the drift-filled valley which, it is suggested, was, prior to the glacial occupation, occupied by West Sixmile, but was subsequently abandoned by that stream in consequence of the deposition of the morainic mass (I, fig. 3) between Rowe and Gilbert Hills (L, U, fig. 2). This mass of moraine, termed here the Moss Creek Moraine, and evidently a stadal moraine, apparently diverted West Sixmile Creek across what may have been the eastern rock wall of the West Sixmile valley and forced it to cut the gorge through which it is now flowing.

#### *Glacial Modifications of the Topography.*

Only the highest elevations in the Upper Sixmile drainage area exhibit outcrops of bed rock, and these are both infrequent and of small exposure. The remainder of the area is mantled deeply with a thick drift deposit

through which streams of even such vigor as East and West Sixmile, and Spur Creeks (O, fig. 2), have not yet cut except in the gorge sections of the first two. All of these streams rise in upland marshes whose soil is a rock flour of glacial grinding interspersed with angular rock fragments of local origin, a colluvial deposit which

FIG. 3.

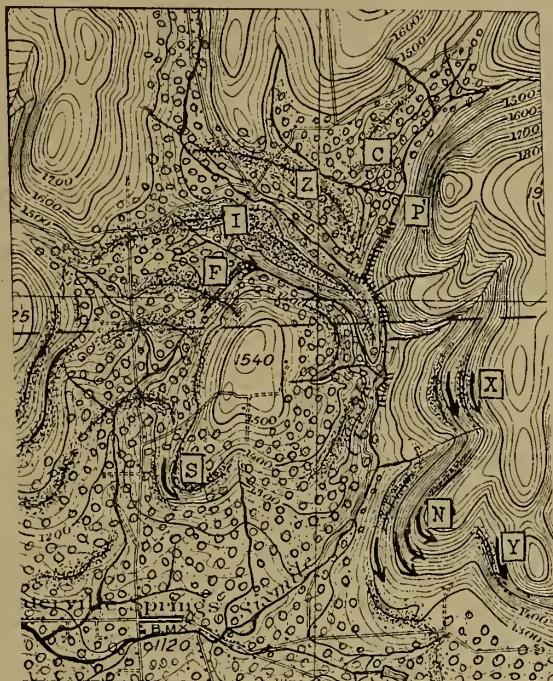


FIG. 3. Key map to the glacial phenomena mentioned in text.

- |                                 |                                   |
|---------------------------------|-----------------------------------|
| F, Moss Creek Outflow Channel.  | X, Marginal Channels.             |
| I, Moss Creek Terminal Moraine. | Y, Marginal Channels.             |
| N, Marginal Channels.           | P, Truncated Spur of Davies Hill. |
| S, Marginal Channels.           | Z, Spur Creek Moraine.            |

Areas unmarked are covered with thin drift. Gorges are shown by lines with cross shading. Stadal moraine loops and ridges are indicated by lines with shading in dots. The other markings indicate thick drift and valley filling.

favors the persistence of swampy areas on the tops of many of the hills.

In the valley bottoms of East and West Sixmile characteristically irregular moraines occur, and between

Rowe and Hunter Hills (V, fig. 2) there extends a roughly parallel series of what appear to be stadal moraines. Chief among these is the largest of the single moraines in this region, the Moss Creek Moraine (I, fig. 2 and 3), whose position and mass is responsible for the diversion of West Sixmile Creek toward the east. Parallel to this, and toward the north, lies the Spur Creek Moraine (Z, figs. 2, 3) that has, in like manner, altered the direction of flow of Spur Creek. Other stadal moraine loops, representing halts of much shorter periods, are readily traceable in the Gravel Creek valley (R, fig. 2) to the south. These moraines are shown in fig. 3.

A rather well-defined glacial outflow channel, the Moss Creek Channel (F, fig. 3), can be seen to the northwest of Rowe Hill, now occupied by the southern tributary of Moss Creek. A mile due south of this point a marginal channel (S, fig. 3) exists, whose southward gradient suggests that its function during the ice occupation was to conduct the water from the Gravel Creek valley, between the ice and Rowe Hill, into the Slaterville valley, that is, after the retreat of the front of the ice lobe below the level of the Moss Creek Outflow Channel. The Gravel Creek Valley itself displays a very complex mass of glacial deposits among whose irregularities of contour the tiny stream is forced to take an extremely tortuous course in its way down to the Slaterville Valley below.

Perhaps the most clearly defined and striking evidences of the presence of an ice lobe in the region of the Upper Sixmile Valley are the marginal channels on the western and southwestern slopes of Davies Hill (N, X, and Y, fig. 3). Here in three principal groups is a series of outlets plainly indicative of the presence of a tongue of ice whose consecutive stages of gradual reduction in thickness by melting, with halts of varying lengths, are marked by the channels in the drift of Davies Hill. In some places the channels have been eroded into the rock wall of the hill. In the largest of these, first described by Rich, a large singularly well preserved fossil fall occurs. On the slopes of the main Sixmile Valley, between Rowe and Davies Hills, lateral moraine ridges are found, more numerous on the eastern than on the western side.

The evidence furnished by the glacial striae found within and near the area and the presence of the trun-



cated spur of Davies Hill (P', fig. 3) indicate that the general direction of the *local ice movement was from the west and southwest*. The position of the numerous stadal and lateral moraines and the marginal and out-flow channels denote that *the retreat by melting was back over a route in the opposite direction*.

### *Interpretation of the Preglacial Drainage Conditions.*

The following interpretation of the preglacial drainage conditions of the Upper Sixmile Valley region is based upon detailed field studies. These have resulted in the collection of data, which logically arrange themselves into the following captions:

- I. The Features of the West Sixmile and Gravel Creek Valleys.
- II. The Significance of the Gorge of West Sixmile Creek.
- III. The Relations of Moss and Spring Creeks and Rowe Hill.
- IV. The Evidence of East Sixmile Creek and its Tributaries.

#### I. THE FEATURES OF WEST SIXMILE AND GRAVEL CREEK VALLEYS.

That West Sixmile has been turned from its normal course has already been suggested. The presence of the massive moraine deposit (the Moss Creek Moraine) lying between Rowe and Gilbert Hills, the abrupt diversion of the stream at this point, and the gorge eroded below Van Pelt's (P, fig. 2) all substantiate this view. Moreover the obvious correlation of the Gravel Creek and West Sixmile Valleys impresses one as strongly in the field as does the manifest disconnection between the latter and the main Sixmile Valley, below Spring Creek.

Gravel Creek Valley is an early mature, preglacial valley filled with drift. At the point where the road trending southwest from Van Pelt's surmounts the first prominent ridge of the Moss Creek Moraine the top of the deposit attains a height of at least 85 feet above the level of the creek, and at Van Pelt's a well sunk virtually at the creek level extends downward for a distance of about 20 feet before the bed rock is encountered. From this we may safely assume that the depth of the Moss

Creek Terminal Moraine at I (fig. 2) cannot be less than 100 feet. There is warrant for concluding, as will be shown later, that the slope of the rock floor from Van Pelt's to the region of the abrupt turning point of West Sixmile (D, fig. 2) is downwards. If this be true the depth of the Moss Creek Terminal Moraine must be taken to be much greater than has been postulated above. Half a mile due south of the point where the road reaches its greatest elevation on the summit of the Moss Creek Moraine there lies a small swamp (R, fig. 2). Near this point Gravel Creek has penetrated to its greatest depth into the drift filling of the valley, a depth of approximately 80 feet, without arriving at bed rock. Neither here nor in any other part of its course has this stream been able to remove the moraine to a depth sufficient to disclose the rock bottom of the old preglacial valley. It is apparently a creek that has come into possession of a valley in the early mature stage of development (the product of erosion by a much larger and more vigorous stream) obstructed by a complexus of glacial moraine fillings.

The position of the moraines, ridges, and loops in the Gravel Creek and Sixmile Valleys indicates that the ice front at its earliest and longest halt in this region stood in the position indicated in fig. 8. Evidence that the ice occupied this position is furnished by the uppermost series of marginal channels on the southern slopes of Davies Hill (N, X, and Y, fig. 3), described by Rich, and it is possible that these served as outlets for the escape of the water of East and West Sixmile Creeks which at that time no doubt flowed against the ice barrier from the north.

It was apparently only after the ice front had retreated to a position just to the south of the present course of West Sixmile that the creek discovered the lowest portion of the Moss Creek Moraine and began to erode its present channel into it. In some localities the course of this early stream across the irregularities of the moraine may have been determined by the position of the ice front, which, forming one of its banks, forced it to become, locally and temporarily, a marginal stream. Its volume may have been much greater then than now, for it seems not unreasonable to suppose that it was augmented by water from the melting ice toward the north,

in the region of the present headwaters. The series of marginal channels, on Davies Hill, to which allusion has been previously made, would indicate that at all stages of the ice occupation of the Gravel Creek Valleys drainage from the north made its escape to the southward around the ice lobe and into the upper portion of the Owego Creek Valley (O', fig. 2). Thus the evidence adduced seems to support for the first part of our conclusion, namely that West Sixmile Creek was at an

FIG. 4.

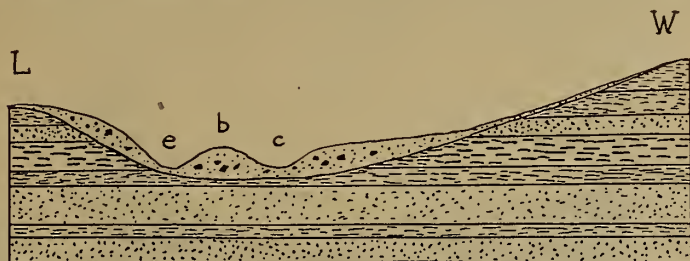


FIG. 4. Cross section between summits of Rowe and Cole Hills, along line L-W (fig. 2) to show modification by drift filling of preglacial valley bottom. e, Moss Creek; b, Moss Creek Terminal Moraine; c, West Sixmile Creek.

earlier date excluded from the lower preglacial portion of its valley (represented now by the Gravel Creek Valley) by a moraine deposit, was turned aside and forced to cut a gorge along its new course.

## II. THE SIGNIFICANCE OF THE GORGE OF WEST SIXMILE CREEK.

The gorge of West Sixmile Creek begins about 150 feet above the point of confluence of that stream with East Sixmile, and at a level of at least 90 feet below the surface of the local glacial drift cover (H, fig. 2). Above the point of confluence the tops of the gorge walls on each side of West Sixmile slope very abruptly westward and disappear beneath the drift. The remainder of the ravine, as far as Van Pelt's, lies entirely in drift and nowhere is the bedrock visible in this upper section. A continuation beneath the drift of the westward slope of the tops of the gorge walls suggests that, at the head of

the ravine at Van Pelt's, the rock floor must be far beneath the surface of the drift filling. This, however, is not the case. A well sunk at Van Pelt's in the lowest portion of the valley, about ten feet from the stream itself, reaches bed rock, as has been said, at a depth of only 20 feet. The nearness to the surface of the bed rock here, and the fact that a quarter of a mile down the ravine the stream has eroded to a depth of at least 65 feet (45 feet below the level of the bed rock at Van Pelt's) before encountering the bed rock, indicates that the slope of the rock floor in this section is eastward. This, no

FIG. 5.

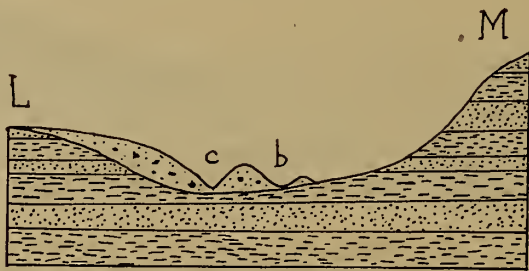


FIG. 5. Cross section between summits of Rowe and Davies Hills, along line L-M (fig. 2), to indicate a possible explanation for the presence of bed rock in the gorge of West Sixmile (b) and its absence in Moss Creek Ravine (c).

doubt represents the older preglacial floor of an early mature valley. How then are we to account for the short gorge at the lower end of West Sixmile?

The probable relationship between the rock floor and the drift filling is given in fig. 4. It is supposed that a line extending between the summits of Rowe and Cole Hills (W, fig. 2) and passing through Van Pelt's indicates the position of the low preglacial divide (reduced to a still lower level by ice erosion) existing between the valleys of East and West Sixmile (fig. 7). Evidence to be adduced later tends to substantiate Tarr's conclusion that East Sixmile has been forced by morainic barriers to flow over its eastern valley slope and has cut a rock gorge down into the former valley side. If this deduction be correct then the gorge of West Sixmile may have been cut into the end of the spur of Davies Hill project-

ing beneath the surface of the drift (fig. 7). According to this interpretation Rowe Hill may quite readily be regarded as representing a remnant of the preglacial divide between East and West Sixmile Creeks, extending in the general direction of a line from Rowe to Spur Hills (*Z'*, fig. 2). This brings us to the consideration of:

III. THE RELATIONS OF MOSS AND SPRING CREEKS AND ROWE HILL.

The largest north-flowing tributary of Moss Creek occupies the beginning of a glacial outflow channel (the Moss Creek Channel) the existence of which was first

FIG. 6.

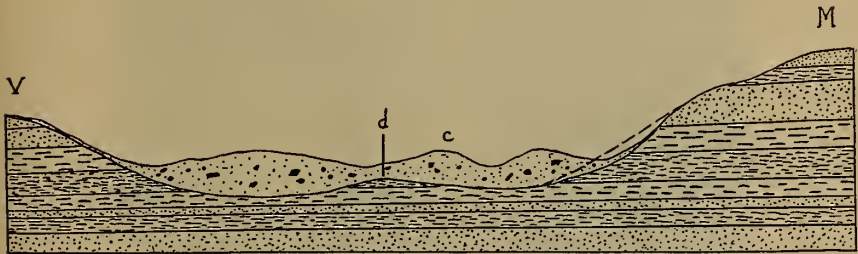


FIG. 6. Cross section between summits of Hunter and Davies Hills, along line V-M (fig. 2), to show probable relation of the drift filling to the preglacial valleys of East and West Sixmile. V-d, preglacial valley of West Sixmile; d-M, preglacial valley of East Sixmile; c, Moss Creek Terminal Moraine. Dotted line shows probable slope of a portion of Davies Hill before truncation had occurred.

made known by Tarr (6). The probable position of the ice front when this channel was formed and in use is indicated in fig. 9. The glacial drainage together with the drainage of the upper slopes of the valley to the north probably developed the present Moss Creek valley through the drift. At this time probably the maximum volume water was flowing around the margins of the ice lobes and no doubt made its way into the upper portion of the Owego Creek Valley (*O'*, fig. 2) through one of the larger marginal channels of Davies Hill, possibly through the one containing the fossil falls which Rich has described.

The post-glacial flow of Moss Creek has since carved a ravine in the bottom of this glacial outflow channel to

a depth, at one point, of over 100 feet and in drift throughout its entire length, without reaching bed rock in the stream bottom. Our explanation for the presence of rock in the West Sixmile gorge and its absence in the Moss Creek Ravine is given in fig. 5.

Spring Creek (K, fig. 2) has likewise carved out a post-glacial ravine in the eastern side of Rowe Hill, in some places from 40 to 50 feet in depth, without revealing the

FIG. 6a.

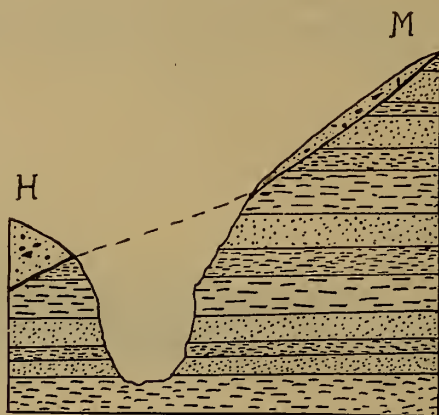


FIG. 6a. Cross section through the gorge of East Sixmile, at H (fig. 2), to show how the gorge at this point has been entrenched into the western rock slope of Davies Hill (M).

bed rock of the hill, nor does the hill itself exhibit traces of its central rock core except in one obscure outcrop near the marginal channel at S (fig. 2).

The evidence, therefore, of the gorge of West Sixmile; the ravines of Moss and Spring Creeks; and the nature of the material exposed on and in Spring Hill all lead to the conclusion that Spring Hill is composed of a small central rock core deeply mantled over with glacial drift, especially towards the east in the region about and south from Spring Creek. The relation of the thin and thick drift is shown in fig. 3.

#### IV. THE EVIDENCE OF EAST SIXMILE CREEK AND ITS TRIBUTARIES.

An extension of the same terminal moraine that has diverted West Sixmile Creek from the lower portion of

its preglacial course has apparently also turned Spur Creek (O, fig. 2) aside toward the east. The preglacial course of Spur Creek seems to have been almost directly south, following the present general trend of its upper valley, i. e., that portion whose bottom is above the 1480

FIG. 7.

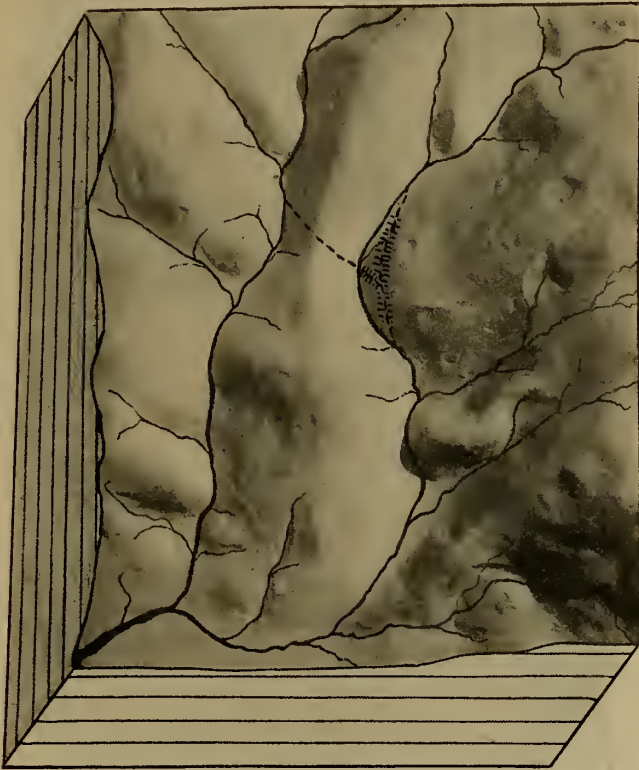


FIG. 7. Restoration of probable preglacial topography and drainage.

Dotted lines show the relation of the present courses of East and West Sixmile to the rock slopes. Present rock gorges are shown by lines with cross shading (near center).

foot level. The lower end of Spur Hill (P, fig. 2) from an altitude of 1560 feet down between West Sixmile and Spur Creeks consists of drift material covering the rock to a depth of at least 60 feet at the point where East and West Sixmile unite. This is shown to be true by the

section of the mass that the gorge of each creek has made near their confluence. The drift is estimated to be from 175 to 200 feet deep on the nose of Spur Hill at points between the 1500 and 1600 foot contours. Spur Creek is

FIG. 8.



FIG. 8. Stage of the glacial retreat at the deposition of the Moss Creek terminal moraine.

nowhere in its valley flowing on bed rock, except in a very small portion of its course near the headwaters where the drift is thin.

The topography of the triangular area included between Spur Creek on the south, the road on the northwest, and East Sixmile on the east, indicates that the



Spur Creek Moraine (Z, fig. 3) was pushed well up into the East Sixmile Valley especially along its western side. No traces of bed rock could be found here, outcropping on the surface, nor did road cuttings, wells, or

FIG. 9.

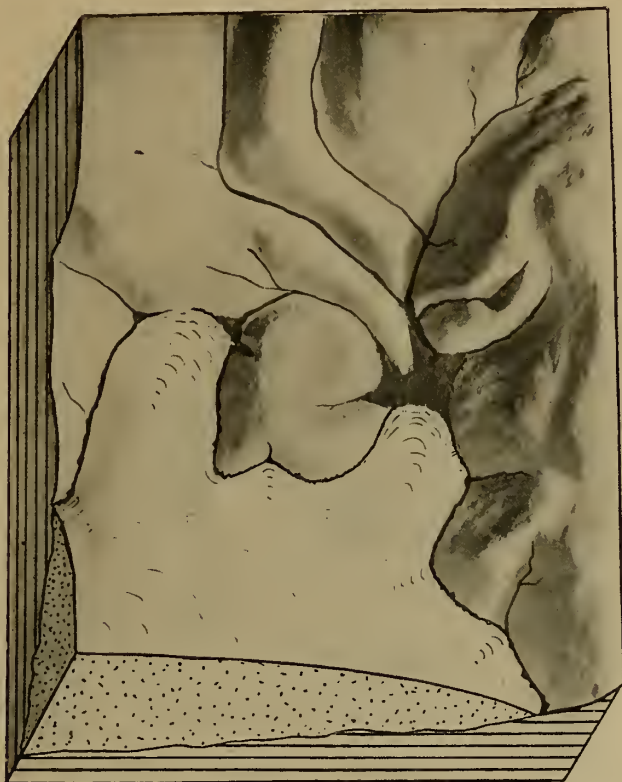


FIG. 9. Stage of the glacial retreat when Moss Creek outflow channel carried glacial drainage.

the beds of either East Sixmile itself or of any of its tributaries reveal anything but glacial drift.

It appears probable, therefore, that East Sixmile Creek has been pushed over to the eastern side of its valley by the Spur Creek Moraine. This is further suggested by the fact that just after the creek crosses beneath the road at the foot of Cole Hill its direction

changes abruptly and turns from the western side of its valley sharply toward the eastern, exactly at the point where the northern end of the Spur Creek Moraine begins to be most characteristically developed, and where the hummocks and kettles begin to appear (C, fig. 3).

FIG. 10.



FIG. 10. Stage of the glacial retreat when Rowe Hill marginal channel carried glacial drainage from Gravel Creek valley to East Sixmile valley.

The fact that lends the strongest support to this interpretation, however, is that at the point where East Sixmile is joined by Spur Creek, the former begins to cut a gorge in the bed rock of the eastern wall of its broader, older valley at the foot of Davies Hill. This gorge

attains its greatest depth between Berry and Diedrich Creeks (B and M, fig. 2). In all places along the gorge the eastern rock wall is higher than the western; the alignment in elevation of the tops of the gorge sides pre-

FIG. 11.



FIG. 11. Postglacial topography and drainage.

servicing the steep gradient of the slopes of the truncated spur of Davies Hill (fig. 6a).

If we suppose East Sixmile to have been diverted against its eastern wall we should expect to find some evidence of this in the valleys of its tributary streams from Davies Hill, for such a diversion would result in the steepening of those slopes of Davies Hill against which the stream had been forced and into which it had

cut its gorge. Such evidence is actually to be found in the change in the direction of the flow of Berry and Diedrich Creeks, and to a less extent in that of Reed Creek (R', fig. 2). It suggests that preglacially all three may have followed in the entire extent of their courses the directions of the upper portions of their present valleys and flowed more toward the south, but turned toward the west after the steepening of their main valley (East Sixmile) and flowed down the steepened slopes in the shortest route to the main stream below. Furthermore in the lower parts of their courses they have all cut diminutive gorges in the bed rock of Davies Hill, and bear all the appearance of streams that have been rejuvenated because of the deepening of their main valley.

The facts that have been adduced, namely: (1) that Spur Creek has been turned from its earlier course by a mass of moraine, (2) that the Spur Creek Moraine continues up the western side of the East Sixmile Valley and has diverted the stream at the road near the foot of Cole Hill, (3) that the East Sixmile gorge is manifestly cut into the side of Davies Hill, causing the rejuvenation of Berry, Diedrich, and Reed Creeks, all seem to justify the conclusion that East Sixmile Creek has been forced to the eastern side of its old preglacial valley by the Spur Creek Moraine and has, in consequence, been compelled to cut a gorge in its earlier valley wall.

#### *Summary and Conclusion.*

Upon the facts gathered in the field and outlined in the foregoing pages the author's restoration of the probable preglacial topography and drainage, as given in fig. 7, is based.

In fig. 8 is represented the theoretical position of the ice lobe at the time of the deposition of the Moss Creek Terminal Moraine. During this stage the impounded waters from the north flowed around the northern edge of the ice front and escaped southward into the upper portion of the Owego Creek Valley through some one of the marginal channels on the higher slopes of the western side and southern end of Davies Hill.

At a later stage, fig. 9, the ice had so far retreated that Rowe Hill was uncovered and the occupation of the Moss Creek Outflow Channel commenced. During this period

a lower series of marginal channels on Davies Hill conducted the water southward into the Owego Valley.

The development of the marginal channel on the southwestern slope of Rowe Hill marks a third stage in the ice retreat (fig. 10). The lobe occupying the present Gravel Creek Valley had now been melted back below the divide between Gravel and West Sixmile Valleys and thereafter the drainage was conducted around the southern end of Rowe Hill into the East Sixmile Valley and from thence into Owego Creek, utilizing probably the lower of the marginal channels near the southwestern base of Davies Hill.

The postglacial topography and drainage is represented in fig. 11.

A comparison of figs. 7 and 11 will give some notion of the great modifications in both topography and drainage that apparently have been occasioned by the occupation of the Upper Sixmile region by the Pleistocene ice. To some extent the readjustment of the streams and the development of new topographic features is due to the effects of ice erosion, but in a much greater degree to the massiveness and frequency of the moraine deposits of various kinds.

It is the object of this paper to indicate how great may be the changes which can be brought about by such processes operating within a very restricted area as a result of ice occupation, and to emphasize the importance of glaciation in the moulding of the topography of the land surface.

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Physiographic Laboratory, Cornell University.

ART. XII.—*The Moisture Content of some Typical Coals*; by G. A. HULETT, E. MACK and C. P. SMYTH.

In a previous article "On the Moisture Content of Coal and some Ideas on the Genesis of Coal," we obtained results which were readily interpreted by assuming that coal is largely in the colloidal state with water as the external phase and absorbed on such a large surface that a measurable portion of it is not removed in the usual analytical method of heating to  $110^{\circ}$  in a drying oven nor even by any process of vacuum desiccation at ordinary temperatures. Indeed it was found necessary to heat coal to near  $300^{\circ}$  C., with a continual removal of the water vapor, in order to secure results which represented the moisture content of the coal. It is probable that all water, which is present as such in coal, is not removed until a temperature of some  $365^{\circ}$  C., the critical temperature of water, is reached; but the amount of water retained by a coal after heating for an hour or so at  $250^{\circ}$  to  $300^{\circ}$  is, we believe, quite negligible. The constituents of coal decompose or "crack" at all temperatures but at ordinary temperatures the reactions are so slow as to require geologic periods to produce measurable results, and even for temperatures well over  $200^{\circ}$  the rate of these reactions is still so slow<sup>2</sup> that it seemed quite possible to heat coal for the time and temperature needed for our purpose without causing a noticeable decomposition or the formation of a measurable amount of water. In view of this situation it has been of interest to make a more detailed study of some typical coals.

Coal in the uncovered seam always appears to be "dry" but immediately it is broken down and exposed to the mine air, there begins a loss or gain of moisture, depending on the kind of coal, temperature, humidity of the mine air, &c. Furthermore, it has been shown<sup>3</sup> that coal, like other colloidal substances, does not possess a definite vapor pressure. When water was removed from a coal by lowering the vapor pressure, the coal showed a continually decreasing vapor pressure as it lost water.

<sup>1</sup> This Journal, 43, 89, 1917.

<sup>2</sup> L. c., p. 103.

<sup>3</sup> Ralston and Porter, Tech. Paper 113, U. S. Bureau of Mines.

On increasing the vapor pressure the coal took up water again, but when the water removed had been returned, the vapor pressure was not that originally shown by the coal but measurably greater. This is a typical behavior of colloids.

The water content of a coal must, therefore, be defined as the moisture that is present as such when the coal is first broken down from the seam, and care must be exercised to avoid loss or gain of moisture during the sampling, collecting, or handling of the samples.

The present work was on four samples typical of American bituminous coals. These samples were secured by engineers of the U. S. Bureau of Mines, reduced to 60-mesh samples and given the regular analysis at the Pittsburgh Station:

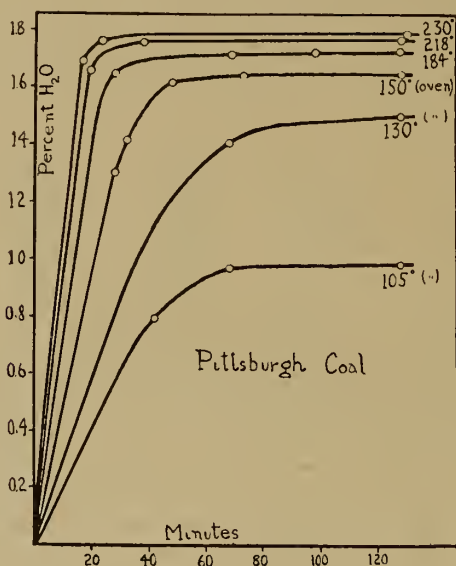
	New River	Pittsburgh	Indiana	Wyoming
Moisture	1.10	1.93	4.55	6.15
Volatile	24.67	36.23	41.65	37.55
Fixed Carbon	69.98	55.42	42.70	52.30
Ash	4.25	6.42	11.10	4.00

Precautions were taken to avoid a loss or gain of moisture after the 60-mesh samples were prepared, but these samples would not comply with the criterion given above, as we do not as yet know the loss or gain of moisture in preparing the 60-mesh samples. The question of local heating due to crushing may play a measurable rôle and must be looked into, and until information on these points is available we can not consider the values we have obtained as representing the moisture content of the coal as mined but only of the 60-mesh samples.

From our previous experiences we were able to materially improve our method and apparatus. The coal was heated in a vacuum so devised that the water was removed from the presence of the coal as fast as liberated. It was found that for a definite constant temperature the moisture came off rapidly at first, then more slowly and finally ceased altogether, thus giving results which were plotted as "percentage loss of water—time curves." These curves showed a rapid evolution of water at first but the curves finally ran practically parallel to the time axis, showing no further liberation of water. Fig. 1 represents the curves obtained at the various indicated temperatures for a Pittsburgh coal. We noticed in the previous work that gases were liber-

ated along with the moisture and that they ceased to come off when the moisture did, so it seemed probable that these gases (mostly  $\text{CO}_2$  with some  $\text{CO}$  and a little  $\text{CH}_4$ ), were also absorbed by the large surface of the colloidal coal in much the same way that the water was. We arranged our apparatus so that we could follow the liberation of these gases manometrically, and were thus able to plot the volume of gas liberated as a function of

FIG. 1.



the time of heating for each temperature. These isothermals were very similar to those previously obtained for the moisture losses as a function of time, and were much easier to determine as it only required manometer readings at convenient time intervals, while in the previous work it was necessary to make a separate determination of the moisture for each point on the curve. In this work we were also able to make a determination of the total water liberated at a given temperature, while the plot of the gas liberation curve showed whether there had been noticeable decomposition.

An idea of the apparatus and method may be obtained from figs. 2, 3 and 4. The coal bucket was made from



very thin walled tubing (.3 mm.) and fitted the heating tube of the apparatus very exactly so as to insure a good heat conductivity. Attached to the bucket is an aluminium wire which carried two disks of aluminium which served to prevent convection currents. The convection currents due to a temperature of  $250^{\circ}$  to  $300^{\circ}$  in the heating tube with  $-78^{\circ}$  in the insert tube, cause excessive

FIG. 2.

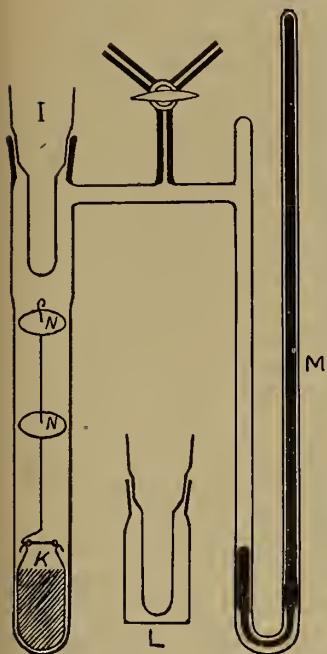


FIG. 3.

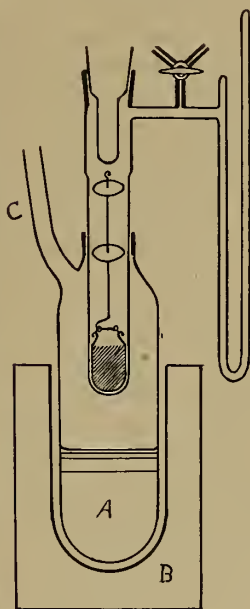


FIG. 4.

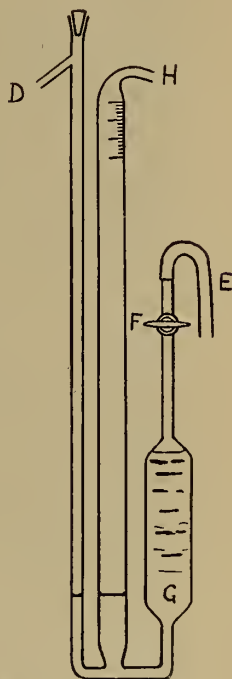


FIG. 2.—I, insert tube. L, insert tube and container for weighing. K, coal bucket. N, N, aluminium disks.

FIG. 3.—A, constant boiling liquid. B, electric heater. C, condenser.

FIG. 4.—D, air or gas inlet. G, concentrated  $H_2SO_4$ . H, connection with apparatus fig. 2.

convection currents even with small gas pressures and it was found best to avoid them and in fact necessary when the volume of the gas was to be measured. The disks had a diameter of about one millimeter less than that of the tube. The partial pressure of the water vapor in the apparatus was kept very low during the heating by condensation on the lower part of the insert

tube. This insert tube contained the solid  $\text{CO}_2$ , which was added from time to time and kept well packed down so that the ice which formed on this tube was maintained at  $-78^\circ \text{C}$ ., thus reducing the partial pressure of the water vapor in the apparatus to about .0005 mm.<sup>4</sup> The moisture formed as a sheath of ice on the lower end of the insert tube, and after dry gas had been allowed to fill the apparatus, this insert tube was removed with its sheath of ice and rapidly inserted into its weighing tube and weighed,<sup>5</sup> the insert tube was loosened and the system placed in a vacuum desiccator until the water disappeared, and then reweighed. In view of the fact that gases and vapors are not soluble in ice, the method is evidently exact and capable of wide application in moisture determinations. If vapors other than water are condensed, their nature and amount may be determined.

After the coal had been inserted and the lower end of the insert tube was at the temperature of  $-78^\circ$ , the air was removed from the apparatus without fear of loss of moisture from the coal, but the rapid liberation of moisture and gas from some of the coals, when first evacuated, caused some of the fine powder to "boil" and be carried along and spread throughout the apparatus. This difficulty was overcome by inserting a wad of dried glass wool in the top of the coal bucket. In order to prevent a loss of gas from the coals during the evacuation of the apparatus, we inserted the end of the tube containing the bucket in a cold mixture ( $-20^\circ \text{C}$ ., or in some cases cooled it to  $-78^\circ$  before evacuating.) Fig. 3 shows the electric heater and vapor bath; it was found most satisfactory to use the condensing vapor of a constant boiling liquid for heating the coal. We were able to find satisfactory materials for the various temperatures needed.

When the tube was first inserted into the vapor of the bath there was, in some cases, such a rapid evolution of water vapor that it was not condensed on the insert tube as fast as liberated from the coal, and the pressures observed were due not only to the gas liberated but to

<sup>4</sup> Dushman, *Phys. Rev.*, 5, 223.

<sup>5</sup> It was found necessary to carefully clean out the inside of the insert tube, and to wipe in a definite way; if very accurate results were desired we found soft filter paper very good. After the ice had melted and room temperature had been attained we allowed the pressure inside and out to equalize, and made sure that the weight was constant.

some water vapor. In a few minutes, however, the water vapor was liberated more slowly than condensation took place and from this point on only the gas pressures were observed. This first part of the curve may be obtained by a short extrapolation, but (this first few minutes of the curves) is not important for our purposes. We secured a series of pressure readings at convenient intervals, but the volume of the apparatus and the temperatures were still necessary for calculating the volume of gas corresponding to each time interval. This seemed to be a difficult problem in view of the wide difference of temperature in various parts of the apparatus. We were able however to get a most satisfactory "temperature-volume" factor to combine with our pressure readings. After the pressure readings had been made, the gas was pumped out of the apparatus and connection was made with the top of the burette of the apparatus represented in fig. 4. Gas was now allowed to fill the apparatus from the burette until the pressure in the apparatus and burette was atmospheric, the various parts of the apparatus were maintained at the same temperatures as in the experiment. The burette readings thus gave the volume of gas at atmospheric pressure and room temperature which filled the apparatus at its temperatures under the pressure of the atmosphere. Obviously the burette volume and temperature may be used in our calculations with each observed pressure reading and thus we were able to calculate the exact volume of gas present at each of the time intervals. It was of course necessary to admit only dried gases into the apparatus and it was also necessary to use an indifferent gas since dehydrated coals at the temperatures employed absorb oxygen very rapidly. We used methane, hydrogen or coal gas, which was forced in through the leveling tube and up through the burette and out through the three-way cock of the apparatus, thus thoroughly drying these tubes. The burette apparatus was designed so that concentrated sulphuric acid might be used in it and thus insured a perfect dryness for the apparatus and gases used. With the aid of the rubber mouthpiece E and the cock F, it was possible to control the acid in the burette apparatus and make all readings with the gas pressure in the burette atmospheric. When the aluminium disks, fig. 2, properly stopped convection currents in

FIG. 5.

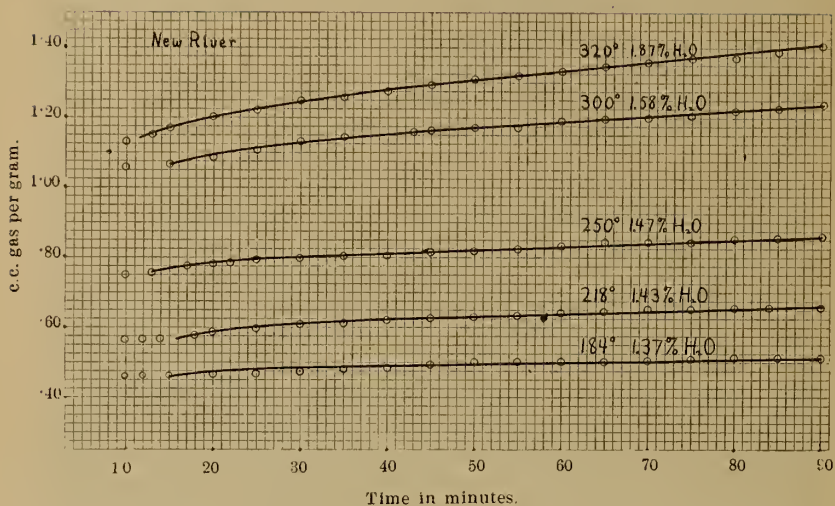


FIG. 6.

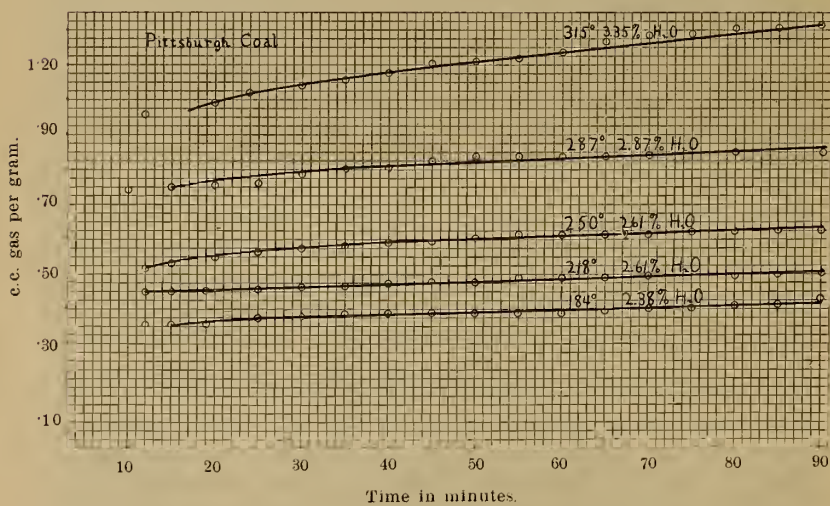


FIG. 7.

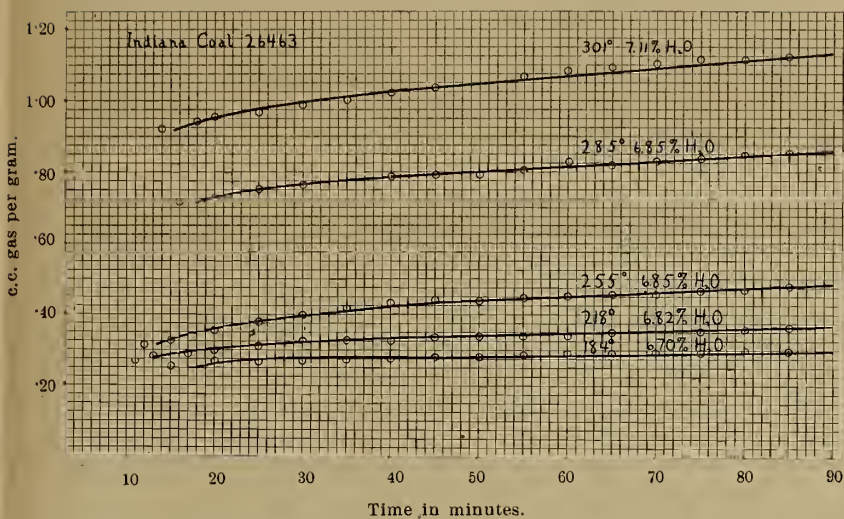
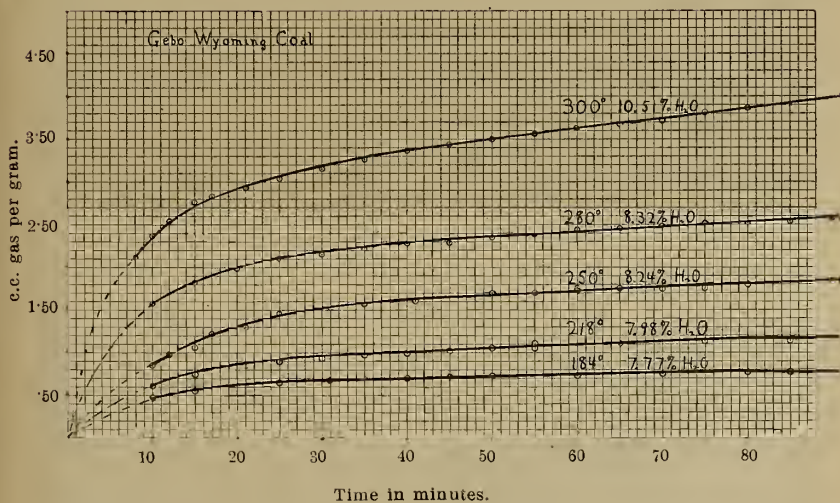


FIG. 8.



the gas in the apparatus, the volume readings were very constant and precise.

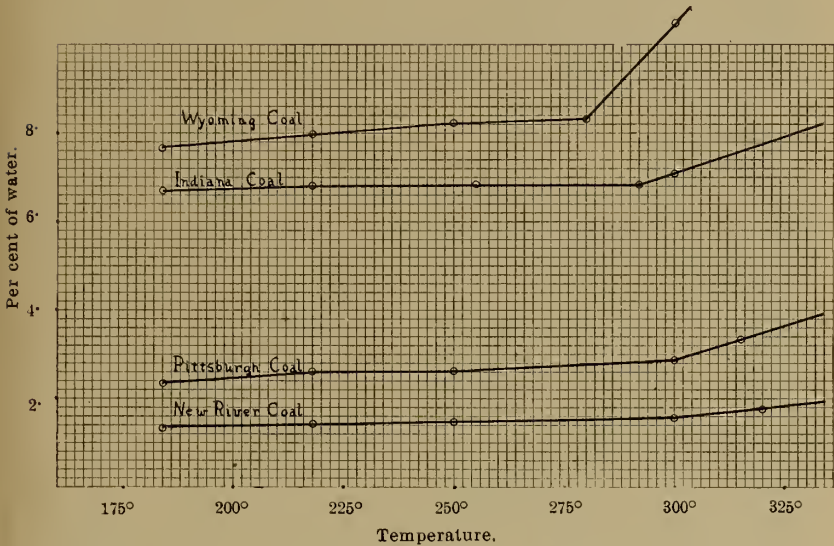
The gas volumes were calculated to standard conditions, after allowing for the (volume) position of the mercury in the manometer. From these values we readily obtained the volume of gas liberated per gram of coal for each time interval, and the plot gave information as to whether measurable decomposition of coal substances has taken place during the heating, while the total moisture liberated during the heating was determined at the end of the experiment. It was found that 90 minutes heating was sufficient for our purpose and on inspection of these isothermal curves, figs. 5, 6, 7 and 8 (the temperature of each curve and total moisture liberated are indicated on each curve), it was seen that the gas generally ceased to be liberated after 40 to 60 minutes and the curves from this time tended to run parallel to the time axis, but at the higher temperatures there are distinct indications of a continual liberation of gas as long as the heating of the coal was continued. This is more marked with some coals than with others and clearly indicates decomposition of coal substances.

The moisture values are seen to be higher, the higher the temperature of the experiment, which is in accord with the conclusions we drew from our previous work on the condition of water in coal. The temperatures used were those of constant boiling liquids and did not give equal temperature intervals, so we plotted water losses against the corresponding temperatures and secured the curves of fig. 9, which represent the water losses when these coals were heated at the various temperatures for 90 minutes in a vacuum which was exceedingly free from water vapor. Longer heating did not make a noticeable difference in the results. Between  $184^{\circ}$  and  $218^{\circ}$  the curves show a noticeable increase in the percentage of water lost in all cases, which we regard as the typical behavior of the loss of water from the large surfaces of the colloidal coal. Above  $218^{\circ}$  this loss is still noticeable but becomes so small in some cases that the curves are nearly parallel with the temperature axis. Above some  $275^{\circ}$  we soon strike a more or less pronounced break in the curves which we attribute to the decomposition of coal substances with the formation of water. These same reactions undoubtedly take place at

lower temperatures, but with such slow rates that the amount of water formed is not measurable. There is no real break in the curves but a more rapid change in direction due to the appearance in measurable quantities of water of decomposition.

It is a comparatively easy matter to pick out from

FIG. 9.



these curves satisfactory values for the moisture content:—

	Moisture Content. c.c. of Gas per Standard Method Gram of Coal. of Moisture.		
New River	1.50	.85	1.10
Pittsburgh	2.45	.60	1.93
Indiana	6.82	.75	4.55
Wyoming	8.20	2.00	6.15

The values are over 30% greater than the standard method of determining moisture, which in view of the situation we have pointed out, would hardly be expected to give the true moisture content of a coal, but the standard method is valuable for commercial purposes.

It is evident from fig. 9 that we may select for our bath liquid any substance which boils between 230° and 275°, and the time of heating may be anything between 1 and 2 hours.

The coals here reported on cover the range of our important coals. The more mature coals corresponding to the New River type are easy to handle. We may safely use temperatures up to 300° before there is a noticeable rate of decomposition of coal substances. With the Pittsburgh type of coal a noticeable rate of decomposition begins at a lower temperature, and the amount of decomposition increases more rapidly with increasing temperature. With still newer types these tendencies begin at progressively lower temperatures and are more marked. Preliminary work with lignites and cellulose materials even more strongly emphasize this tendency.

This seems to be clearly in line with the view expressed in the previous article on the genesis of coal. Starting with woody material or peat, the various substances are undergoing normal chemical reactions at ordinary temperatures, not on account of the pressure of superimposed materials, but in spite of it. The rate of these reactions are so slow that measurable results appear only in geologic periods, but even these slow reaction velocities are of different orders of magnitude and evidently the cellulosic substances largely disappear, while the resinous and other substances with slower reaction velocities have only partially run their courses.

The volume of gases evolved with the moisture, taken from the curves figs. 5, 6, 7, 8, are given in the table. Here again the values are for our 60-mesh samples. Probably the loss of gases in preparing these samples is proportionally greater than that of the water. It will be of considerable interest to know the real amount of these gases in various types of coal and also their composition. From the work of Taylor and Porter (l. c.), coals heated to 250° in a vacuum for several hours give gases which were mostly CO<sub>2</sub> (40–70%), with some 10% of CO, a little methane, and traces of other hydrocarbons. Some coals are known to liberate considerable quantities of methane at ordinary temperatures. More exact information on this subject would be of interest.



ART. XIII.—*The Formation of Dolomite and its Bearing on the Coral Reef Problem*; by ERNEST W. SKEATS, Geological Department, University of Melbourne.

*Introduction.*

THE origin of dolomite is a problem which has been discussed for a century. Most of the attempts to solve the problem have been from the experimental and chemical sides. The modes of occurrence of dolomite among calcareous rocks and the geological aspect of the problem have received more attention in recent years. The recognition of the fact that coral limestones are sometimes dolomitized was first due to the observation of Dana\* at the island of Metia, but it was not till the detailed chemical examination of the material of the Funafuti bores,† and of limestones from upraised coral islands,‡ was undertaken that it was realized how widespread was the process of dolomitization among coral islands. In the course of these investigations the writer was led to the conclusion that the process of dolomitization of the limestones of coral islands was effected in shallow water,§ and in a later paper|| on the Dolomites of S. Tyrol, he amplified these conclusions. Subsequent writers on the dolomite problem appear to have overlooked this later paper; at any rate, no discussion of the views therein presented has come under his notice.

It is, of course, well known that dolomitization may be local, that is restricted to the neighborhood of joints, bedding plants or mineral veins. Dolomites of this restricted occurrence are not here under discussion. On the other hand, "regional" or widespread dolomitization occurs among ancient limestones and among recent coral limestones. Certain dolomites usually associated with gypsum salt deposits are regional in character, but appear to have been formed in land-locked areas and under conditions of concentrated solutions. With such dolomites this paper is not directly concerned. In this communication discussion will be limited to those "regional" cases of dolomitization such as are represented by certain recent coral limestones where no concentration of sea water or elevation of temperature can be postulated.

Extensive references to the literature of the subject will be found in the following papers:

\* J. D. Dana, *Geology of United States Exploring Expedition*, p. 153, 1849.

† J. W. Judd, *The Atoll of Funafuti*, London, pp. 362-389, 1904.

‡ E. W. Skeats, *Monograph of Christmas Island*, pp. 265-8, 1900; *Bull. Mus. Comp. Zool.*, Harvard, vol. xlii, 53-126, 1903.

§ E. W. Skeats, *op. cit.*

|| *Idem*, *Q. J. G. S.*, lxi, 97-141, 1905.

- E. W. Skeats, Bull. Mus. Comp. Zool., Harvard 1903, pp. 53-126.  
 W. Meigen, Sonderabdruck, Geol. Rundschau, Leipzig, Bd. i, pp. 121-126, 1910.  
 Steidtmann, Jour. Geol., pp. 323-45, 392-428, 1911.  
 F. W. Clarke, Data of Geochemistry, Bull. 330, U. S. Geol. Sur. 20, pp. 480-490, 1908.  
 F. M. Van Tuyl, this Journal, xlii, 249-260, 1916.

A study of the mode of occurrence of dolomites among the older limestones was undertaken by the writer to see if the independent evidence of associated organisms or characteristic structures would throw any light on the conditions of the formation of dolomite, and the result has been to substantiate the view of its formation in shallow water. The object of this communication is to review some of the experimental work on the formation of dolomite, to correlate the evidence of its distribution among recent and upraised coral limestones, and to bring together some geological facts of distribution bearing on the conditions of formation of the mineral, and finally to indicate the bearings of the conclusions drawn from these various lines of enquiry, upon the conditions of formation of the atoll of Funafuti among other coral islands.

*Experimental evidence of the formation of dolomite.*

The literature on this subject has been summarized by Pfaff\* and Steidtmann.† Marignac, Durocher, C. Saint Clair Deville, A. von Morlot, and T. Sterry Hunt, among others, claimed to have formed dolomite experimentally by various processes generally involving great heat and considerable pressure. It is not, however, always clear in the case of these early researches whether the product was a mixture of calcium and magnesium carbonates or the definite mineral compound dolomite. Klement's experiments showed that aragonite organisms and aragonite heated in a closed tube with a concentrated solution of magnesium sulphate at 60° C., readily took up magnesium carbonate to the amount of 41.5 per cent of MgCO<sub>3</sub>, while calcite was but little affected. The product, however, was a mixture of the two carbonates and not the definite compound dolomite. Pfaff,‡ as the result of certain experiments, claims that the formation of dolomite in nature occurs at great depths and pressure. He treated powdered anhydrite (gypsum gave negative results) in a concentrated solution of MgCl<sub>2</sub> containing NaCl, to the action of Na<sub>2</sub>CO<sub>3</sub> for a long time under pressure, and got a residue, difficultly soluble in 5 per cent acetic acid,

\* F. W. Pfaff, N. Jahrb., Beit. Bd. xxiii, p. 529, 1907.

† Steidtmann, op. cit.

‡ Op. cit.

which showed under the microscope small rhombohedra, difficultly soluble in H.Cl. In the solution Mg was detected, but the amount was too small for analysis. The anhydrite was never completely converted and sometimes the reaction was entirely absent. Similar results were obtained from a solution of NaCl and anhydrite. Another reaction was that of  $MgCl_2$  and NaCl on  $CaCO_3$  under a pressure of 60–100 atmospheres and a temp. from  $4^\circ$  to  $14^\circ C$ . A residue insoluble in 2 per cent acetic acid was obtained, and in one case the residue had the composition of dolomite.

G. Linck,\* by adding  $Am_2CO_3$  to a solution of Mg salts and then adding  $CaCl_2$ , obtained first an amorphous precipitate, which on long standing became small crystalline spherulites of the composition of dolomite but having a + optical sign, and decomposing when boiled with water. On heating these spherulites with their mother liquor in sealed tubes for several hours to  $40^\circ$ – $50^\circ C$ . the spherulites showed – optical sign and only slowly dissolved in dilute acetic acid. The analysis showed 44.8 per cent of  $MgCO_3$ , which indicates an excess of  $MgCO_3$  as compared with normal dolomite. Meigen† has repeated these experiments, but has failed to obtain a precipitate of similar composition.

Phillipi‡ disagrees with the views of Pfaff and agrees with those of the writer that dolomite is formed in shallow water. He instances the case of the calcareous nodules with dolomite cement dredged from the Seine Bank N.E. of Madeira at a depth of 150 meters. He argues that the dolomitization of these nodules took place in shallow waters near the surface, and that the bank has since then subsided, since at the present depth not only is dolomitization not in progress, but solution and disintegration of the nodules is occurring.

Van Tuyl§ tried the effect of known concentrates of  $MgCl_2$  and  $MgSO_4$  and of mixtures of the salts both with and without the presence of NaCl on powdered aragonite. Tested after six months and again after three years the results were negative. Attempts made by Van Tuyl to obtain dolomite as a direct chemical precipitate by evaporating for a month solutions of the bicarbonate of calcium and magnesium in molecular equivalent proportions, resulted in the separate precipitation, first of  $CaCO_3$  and later of  $MgCO_3$ . Even when the solution was inoculated with a crystal of dolomite the results were negative.

A careful consideration of the results of these experimental investigations leads the writer to agree with the conclusions of

\* G. Linck, *Moustsber Deutsch. Geol. Ges.*, pp. 230–241, 1909.

† Meigen, *op. cit.*

‡ Phillipi, *Neues Jahrb.*, Festband, pp. 397–445, 1907.

§ F. Van Tuyl, *op. cit.*

Van Tuyl.\* “Dolomite has been frequently prepared artificially under conditions of high temperature and high pressure or both but it has been produced in the laboratory at ordinary temperature and pressure only in rare instances and then in minute amounts and under conditions which doubtfully operate in nature, at least on a large scale. It must be conceded then that these experiments furnish little evidence as to the actual conditions obtaining when extensive beds of dolomite are formed naturally.”

*The chemical precipitate hypothesis of the origin of dolomite.*

As pointed out by Van Tuyl† many geologists have advocated the view that dolomite is a direct chemical precipitate, including Boué, Bertram-Geslin, Coquand, Zirkel, Fournet, Loretz, Forchammer, Hunt, Vogt, Daly, Linck, and Suess.

Some of these writers have been led to this conclusion by the existence of fine-grained structureless dolomites apparently devoid of organisms. This conclusion may be partially correct in the case of certain dolomites formed in restricted seas under conditions of concentration and this view may apply to the formation of parts of the magnesian limestone of the North of England, to parts of the Raibl dolomites in the Tyrol‡ and some dolomite-bearing rocks in the Triassic rocks of Britain.

Dr. Cullis,§ for instance, has explained the presence of minute rhombohedra of dolomite in some of the Keuper marls of Britain as being due to direct chemical precipitation.

Modern work on the limestones and dolomites of coral islands has shown however|| “that fine grained structureless dolomites occur among reef limestones, and have arisen by complete recrystallization and metasomatic alteration of limestones originally composed of calcareous organisms.”

Zirkel’s¶ observations that crystals of dolomite occurring in veins and druses indicate its possible chemical deposition on a larger scale in nature is not borne out by the detailed examination of coral island limestones made by Dr. Cullis\*\* and the writer,†† who found at Funafuti and among upraised coral limestones respectively that while primary deposition of dolomite occurs, it appears to be limited to the formation of small quantities of dolomite occurring as rhombohedra lining calcite crystals in cavities in the limestone or as occasional layers alter-

\* Op. cit.

† Op. cit.

‡ Skeats, op. cit.

§ Cullis, Rep. Brit. Asso., 1907, pp. 506-507.

|| Skeats, Bull. Mus. Comp. Zool., Harvard 1903; Cullis, Funafuti Reports, London 1904.

¶ Zirkel’s Lehrbuch der Petrographie, 2nd ed., vol. ii, p. 503.

\*\* Op. cit.

†† Op. cit.

ning with calcite in certain stalagmitic or agate-like deposits lining cavities in certain parts of the reef limestones.

We may conclude then that our present knowledge suggests that direct chemical precipitation of dolomite in nature, while known, is of restricted occurrence, and of limited geological significance.

*The Clastic Theory of Dolomite Formation.*

Lesler, Phillipi, and Grabau, among others, have suggested that certain dolomites represent either mechanical sediments derived from an older dolomite or from the residuum of limestones low in magnesia. No claim, however, is put forward that this method of formation is in any way widespread and the first hypothesis necessarily presupposes the existence of older dolomites from which later clastic deposits of similar composition could be formed.

*The formation of dolomite by differential leaching of slightly magnesian limestones in carbonated water.*

This hypothesis is based on the observation that in slightly magnesian limestones water containing  $\text{CO}_2$  will dissolve calcium carbonate while magnesium carbonate is only slightly affected. The solubility of calcium carbonate in sea water is very small and has been variously estimated at from 1 in 10,000 to 1 in 136,000. In sea water containing  $\text{CO}_2$  in solution the solubility, no doubt, is much greater. Bischoff's and Hardman's experiments show that, when powdered slightly, magnesian limestone is attacked by water saturated with  $\text{CO}_2$ ; at atmospheric pressure the calcium carbonate is readily dissolved, and very little of the magnesium carbonate goes into solution.

This process of leaching of slightly magnesian limestones may be pictured as occurring either under subaerial or under submarine conditions.

Grandjean\* in 1844 appears to have been the first to suggest subaerial leaching as a method for the formation of dolomite, and utilized this theory to explain the production of the dolomites of the Lahn district. Hardman,† following Bischoff, later accepted this process after experimental tests, to explain the origin of the dolomites of the Carboniferous limestone of Ireland. Hall and Sardesen‡ adopted the same view with regard to the origin of the Lower Magnesian series of the Upper Mississippi Valley. Hagboni,§ however, regards surface

\* Grandjean, Neues Jahrb., 1844, p. 543.

† Hardman, Proc. R. Irish Acad. Science (2), ii, p. 705. 1877.

‡ Hall and Sardesen, Bull. Geol. Soc. Amer., vi, 167, 1895.

§ Hägboni, Neues Jahrb., 1894, i, p. 262.

leaching as of minor importance, and emphasizes the effects of marine leaching. He has studied the marine marls derived from the Silurian limestones of Bothnia, and deposited in a southerly direction. Analyses show that as one goes further from the Silurian source, the composition of the marls progressively changes in two ways. Firstly, it is noticed that the percentage of carbonates to argillaceous matter steadily falls in a southerly direction, but in addition, when the carbonates are analyzed it is found that the proportion of magnesium to calcium carbonates steadily rises in the material deposited further and further from the parent source. This result is attributed to the greater solubility of calcium carbonate as compared with magnesium carbonate under the conditions of marine leaching in carbonated sea water.

Professor Judd\* accepted this hypothesis of marine leaching in regard to the upper part of the Funafuti bore, where at the surface the limestone contains only about 2-3 per cent  $MgCO_3$ , while at 15 feet below the surface, the  $MgCO_3$  percentage has risen to over 16. Professor Judd believed that this increase in  $MgCO_3$  was not due to the introduction of  $MgCO_3$  from the sea water, but to the removal of  $CaCO_3$  by leaching in carbonated sea water.

In discussing the validity of this hypothesis of the formation of dolomite by differential leaching of the two carbonates it is important to realize that the normal fresh limestone composed of calcareous organisms, such as a coral limestone, ordinarily contains not more than about 1 per cent of  $MgCO_3$ . The author† has pointed out that if the original limestone contains 1 per cent of  $MgCO_3$  and assuming that only the  $CaCO_3$  is dissolved by carbonated water, 80 per cent of the original rock must be removed by solution before the  $MgCO_3$  of the remainder reaches 5 per cent, 90 per cent must be dissolved before it reaches 10 per cent, and over 93 per cent before the  $MgCO_3$  reaches 16 per cent. That is to say, long before the rock is completely dolomitized it must be reduced to a quite structureless mass, and all traces of organisms must necessarily disappear. This result appears to have been overlooked by the authorities quoted above who have involved the leaching hypothesis to account for the formation of dolomites.

While it is true that the process of dolomitization tends to obliterate the organisms formerly present in a limestone, traces of their outlines in undisturbed condition can usually be seen under the microscope, and in many of the dolomites of the Carboniferous limestone in Britain and Ireland traces and casts of organisms are commonly to be seen either in the mass or

\* Judd, Funafuti Report, London, 1904, p. 384.

† Skeats, Q. J. G. S., lxi, 132, 1905.

under the microscope. Such dolomites clearly could not have originated by the process of differential leaching.

In the case of recent coral limestones the author\* has shown by chemical analysis that specimens from the elevated fringing reefs at Christmas Island, Niue, and elsewhere contain from 8-13 per cent of  $MgCO_3$ , but shown no sign of dolomite. Further, the limestones appear fresh, one contains up to 1.5 per cent of organic matter still remaining and the organisms are beautifully preserved. There is therefore no sign of differential leaching having taken place; on the contrary, microscopic examination shows that there has been notable deposition in cavities of the rock of secondary carbonate, sometimes in the form of aragonite, sometimes of calcite. Precisely the same evidence is to be noted in that part of the Funafuti bore, between 15 and 25 feet from the surface, where the  $MgCO_3$  reaches 16 per cent, and for which high percentage of  $MgCO_3$  Prof. Judd advanced the explanation of differential leaching.

The writer is quite sure that if Prof. Judd had been as familiar with the mineralogical evidence as was Dr. Cullis, who described the mineralogical changes in the Funafuti bore, he would not have put forward the leaching hypothesis. Dr. Cullis's descriptions and drawings from this part of the bore shows clearly that, however the  $MgCO_3$  may be present, no dolomite occurs, the organisms are wonderfully fresh, over 1 per cent of organic matter is present, and a considerable amount of secondary carbonate having the form of calcite and aragonite has been deposited in the interstices of the coral limestone.

It is clear, therefore, whatever be the explanation for the presence of 10-16 per cent of  $MgCO_3$  in certain recent coral limestones, it is not due to the process of selective leaching by carbonate water and that a general theory of dolomitization based on the process of differential leaching is opposed to the known facts.

#### *Dolomitization by Metasomatic Replacement.*

The presence of corals and other organisms replaced by dolomite in many dolomitized limestones has for long made it clear to field geologists that replacement of calcium carbonate by magnesium carbonate has occurred in many limestones. That this is the dominant process in regional dolomitization has been made clearer by the detailed microscopic examination of limestones, especially coral limestones, in recent years. Various stages in the process have been described by the author† and by Dr. Cullis.‡ The Funafuti evidence, apart from the

\* Skeats, Bull. Mus. Comp. Zool. Harvard, 1903; Q. J. G. S., lxi, 132, 1905.

† Skeats, op. cit.

‡ Cullis, op. cit.

evidence of limestones from unpraised coral islands, has made it clear that in such cases of regional dolomitization the process has gone on beneath the sea, and the only possible source of magnesium consists in the salts in solution in sea water. In the case of certain coral limestones such as those between 15 and 25 feet in the Fnnafuti bore, and others from elevated fringing reefs at Christmas Island, Niue, etc., it is clear that  $MgCO_3$  has replaced  $CaCO_3$ , up to 10–16 per cent, without the production of definite crystals of dolomite. The shapes of aragonite and calcite have persisted, in spite of the introduction of  $MgCO_3$ . Microscopical examination of limestones richer in magnesia has shown that when dolomite crystals are developed the process usually proceeds on definite lines. The structureless matrix of the limestone is dolomitized before the larger crystals or the organisms.

The organisms are attacked in a definite order, those whose constitution was originally aragonite such as the corals, Halimeda, and gastropods being dolomitized before organisms built of calcite, such as most of the foraminifera, Lithothamnion, echinoderm spines, etc., while among the organisms built of calcite, those like Lithothamnion in which a considerable amount of organic matter is present are usually dolomitized before organisms such as echinoderm spines in which little or no organic matter is present. The process of dolomitization is therefore selective, and most of the stages in the introduction of  $MgCO_3$  and of replacement of  $CaCO_3$  by dolomite can be followed in a series of rock sections of limestones in which the change has taken place. Ultimately a dolomite may be formed which is quite structureless, in which all traces of organisms have disappeared, but that they were formerly present is reasonably certain from the study of the stages less complete where traces of the outlines of the organisms remain as "dirt lines" or "ghosts" defining their boundaries. No one who has made a microscopic examination of such dolomitic limestones can doubt that the change from a non-magnesian limestone to a dolomite has taken place by a gradual introduction of magnesian salts from the sea water involving a corresponding solution and removal of  $CaCO_3$ .

Furthermore, since in the formation of these marine limestones the sea is the only possible source of magnesium, it follows that the dolomitization of the limestone followed so closely on its formation as to be almost contemporaneous with it in a geological sense.

In this respect we may distinguish between these regional "contemporaneous" dolomites and the local or subsequent dolomites occurring generally along joints or mineral veins which have been formed by the passage of magnesian solutions along



definite channels, long after the formation of the limestone, and usually after it has been elevated above sea level.

The important questions as to the distribution of dolomites among geologically recent coral limestones and the conditions under which replacement can take place beneath the sea remain for discussion.

*The distribution of dolomites in coral islands.*

*The Evidence of Funafuti.*—When Dr. Cullis made a mineralogical and chemical examination of the core of the main boring at Funafuti, it was at first confined to the upper 698 feet from the surface, the depth reached by Professor David's Expedition.

In this part of the bore the mineral distribution appeared to be regular, aragonite being practically limited in its occurrence to the upper part above 150 feet, calcite occurring alone between the lower limit of aragonite and a depth of about 635 feet, while below this depth to the bottom of this part of the core at 698 feet, dolomite was represented almost to the exclusion of calcite. It appeared at that time as if there existed three zones of aragonite, calcite, and dolomite, respectively, whose formation and limits could most easily be explained as being conditioned by depth beneath the sea surface, that is, by pressure.

But even at that time, before the deeper cores were available for examination the idea that dolomitization was produced only at considerable depth and considerable pressure, was rendered doubtful by the fact that in the upper part of the aragonite zone, at depths of 15 to 25 feet only below the top of the bore, although the mineral dolomite was not present yet introduction of  $MgCO_3$  and replacement of  $CaCO_3$ , had gone on to the extent of 10 to 16 per cent. This relatively high magnesian content in the coral limestone near the surface was not a localized and sporadic occurrence but was evidently widespread beneath the surface of the atoll, since in both of the shallow bores put down by Prof. Sollas, one of which is a mile and a quarter from the main boring, a similar rise in the magnesian content of the coral limestones was found to occur at about the same depth. When the cores from the deeper part of the boring between 698 feet and the bottom at 1114 feet, came to be examined mineralogically and chemically, it became clear that the apparently simple relations of the upper part of the bore did not continue indefinitely. The downward continuation of rocks consisting entirely of dolomite below 698 feet was interrupted between the depths of 820 and 875 feet, and again between 1050 and 1070 feet. At 826 feet, a rock containing only 4.83 per cent of  $MgCO_3$  was met with while

at 1061 feet a dolomitic limestone occurred containing only 26.63 per cent of  $MgCO_3$ .

Dr. Cullis found by microscopic examination that in each of these lower parts of the core where the magnesian content was noticeably lower than above or below them, that the rocks at these places had been partially or completely dolomitized, but subsequently their numerous cavities had been lined or filled with later deposited layers, mainly of calcite but to some extent of dolomite, thereby reducing their magnesian content to the values found.\*

#### *The evidence from upraised coral islands.*

While the examination of the Funafuti bore cores was in progress, the author was examining by the same methods, limestones from various upraised coral islands in the Pacific and Indian Oceans collected by Prof. Agassiz, E. C. Andrews, Professor David, and Dr. C. W. Andrews. Some limestones were found to consist mainly of aragonite, others of calcite, and others of dolomite. Reference has been made above to the fact that from some of the elevated fringing reefs of Christmas Island, of Niue and elsewhere aragonitic limestones, as in the shallow part of the Funafuti bore, were found to contain from 8 to 13 per cent of  $MgCO_3$  without any development of the mineral dolomite. In the case of those upraised coral islands in which dolomite was found, its zonal distribution measured by height above sea level at which it occurred appeared at first to be quite capricious. The limestones of certain of the islands have been dolomitized from top to bottom. Ngillangillah and Vatu Vara belong to this class, and Yathala and Kambara may also belong here. In several of the islands no dolomite was found. Niue, Vavan, Tongatabu, Niau, and Guam are of this type. Non-magnesian limestones are associated with dolomitic limestones in Christmas Island, Mango, Namuka, and Eva.

In these, dolomitization may recur at two or more horizons. This is the case in Namuka, Christmas Island, and Mango.

#### *The shallow water origin of dolomite.*

Certain considerations in the distribution of dolomite in coral limestones point strongly and the writer thinks unmistakably to its origin in shallow water. At Mango, Vatu Vara, Ngillangillah, and Christmas Island, some of the *most elevated* of the limestones have been dolomitized. This implies that such limestones were the youngest and the only movements of which we have evidence since their formation are movements

\* Cullis, Funafuti Report, London 1904, p. 410, fig. 44; p. 414, fig. 48.

of elevation which raised them above the sea, the source of their magnesian content. The evidence at Christmas Island is very significant. Dr. Andrews\* refers to the "thick beds of nearly pure phosphate of lime, which cap several of the higher hills. This substance is probably derived from ancient (? Pliocene) guano beds formed on the low islets which existed before the first elevation of the island and is the insoluble residue of beds of limestone altered by this guano." The significance of this observation lies in the fact that immediately below the beds of phosphate and in sharp contact with it, analyses by the writer showed that the limestone had been completely dolomitized. The inference is clear that this dolomitization took place in very shallow water at the time when low islets rose above the lagoon, and formed the resting place for birds to deposit guano. This view of the shallow water origin of dolomite receives support also from the occurrence of dolomitic limestones from the raised island cliffs and terraces at Christmas Island and Eva which are probably, but not quite certainly, raised fringing reefs.

In this connection it is significant as recorded by Walther† and Hume,‡ that in places, the upper raised fringing reefs of the Red Sea have been dolomitized. The only movement known to have affected this reef which was formed just below sea level, is one of elevation. Its dolomitization must therefore have occurred under very shallow water conditions. The writer§ believes he was the first to develop this hypothesis of a very shallow water origin for "contemporaneous" or regional dolomites. This view was amplified by him in a subsequent paper,|| and since then has been adopted by several geologists. The hypothesis can be further tested by considering the distribution of "contemporaneous" or "regional" dolomitization among older limestones, and noting whether the parts which are dolomitized are specially associated with shallow water conditions as indicated by fossil content or special structures such as false bedding, oolitic structure, conglomerates, etc.

*The association of dolomites in older limestones with independent evidence of shallow water conditions.*

The chalk is a special limestone now generally believed to have been formed at moderate depths. It is nearly everywhere a fairly pure limestone with low content of  $MgCO_3$ . The one

\* C. W. Andrews, Monograph of Christmas Island, p. 271.

† J. Walther, Abhandl. Math. Phys. K. Sächs. Ges. Wiss., xiv, p. 494.

‡ W. F. Hume, The Rift Valleys of E. Sinai, Int. Geol. Cong. Paris, 1900, pp. 32-40.

§ E. W. Skeats, Bull. Mus. Comp. Zool., Harvard, vol. xiii, 125, 1903.

|| E. W. Skeats, Q. J. G. S., lxi, pp. 131-137, 1905.

exception to this condition which the writer can find in the literature of the subject is in the island of Faxoe off the Danish coast. This has been the subject of papers by F. Johnstrup,\* translated into German by A. Stelzner, and by E. M. Noerregaard.†

In these papers it is shown that the Faxoe chalk, of Danian age, is of specially shallow water origin since it is in part composed of coral reefs and of bryozoan limestones and it is stated that the coral reefs are in part dolomitized. That is to say dolomitization of the chalk is only recorded where the independent testimony of the organisms shows that the chalk has been formed in shallow water and not, as is customary, in water of moderate depth. In the Keuper marls of Britain, a rock clearly of shallow water origin, Cullis‡ has described the occurrence of minute rhombs of dolomite. In the West of England Sir A. Geikie§ states, "At the base of the Keuper series in the region of the Mendip hills a remarkable littoral breccia or conglomerate occurs. . . . Its matrix being sometimes dolomitic it has been called the Dolomite conglomerate. . . . It represents the shore deposits of the Trias salt lake or inland sea." Perhaps the Carboniferous Limestone of the British Isles provides the best authenticated illustrations of "contemporaneous" dolomites associated with independent evidence of shallow water conditions.

References to some of these were made in a discussion on the author's paper to the Geol. Soc. of London, 1905. E. L. Dixon referred to the evidence that some dolomite in the Carboniferous Limestones of Pembrokeshire and Caermarthenshire is associated with shallow water conditions. Prof. Watts drew attention to the probably shallow water dolomites near Charnwood Forest, and to the base of the Carboniferous Limestone in Ireland, frequently either a dolomite or a conglomerate or grit cemented by dolomite.

The writer remembers asking the late Dr. Vaughan, who did such valuable paleontological and field work in the zoning of the Carboniferous Limestone in the West of England, during the course of his work, whether he found that the fossil evidence showed specially shallow water conditions where the limestone had been dolomitized. He replied that his results definitely supported that conclusion but expressed surprise that it should be known as his results were still unpublished.

Frequent references will be found in his papers as well as in those of other writers like Sibly and Dixon among the same

\* F. Johnstrup, translation by A. Stelzner, *Neues Jahrb.*, xxxviii, 542-575, 867.

† E. M. Noerregaard, *Meddel. dansk. Geol. Forch.* No. 10, 1904, pp. 85-106.

‡ C. G. Cullis, *Rep. Brit. Assoc.*, 1907, pp. 506-507.

§ A. Geikie, *Text Book of Geology*, 1903, vol. ii, pp. 1092-1093.

rock series to the close association of dolomites with rocks showing oolitic structure. While some oolites have been claimed to be of æolian origin most examples are clearly of very shallow marine origin and by many geologists are regarded as having been formed between high and low tide levels. From these writings the following remarks are taken :

"The\* dolomitized rocks (Lower *Syringothyris* Zone C.) clearly were originally crinoidal and foraminiferal limestones . . . . . As regards the conditions of formation of these dolomites, the facts appear to be in conformity with the now generally accepted view . . . . . that they originated by the practically contemporaneous alteration of limestone under shallow water conditions. It is a well established fact that shallowing of the water of the Carboniferous Limestone Sea took place throughout the main part of the Southwestern Province in Middle Avonian times ; and the occurrence of these dolomites on the same general horizon as the shallow water beds elsewhere, is evidence that the shallowing extended to the Mendip area." Dixon and Vaughan,† referring to the characters of the S<sub>2</sub> or "*modiola*" phase of the Carboniferous Limestone of the Gower Peninsula in South Wales, remark :—

"Contemporaneous erosion is evidenced in some of the oolites by irregular fragments, also of oolite, measuring up to 2 feet in length ; in such beds, dolomite, if present, is more abundant in the matrix than in the fragments."

Sibly,‡ referring to the Carboniferous Limestone of the West of England, states—"In the Bristol area shallow water prevailed during the greater part of *Syringothyris* time, as evidenced by the extensive development of pure oolite, shales and dolomites in the *Syringothyris* zone . . . . . In the Mendip area the *Syringothyris* zone, which is considerably thicker than in the equivalent part of the Bristol zone, consists entirely of fossiliferous limestone. The Weston-Super-Mare district between the Bristol and Mendip areas exhibits an intermediate type of development of the *Syringothyris* zone. The lowest zone is appreciably dolomitized, and is succeeded by a thick band of pure oolite . . . . ."

Dixon,§ describing the dolomitization of the Carboniferous Limestone of the Gower Peninsula, remarks as follows :—

"Laminosa dolomites occur in the Bristol district, in Gower, and West of Tenby, and throughout this long extent dolomites replace a variety of limestones . . . . . Further South, however, in the Mendips and South of Tenby, limestones on the

\* Reynolds and Vaughan, Q. J. G. S., lxxvii, 348-349, 1911.

† Dixon and Vaughan, Q. J. G. S., lxxvii, 488, 1911.

‡ Sibly, Q. J. G. S., lxxii, 356, 1906.

§ Dixon, Swansea, Memoir, No. 247, Geol. Sur. of Gt. Britain, 1907, pp. 15-17.

same horizon are much less dolomitized but it will be remembered that these onterops are *further removed from the shore line of the Carboniferous limestone sea.*"

Later, on p. 17, he states, "Both groups of strata in which contemporaneous dolomite occurs appear to have been formed in shallow water. The Mumbles Head Beds throughout a large tract of country contain a thin coal and marl with underclay which can only have been formed in the shallowest water, while the "laminosa" dolomites may be inferred to have had a shallow water origin from the fact that they are represented at Pendine by a conglomerate which there is reason to believe was actually a beach deposit."

Dr. A. Strahan\* has described the lateral passage of a seam of coal into dolomite at the Wirral Colliery in Cheshire. He pictures both coal and dolomite as having been deposited below sea level in quite shallow water.

F. M. Van Tuyl† in a paper entitled "A Contribution to the oolite problem" describes the sequence of the basal Ordovician beds of northeastern Iowa as follows:—

Prairie du Chien Dolomite  
Oolite  
Saint Croix Sandstone

and states that the oolite is in places dolomitic, in places siliceous.

Steidtmann‡ in his discussion of the dolomite problem states: "Many dolomites have very obvious earmarks of shallow water deposition, such as ripple marks, cross bedding, and interstratification with coarse sands."

The above references to the occurrence of dolomites in the chalk, the Trias, the Carboniferous and the Ordovician rocks of different areas show that in each case there is independent evidence of shallow water conditions. These consist of changes in the organisms as in the chalk and Carboniferous Limestone, the association with conglomerates as in the Trias and the Carboniferous limestone, the passage into a coal seam as in the Carboniferous, and the association with oolitic structure as in the Carboniferous limestone and the basal Ordovician series.

It may be stated therefore that the modes of occurrence of dolomite among the older sediments, so far as known to the writer, yield powerful evidence in support of the hypothesis of the shallow water origin of dolomite originally developed by the writer from a study of its distribution among recent and unraised coral limestones.

\* A. Strahan, Q. J. G. S., lvii, 297-306, 1901.

† F. M. Van Tuyl, Journ. Geology, xxiv, 794, 1916.

‡ E. Steidtmann, Jour. Geology, xix, 338, 1911.

*Chemical explanation of shallow water origin of dolomites.*

The author\* has in a previous paper attempted to suggest an explanation of the shallow water origin of dolomite based upon the varying solubilities of calcium and magnesium carbonates, respectively, in water containing  $\text{CO}_2$  in solution. There is considerable experimental evidence to show that under atmospheric pressure calcium carbonate is more soluble than magnesium carbonate in carbonated water. However, under increased pressure the solvent action of carbon dioxide on the magnesium and calcium carbonates is reversed.†

Based upon this principle a process was for some time employed for the commercial formation of Epsom salts by the extraction of nearly pure magnesian salts from dolomite. This consisted in subjecting the rock when finely ground and mixed with water, to the action of  $\text{CO}_2$  under a pressure of about *four atmospheres*. Under these conditions the magnesian carbonate passed readily into solution while very little calcium carbonate was taken up.

As at atmospheric pressure calcium carbonate is more soluble than magnesium carbonate in carbonated water, while under four atmospheres pressure the reverse conditions obtain, it should follow that at some pressure between 1 and 4 atmospheres carbonated water should dissolve the two carbonates in molecular proportions. At such a pressure, under conditions of saturation, dolomite may be deposited, and such a pressure may well afford the most favorable conditions for the replacement of calcium carbonate by magnesium carbonate up to 45.65 per cent, the composition of dolomite.

In the sea, especially where organic decay is going on round coral reefs, carbon dioxide will be present and such a pressure as indicated above will occur not far below the surface.

The zone in the Funafuti bore between 15 and 30 feet below the surface may very well represent this favorable zone since in all three borings at about this level, while no dolomite crystals have developed,  $\text{MgCO}_3$  is present in the coral limestones up to about 16 per cent. It seems probable therefore that the limestones at this depth are now passing through an early stage of dolomitization.

Since it is notorious that all shallow water limestones do not become dolomitized the question arises as to what circumstances may retard or facilitate the process. In the present state of our knowledge it is only possible to suggest one or two factors which may operate in nature.

The activity of bacteria‡ has been suggested by some writers as influencing the formation of dolomite. Time certainly is an important factor. The process of replacement is probably slow

\* E. W. Skeats, Q. J. G. S., lxi, 135, 1905.

† Dingl. Polyt. Jour., cix, 467; abstract, Chem. Soc. Jour., xii, 96.

‡ Walther, Geschichte der Erde und des Lebens, p. 90.

and if the rate of subsidence, of a coral limestone, for instance, exceeds a given value, little or no replacement may take place, since the limestone will then subside too rapidly below the favorable zone.

Porosity too may well be an important factor in the process since a porous limestone will be readily permeated by sea water and become dolomitized if other conditions are favorable while a relatively dense and impervious limestone may remain undolomitized.

*Relation of the distribution of dolomite to the formation of the atoll of Funafuti.*

The author regards the evidence of dolomitization of fringing reefs of coral islands, the occurrence of dolomite immediately below phosphate beds, on the hill tops of Christmas Island, the rise in the magnesian content of the limestones of the Funafuti bore between 15 and 30 feet, as definite and strong evidence of the shallow water origin of dolomite in coral islands. It is claimed that this view is consistent with the chemical evidence quoted above of the reversal of the solubilities of calcium and magnesium carbonates in carbonated water between the pressures of one and four atmospheres. In addition, the evidence, cited above from more ancient dolomites showing their intimate associations with independent evidence of shallow water such as fossils, current bedding, conglomerates, and oolitic structures, is so consistent and so in accordance with the evidence from modern coral limestones, that the author takes the view that wherever a "contemporaneous" or regional dolomite is found to occur, it may be regarded as having originated in shallow water. If this be granted, it follows that such upraised coral islands, like Ngillangillahi now 510 feet high, and Vatu Vara now 1030 feet high, which are dolomitized from top to bottom, must have originally been formed of shallow water limestones accumulated by subsidence to at least 500 and 1000 feet respectively before elevation set in. The atoll of Funafuti whose surface is practically at sea level must also have been built up of shallow water limestones accumulated during subsidence, which must have amounted to about 1100 feet at least since the cores from 635 feet to 1114 feet consist entirely of limestones which have passed through the process of dolomitization.

In the discussion, therefore, of this chemical and mineralogical problem, apparently so remote, on first consideration, from the question of the origin of atolls, there is brought forward independent testimony in favor of the validity of Darwin's theory of subsidence for the formation of the atoll of Funafuti as well as of several upraised coral islands. This testimony is advanced with the more confidence since it is in agreement with the evidence of the organisms and of structures set out in a preceding paper.



ART. XIV.—*On the Etching Figures of the Dihexagonal Alternating Type*; by ARTHUR P. HONESS.*Introduction.*

While the dihexagonal alternating crystal type includes a variety of mineral species, calcite, due to its abundance of forms, is perhaps more representative than any other. For this reason the etchings of calcite form the basis of this investigation; and, although some work has been done on the rhombohedrons of this species, by other authors, an extended study of calcite, with a view to the correlation of the results arrived at geometrically and those obtained by the etch method, has not hitherto been made. Consequently, a more detailed examination of the etchings of this important mineral, and their relation to the symmetry content, may be of some interest.

Tschermak<sup>1</sup> in his article, "Ueber die Isomorphie der rhomboëdrischen Carbonates und des Natrium-salpeters," gives the result of his investigation of several of the more common isomorphous carbonates.

The results upon calcite are in perfect accordance with what is expected,—HCl produced curved triangular forms, with the point turned upward, revealing a vertical plane of symmetry. With H<sub>2</sub>SO<sub>4</sub> he obtained rhombic forms identical in form and position with the rhombohedral face itself, also symmetrical with regard to a vertical plane.

For the purpose of comparison Tschermak etched magnesite, siderite, rhodochrosite and sodium nitrate, but was unable to secure suitable smithsonite crystals for this purpose.

Magnesite was etched with HCl, and very dilute H<sub>2</sub>SO<sub>4</sub>, two kinds of figures resulting. Most of them were simple symmetrical triangular forms, but a few asymmetric figures were noticed. Thinking the iron content of his Zillertal crystals might be the cause of this variation, he obtained pure magnesite from Snarum, and etched this, only to obtain similar results; explained by the fact that the crystals were mixed: in part rhombohedral, in part tetartohedral.

<sup>1</sup> Min. petr. Mitt., 4, 99, 1881.

Siderite reveals the same peculiarities; occasional asymmetric forms accompanied by many symmetrical ones. Baumhauer<sup>2</sup> observed only monosymmetrical forms, Dilute HCl produced figures very similar to magnesite, but which do not resemble so closely the siderite figures obtained by the writer, which, although long and monosymmetrical and pointed, are bounded by two long curved sides which are absent in Tschermak's. According to Tschermak, the number of asymmetric forms occurring is greater than that on magnesite, and many are enantiomorphic. H<sub>2</sub>SO<sub>4</sub> produced triangular forms, the most of which are monosymmetrical,—a few asymmetric, revealing a complex crystal, or at least a doubtful result due probably to a rhombohedral siderite containing a few tetartohedral particles.

Rhodochrosite, according to Tschermak (*Min.-Petr.*, p. 116), gave asymmetrical figures which does not accord in the least with the results obtained by the writer (see photographs).

While the figures produced on the various carbonates differ more or less, as also obtained by the writer, Tschermak in his investigation observed a greater similarity between calcite and sodium nitrate and between magnesite and siderite.

Otto Meyer<sup>3</sup> also investigated Iceland spar, obtaining well-defined figures with HCl and acetic acid. The HCl figures are very similar to those described by Baumhauer but the acetic acid forms are five-sided, with the sharp angle turned upward; a mixture of the two acids gave different results, some of the figures being semicircular, others slightly oval with four and five bounding faces.

J. S. Pratt<sup>4</sup> observed etch figures on the base of Montana sapphires. The figures are very perfect, and although they show different forms they reveal the dihexagonal alternating symmetry. The most common form is the simple triangular depression, bounded by three planes, the intersections of which with the base are straight well-defined lines. The rhombohedral depressions were measured and the faces calculated as (10 $\bar{1}$ 7).

Occasionally these triangular forms possess a fourth face of varying size, lying at the bottom; the larger fig-

<sup>2</sup> *Berichte der deutsch. Chem. Ges.*, 1872, p. 857.

<sup>3</sup> *Jb. Min.*, 1, 74, 1883.

<sup>4</sup> *This Journal*, 4, 424, 1897.

ures often reveal small triangular pits implanted in them, producing a figure within a figure, with the same shape and orientation. In many cases the outer contour is curved, this variety of figure usually being the deeper one.

Bauer<sup>5</sup> also observed similar figures upon the base of Burma rubies.

#### *Artificial Etchings.*

The writer in his investigation of the etch figures of this type selected five of the isomorphous carbonates, calcite, magnesite, siderite, rhodochrosite and smithsonite. These were etched and studied with a view to comparing and contrasting the solubilities and etchings produced under similar conditions. Unfortunately calcite is the only one of the five minerals which offered a variety of forms for study. Consequently the work done in this connection deals principally with the behavior of the unit rhombohedrons when acted upon by acids, the other forms being so very rare, or so corroded, as to be useless for etching.

The calcite crystals used were taken from beautiful crystal clusters collected at Cumberland, England; the crystals are very bright, and transparent, varying from 5mm. to nearly an inch in length; they are attached by the base, and terminate by either  $r$  ( $10\bar{1}1$ ) or  $e$  ( $\bar{1}101$ ) and the scalenohedron  $v$  ( $21\bar{3}1$ ); two prisms,  $10\bar{1}0$  and  $11\bar{2}0$ , occur, the  $10\bar{1}0$  form being much the larger;  $11\bar{2}0$  is deeply grooved parallel to its intersection with the scalenohedron. These crystals were used for etching the unit prism and the scalenohedron principally, as these forms were more perfect. For the base and second-order prism, small transparent crystals from Patterdale, Cumberland, England were used, which showed only the two forms mentioned. A cleavage piece of Iceland spar gave the etch figures on the unit rhombohedron. The remaining two forms, the hexagonal pyramid and the dihexagonal prism, due to rarity, could not be obtained and for that reason were necessarily omitted in this work. Cleavage pieces of a very clear magnesite, locally unknown, were found very desirable for etching.

Siderate crystals were not so easily obtained, although several fine specimens from the museum were examined.

<sup>5</sup> *Jb. Min.*, p. 209, 1896.

and in fact etched, but the rhombohedral crystals, whose surfaces are curved, did not reveal well-defined etchings, and consequently were rejected. The best results were obtained on brown rhombohedral cleavage plates from Greenland, which, if cleaved sufficiently thin could be readily examined under the microscope.

The smithsonite used for this purpose was obtained from Altenberg, Saxony; it occurs as a crust of exceedingly small transparent rhombohedral crystals, possessing a high luster and fairly smooth faces. The rhombohedral faces are decidedly the better although the unit prism did occur on several, sufficiently developed, as to permit of etching.

Rhodochrosite also could be obtained only in rhombohedral form, so that brilliant cleavage fragments from Alicante, near Leadville, Colorado were used for the purpose of etching.

From the foregoing, it will be readily understood that the chief difficulty in the comparison of this isomorphous series of carbonates lies in the rarity of forms desired, and as the only available material did not possess the necessary variety, a comparison of the one form only must of necessity be more or less incomplete. Nevertheless the results obtained are interesting, and may be accepted as a minor contribution to the vast literature on etch figures.

The Cumberland calcite described above, upon immersion in 10 percent dil. HCl for a period of a few seconds, revealed a great difference in the solubility of the various faces. The unit rhombohedron was the first form to etch, followed immediately by the unit prism; the second order prism, when present, etched later; but the scalenohedron, strangely enough, did not etch at all. One could hardly say that the face had not been acted upon by the acid, because it was very apparent that the face had undergone a change, as the edges were rounded and the whole face appeared glassy but not revealing the slightest indication of an etch pit. Repeated immersions produced good figures upon the rhombohedron and the unit prism, also upon the second-order prism, but still the scalenohedron maintained its glassy luster and did not decrease much in size, and only disappeared through the action of the solvent, after the other forms had been completely corroded and eaten away.

Large well-defined etchings were obtained upon the unit prism after immersion of 10 seconds in warm 10 percent HCl (see fig. 1). The figures are bounded by four faces, two lateral, one large basal plane, and a small face at one end. The figures are quite unique in form, differing more or less in the primitive and ultimate stages. In the primitive stage the figures appear as relatively deep pits, from which there extend, above or below as the case may be, but always in the same direction on the same face, a face parallel to  $c$  ever widening as it extends farther and farther from the pit, and at the same time gradually approaching the surface, its intersection with which is barely discernible, and in some cases cannot be seen at all. This face finally becomes the base and the most prominent plane of the mature figure. It is readily recognized as a triangular form lying in the scalenohedron zone and resembling a face of that form. The intersections of this face and the lateral faces of the figure can be easily distinguished under the microscope, consequently the angle at the apex of this basal plane was measured on several figures, large and small, the readings averaging to  $25^{\circ} 35'$ . These measurements were very suggestive, as the average reading seemed to correspond with the facial angle at the apex of the scalenohedron  $v$  ( $21\bar{3}1$ ) which form occurs on the crystal etched. Repeated measurements of the facial angle proved this to be a fact, and that the two readings are almost identical, the face being  $26^{\circ}$  and the figures  $25^{\circ} 35'$ , indicating that the face of the figures is parallel to the actual scalenohedron occurring on the crystal. The two converging edges of these basal planes meet the edge  $10\bar{1}0/21\bar{3}1$  at approximately  $45^{\circ}$  which corresponds to the angle produced by the convergence of the two adjacent edges  $10\bar{1}0/21\bar{3}1$ , placing the lateral bounding planes of the figure in the  $10\bar{1}0/21\bar{3}1$  zone. The plane bounding the smaller end of the figure appeared to be slightly rhomb-shaped, with the large angles turned down to meet the apex of the base. The center of this end face seems to contain a faint groove extending downward, which becomes invisible before it reaches the bottom. Thus the figure in general is much deeper at the narrow end, and is symmetrical with regard to a vertical plane. Figures on adjacent faces are inverted with respect to one another thus revealing the alternating axis of symmetry.

As a further comparison, the unit prism was etched with 10 percent  $\text{HNO}_3$ , which acted upon the crystal in a manner very similar to  $\text{HCl}$ . After immersion for 15 seconds in the acid good figures were obtained (see fig 2); several distinctions, however, are to be made. In the first place, the basal plane, which is so prominent in the  $\text{HCl}$  figures, is much reduced in size; it does not extend completely to the pit of the figure, but the two convergent lines bounding it meet to form the apex at the center of the figure and continue to the opposite end as a groove, coincident with the intersection of the two lateral faces of the figure. The apex angle as measured before varies from  $12^\circ$  to  $14^\circ$ . This is much smaller than the angle of the  $\text{HCl}$  figure, which measured approximately  $25^\circ$ . This face, still triangular, is reduced to such an extent by the development of the two lateral faces, that one may call it the fourth lateral face lying opposite the deeper end of the figure. Its intersection with the crystal face is a straight line more distinct than that observed on the  $\text{HCl}$  etchings. The figures are elongated parallel to  $c$  with the lateral boundaries curved outward, a distinction from the  $\text{HCl}$  figures, which are slightly curved inward or straight. Although the ends of the figures are alike in width, the two faces occupying this position are very different; the one, four-sided, with a slight vertical groove extending downward, descends very abruptly to the deepest part of the figure; the other is an elongated triangle, described above, which descends very gradually to the bottom of the pit. The two lateral faces are decidedly enlarged as compared to the  $\text{HCl}$  figures, and lie in the prism zone. These figures also reveal a vertical plane of symmetry, and an alternating axis  $c$ . The action of  $\text{HNO}_3$  upon the other forms of the crystal was much like  $\text{HCl}$ , the scalenohedron remaining unetched. The figures produced by 10-percent  $\text{HNO}_3$  upon the various faces will be taken up in order.

Another crystal, similar to those etched before, was immersed in hot concentrated citric acid for about five seconds, with good results. The rhombohedron was the first form to etch, the  $11\bar{2}0$  prism immediately after, followed by the scalenohedron; the  $10\bar{1}0$  prism at this stage had not etched, but did show a slight action of the acid in fine striations or grooves extending parallel to the cleav-

age lines. Repeated attempts were not successful in etching the unit prism, which appeared quite glassy and rough, so that a 20-percent cold citric acid was tried, which at first showed no trace of etching, and satisfactory figures were obtained only after an immersion of 20 minutes (see fig. 3). They appear well scattered over the face of the crystal; the primitive and mature figures are very much alike. The more distinct etchings reveal eight sides, and six bounding faces. One end of the figure is very narrow, almost a point, from which the four larger faces extend outward and upward. The three grooves formed by the intersection of these four larger faces appear to meet in a common point, forming triangular faces of the two central and lowermost faces, the apex of which measures approximately  $27^\circ$  very near the angle of the basal form of the HCl figure and apex of the actual scalenohedron face. The narrowest portion of the figure is decidedly the deepest, similar to the HCl figure. Also the narrow end is occupied by a four-sided face, slightly grooved vertically in the center, and dipping abruptly to the pit of the figure. In outline the figures are fan-shaped, and are symmetrical with regard to a vertical plane. The figures of adjacent faces indicate by their relative positions an alternating vertical axis, which is characteristic of the type. Several of the figures possess but six bounding lines but this only indicates an absence of the two small lines at the apex, and does not alter the shape of the figures to any very noticeable degree.

Another solvent was prepared by mixing the HCl and  $\text{HNO}_3$ , used for etching, in a 1:1 mixture. One of the crystals was immersed for about 20 seconds, with fairly good results. The figures produced upon the unit prism  $10\bar{1}0$  are very similar to the  $\text{HNO}_3$  forms, except that they are more elongated with the lateral boundaries less curved. The apex of the triangular basal plane, as in the  $\text{HNO}_3$  figures, measure between  $12^\circ$  to  $14^\circ$ . The primitive forms are not all symmetrical, in fact many of them appear hooked at the narrow end, which is due to unequal development of the lateral planes. As development continues, however, the figures become symmetrical to a vertical plane and reveal by their relative positions an alternating vertical axis.

On the whole, then, four different solvents were used for the purpose of etching the unit prism, and four differ-



FIG. 1  $\times 310$



FIG. 2  $\times 310$



FIG. 3  $\times 310$



FIG. 4  $\times 120$



FIG. 5  $\times 310$

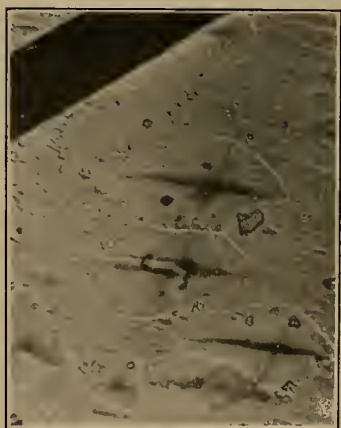


FIG. 6  $\times 310$



ent figures were produced. The etchings produced by the three solvents HCl, HNO<sub>3</sub> and the mixture of the two acids, are very much alike, but the solvent composed of the mixture of the two seems to favor the HNO<sub>3</sub> in the form of the figures. The fourth solvent was citric acid, and this being very unlike the other acids, produced figures which are unique and unlike, in form, any of the preceding figures. However great the difference in the etchings they are alike in that they all reveal a vertical plane of symmetry, and indicate by their relative positions the alternating axis *c*, which corresponds with the calcite type.

*Second Order Prism, 11 $\bar{2}$ 0*—The 11 $\bar{2}$ 0 prism occurring on the scalenohedral crystals from Cumberland, England, was not well developed and too much striated for etching, consequently, simple crystals from Patterdale, Cumberland, which possessed only the second-order prism and the base, were used in the investigation of this form.

10-percent HCl etched the second-order prism and the base after about 20 seconds. The figures of the 11 $\bar{2}$ 0 form were rather slow in developing, but the face was quite readily attacked by the acid, as deep solution lines running parallel to the cleavage lines could be easily distinguished long before the figures had attained the mature stage of development. The grooves are of two kinds: one, very narrow and shallow, and very straight; the other, deep, and broad with edges quite irregular. These elongated depressions are formed by the intergrowth of etch figures, and extend in a diagonal direction (fig. 4). The lighter grooves extend parallel to two of the four edges of the etch figures, and meet the prism edge at an angle of 45°, and on the adjacent face it continues at right angles to its former direction.

The large grooves are also formed by figures, but in this case, solution has continued across the face at right angles to the longer diagonal of the rhombic figures, which can be clearly distinguished in the bottom of the groove. In the other case it will be remembered the solution proceeded in a direction parallel to two sides of the rhombohedron, consequently the elongated depressions vary in size. The deeper groove makes an angle of about 60° with the prism edge, and about 69° with the smaller groove. The rhombohedral cleavage cutting the prism face measures about 45°, so it is probable that the light

groove is due to solution along the cleavage plane, and the direction of the deeper depressions is governed possibly by microscopic striations.

The figures, while they are generally rhombic, vary a little in shape: some of the forms are considerably rounded, while others are quite angular (see fig. 5). The larger angle of the rhomb measures, for an average of eleven readings,  $136^\circ$  and the longer diagonal of the figure extends in a direction approximately  $27^\circ$  with the prism edge. The two longer sides vary but  $7^\circ$  from a parallel position with the prism edge; thus it is readily seen that the figures are not only asymmetric, but asymmetrically placed as well. While the figures are simple they are unique in that any one of the four faces may be extended as a groove at the acute angle, and appears as an appendage curved toward the figure and varying in length with the stage of development. Very often a figure contains two, one at each acute angle. The general direction of these modifications is always parallel to the prism edge. The majority of the figures possess but two curved planes, meeting at the bottom of the pit to form a line parallel to the longer diagonal (see fig. 4). Closer observation reveals a direct connection between the two-winged form and the larger grooves mentioned above; in many instances a large figure can be seen occupying the end of the elongated depression, with the attached appendage on either side, extending outward to the edge of the groove, and turned in direction opposite to that in which the groove is proceeding. Thus it seems to be a peculiar manner of growth, which continued with repeated immersions. Those figures possessing the attachments turned in opposite direction on two parallel sides, usually develop the smaller groove which extends across the prism face at an angle of  $45^\circ$ .

The figures produced on  $11\bar{2}0$  by concentrated citric acid are much less symmetrical than the HCl figures, they are more rounded and slightly elongated, but their general direction is quite the same. They are composed of two warped faces intersecting in an S-shaped curve and asymmetrically placed. The canals or grooves which occur on the prism etched by HCl also occur on this crystal etched by citric acid and are produced in a like manner.

Another crystal was etched with a cold 25-percent citric

acid for 20 minutes; the results obtained are quite different; the figures are quadrilateral forms composed of four distinct faces, triangular in form and meeting at a common point in the center of the figure (see fig. 6). The outer contour is represented by a very fine line more or less irregular and indistinct. The figures have little depth, are blunt at one end, acute at the other and are elongated horizontally. The figures are asymmetric and asymmetrically placed. By heating the acid used in this experiment, and immersing another crystal for two minutes, very peculiar S-shaped figures were produced, which are composed of two and four faces—those possessing but two faces appear to be the primitive forms; they possess no plane lying at the bottom of the pit, but the two faces composing the figure meet to form an S-shaped line, whose general direction is inclined to the prism edges. The more mature figures reveal four planes, triangular in shape, meeting as a spiral at the center (see fig. 7). The figures are elongated and are inclined to the prism edges. Canals or grooves are also present on this crystal, which are composed of a series of etch figures in parallel arrangement, elongated in a direction  $90^\circ$  to the direction of the groove; these canals meet the prism edges at an angle of  $45^\circ$ .

Immersion in hot concentrated citric acid for one minute gave still different figures (see fig. 8). These are quite regular, and bounded by four triangular faces, which are arranged in pairs, the two larger faces occupying similar positions above and below, the two smaller ones lying adjacent above and below, so that the figures are slightly bulb or leaf-shaped, and bounded by four curved lines, the two longer ones meeting to form the sharper end of the etching. The longer diagonal varies but a few degrees from a vertical position to the prism edges, while the shorter one runs nearly parallel to the edge of the prism. Although these figures are more symmetrical in form and position than any described on this (11 $\bar{2}$ 0) form, they do not conform strictly to any planes of symmetry, and are so placed on adjacent prism faces as to indicate an alternating *c* axis; thus they accord with the type. The canals cutting the face are very similar to those previously described. Various exceedingly dilute solutions of this acid were used, but they did not etch the crystals so satisfactorily, due to the easy solubility of the

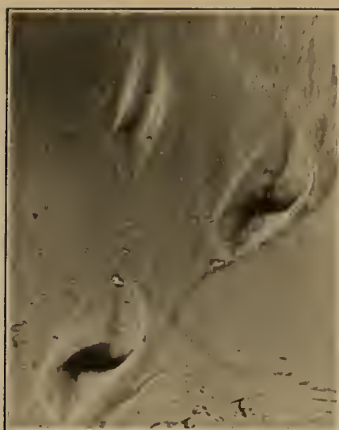


FIG. 7



FIG. 8 × 310

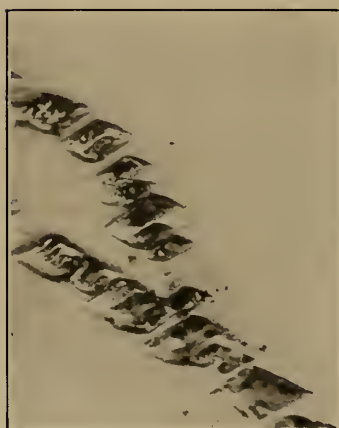


FIG. 9 × 180



FIG. 10 × 120

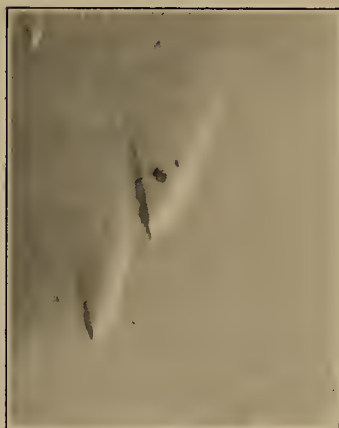


FIG. 11 × 310

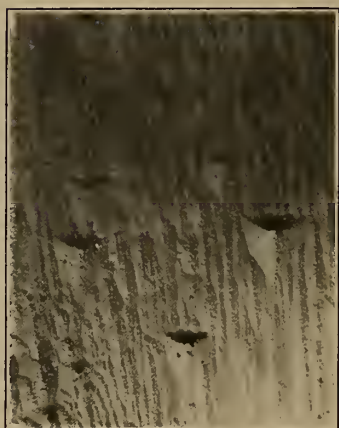


FIG. 12 × 310

crystal along the cleavage lines, which rapidly developed into deep canals, before definite figures could be seen. It is readily noticed, however, that a change in the concentration of the acid produces a very apparent change in the shape and position of the figures, but none of them reveals any planes of symmetry.

The third solvent used was  $\text{HNO}_3$ . This was prepared by taking a few c.c. of conc. C.P.  $\text{HNO}_3$  and diluting it to ten times its volume with water. This was also the strength of the  $\text{HCl}$  used for the purpose of etching this form. Twenty seconds' immersion produced well-formed figures, very similar to the  $\text{HCl}$  forms (see fig 9). They are irregular, rhombic in shape, slightly elongated parallel to the  $c$  axis. A few of the figures are bounded by parallel faces, but the most of them possessed but a single pair of faces lying in parallel position, the larger faces often being slightly divergent. Occasionally several figures are intergrown producing a large irregular four-sided pit, very often containing small figures. The appendages occur on a few figures, but they are very rare, as the longer sides of the figures are quite straight and not curved as are the  $\text{HCl}$  forms. The canals running across the face bear the same relation to the etch figures as do those produced by  $\text{HCl}$ , the more regular depressions extending parallel to the cleavage. The figures possess no plane of symmetry and indicate by their positions on adjacent faces an alternating axis of symmetry  $c$ .

Thus the great similarity of the  $\text{HNO}_3$  and  $\text{HCl}$  figures is again shown in the etchings occurring upon the second-order prism; the figures produced by citric acid are essentially different, due to the difference in the acids, but there is a general likeness to be observed among the etchings of all acids used, especially when compared to the etch figures produced upon the unit prism 1010 by the same solvents. As one would expect, there is a tendency toward a greater similarity in the figures produced upon the same face by different solvents than upon different faces by the same solvent.

*Scalenohedron*—The scalenohedron, 2131, could not be etched successfully with any of the common laboratory acids, although different concentrations and temperatures were tried. It was very apparent, however, that the face had been attacked, but the action had been more or



FIG. 13 × 180



FIG. 14 × 310



FIG. 15 × 180

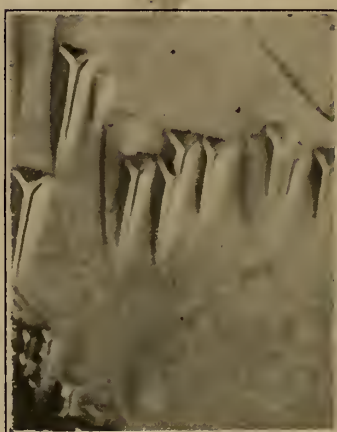


FIG. 16 × 180

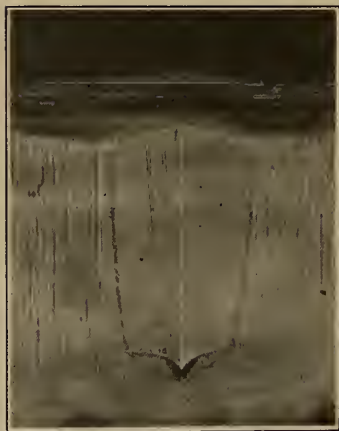


FIG. 17 × 30

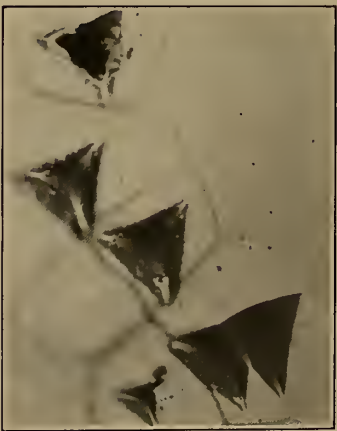


FIG. 18 × 180

less the same over the entire face, producing a glossed, fused appearance. Good results were obtained only by hot dilute citric acid; although figures appeared after the first few seconds, immersion for approximately one minute was necessary to produce well-defined forms (see figs. 10 and 11). The etch figures are somewhat similar to those produced by the HCl on the  $10\bar{1}0$  prism; the basal plane is very similar in the two figures, varying only about  $4^\circ$  in the apex measurement from the reading of the HCl figure, this being approximately  $30^\circ$ . The deeper portion of the figure is the apex, from which there arises the five bounding planes of the pit; the basal plane ascends very gradually to the surface of the crystal, its intersection being almost invisible. The two smaller faces rise abruptly from the pit to form the point of the figures, which angle is about  $65^\circ$  and turned upward. From the apex of the figure, the two lateral bounding planes extend downward, gradually becoming narrower, due to the rise of the basal plane which it intersects, and finally becomes invisible without a definite bounding line. These two planes differ in size, the left being longer than the right. The left side of the figure extends parallel to the intersection of the  $10\bar{1}0$  and  $21\bar{3}0$ , while the right side extends parallel to the left scalenohedral edge upon which it occurs. The figures are asymmetric and asymmetrically placed.

*Rhombohedron*—The unit rhombohedron *r* was successfully etched with practically all of the common acids,  $\text{HNO}_3$ , HCl and citric acid giving the best results. The HCl figures were obtained after two or three seconds' immersion, and are very simple, triangular forms, with the sides slightly curved, giving the figure a rounded appearance (fig. 12). The apex is turned upward. The figures are usually formed of three planes or faces, but occasionally one possesses a basal plane; the figures are symmetrical to a vertical plane cutting the rhombohedral face.

At this point it may be well to consider the rhombohedral figures of the other minerals of the series before giving the results of the other solvents on the calcite rhombohedron.

Magnesite is not so readily soluble as calcite, consequently strong HCl diluted to one-tenth its strength with water attacked this carbonate but slightly, and where

immersion of ten seconds in the boiling acid was amply sufficient to etch the Iceland spar, it was found necessary to boil the magnesite for nearly a half hour in a solution of the same strength before suitable etchings were obtained (fig 13). The etch figures are very similar in shape and orientation to those of calcite; the outer contour of the magnesite forms is always a straight line, while those of the calcite are slightly bulging; a face at the bottom of the figures is common in both carbonates. All figures are symmetrical to a vertical plane.

Siderite, being more easily soluble, required a shorter immersion in the acid, which had been used for the former carbonates; good figures were obtained after an immersion of one minute, and while they are oriented as are the calcite and magnesite figures they are much longer and not so wide. The calcite figures are about as wide as long, while the length of the siderite figures is four or five times its width and the sides almost straight; very few possess basal planes.

Siderite figures, examined after 10 seconds' immersion in dilute HCl, appear shorter and broader with a deep basal groove extending almost the entire length of the figure (see fig 14). At this stage the one-minute figure and the 10-seconds figure are about the same width, which indicates that solution is more rapid at first in a direction at right angles to the *c* axis, and that the more mature stage represents an elongation of the primitive form. If solution be allowed to continue for several minutes the figure becomes rounded, and resembles in a small degree the calcite figure.

The cleavage fragments, having rather an irregular surface, became grooved along certain cleavage lines, and figures starting from these depressions very naturally developed into asymmetric forms, due to the inclined position of the basal plane. Occasionally these grooves intersect, and, due to the solution eating out the intervening space, large figures are produced, which are very different from the ordinary type, but still they indicate the symmetry of the face.

The cleavage pieces of rhodochrosite were next investigated. A solution of HCl of the same strength as that used for the three preceding carbonates, was brought to act upon the more vitreous pieces of the mineral for 20 seconds. It was readily observed that rhodochrosite



acted very much like the calcite when in contact with the acid, and upon examination revealed figures very similar to the calcite figures (fig 15); they are triangular and the majority are bounded by the three faces intersecting in a manner very much like calcite and siderite; the shorter side or face, however, dips more abruptly than does the calcite form. Occasionally there is a basal plane present, but this is usually small and rare.

Increase in time from 20 to 30 seconds' immersion does not change the shape of the figure to any great degree, but merely enlarges it. Like the other carbonates the face is well cut with solution grooves along the cleavage lines. The figures are symmetrical to a vertical plane cutting the rhombohedral face.

The small transparent crystals of smithsonite were exceedingly soluble, even more so than the calcite, consequently immersion for two seconds was sufficient to etch completely the well-formed rhombohedrons and the poorly developed unit prism  $10\bar{1}0$ . Examination revealed a striking resemblance between the unit prism figures of calcite and those of the smithsonite, and still a more striking contrast in the rhombohedral figures of the two minerals. The prism being very small with a very imperfect surface could not be etched so satisfactorily, but the few figures studied seem to be almost identical in form and orientation with those of calcite. The figures of the rhombohedral faces are very unique, unlike any other figure produced throughout the entire investigation; they are very angular and composed of but two triangular planes, intersecting to form the basal groove which extends parallel to the short diagonal of the rhombohedral face. The apex was turned upward and in most cases was approximately  $90^\circ$ ; some were less. The deepest portion of the figure appeared to be at this point, with the two triangular faces gradually ascending from it. All boundaries are straight and with very sharp angles. The figures are symmetrical to a vertical plane.

On the whole, then, there is not found to be the resemblance which might be expected in the etch figures of the rhombohedrons of the isomorphous series of carbonates, even when the conditions of etching were about the same for all minerals. If there is a resemblance to be noted it must involve calcite, magnesite and rhodochrosite; and yet, while siderite is in some ways distinctly different

from the three species named, it has many properties in common with these species and may be comparable to them. Calcite and rhodochrosite are much alike; smithsonite is comparable to none. This may be a sufficient summation of the results of the HCl solvent.

A similar investigation of the five carbonates was made with 10-percent  $\text{HNO}_3$ . The calcite, magnesite, siderite, and rhodochrosite figures were not noticeably different from those produced by the HCl of the same strength. The smithsonite figures differed somewhat as they possessed a large basal plane, and the four bounding lines slightly curved, giving the figure a rounded appearance. The lateral faces are four in number and dip almost perpendicularly to the basal plane. The HCl figure is composed of but two planes meeting to form a basal groove, with no distinct lateral faces; hence the  $\text{HNO}_3$  figures of smithsonite differ from the HCl etchings, and the same comparison holds for both acids.

If a cleavage piece of magnesite be immersed in hot 50-percent  $\text{HNO}_3$  for fifteen minutes, a figure is produced which is much elongated and narrow; it is composed of three faces forming a triangular pit, symmetrical to a vertical plane. The bottom face may be present (see fig. 16).

For the last experiment upon these minerals, a concentrated citric acid was used, but its action upon siderite, magnesite, and rhodochrosite was so slight that good figures were not obtained upon these minerals after repeated immersions of long duration. The calcite rhombohedron *r* etched beautifully after a half minute, the figures being half as large as the rhombohedral face and perfectly symmetrical (fig 17). They are composed of two large faces, lying parallel to the shorter diagonal, and two small faces, bounding the lower end of the figure. The large faces are very smooth and represent, by their position, the negative unit rhombohedron; their intersections with the surface of *r* are practically straight and slightly divergent, until they reach the upper end of the figure, where they converge abruptly forming two rounded corners and a very blunt point; these faces intersect to form the basal groove, which extends parallel to the shorter diagonal. The two smaller faces dip quite abruptly to the bottom of the figure; the intersection of these planes with the two large ones is a curve, and the

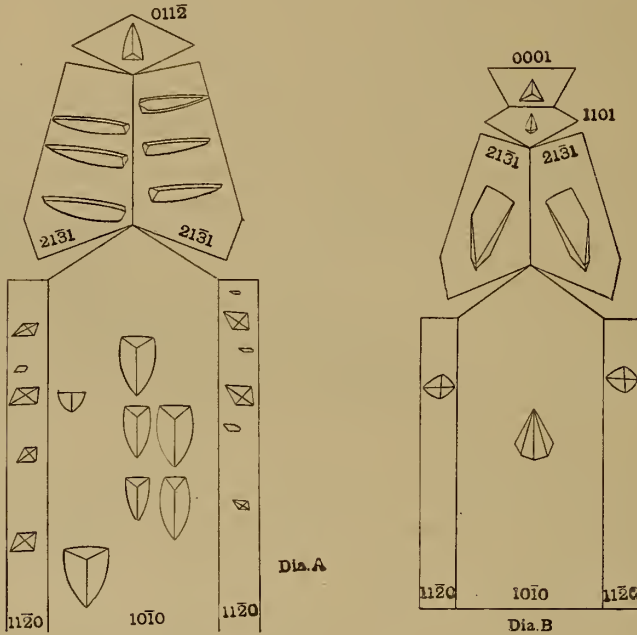
intersections with the crystal face are lines extending parallel to the adjacent edges of the rhombohedron. Two of these figures were produced upon the rhombohedral face, and there was no trace of others. A solution groove developed along the cleavage line of the face, extending parallel to the longer diagonal and extending the entire length. The figures are oriented with the broader end poleward similar to those of smithsonite, but unlike any figures produced by other solvents upon calcite. They are symmetrical with regard to a vertical plane which accords with the symmetry of the face.

Smithsonite, upon immersion in hot concentrated citric acid, for 15 seconds, acts very much like calcite, and the figures produced are quite similar in shape and position,—the etchings are so very small due to the size of the crystal face, that no measurements could be made. Thus, while calcite and smithsonite differ considerably when etched by HCl and HNO<sub>3</sub>, the citric acid figures are quite alike. The unit prism which was so poorly developed on smithsonite failed to etch perceptibly, although it is quite probable figures could be obtained with citric acid if good faces were available. The rhombic carbonates then do differ some in their etching but in general there is a likeness between the calcium, magnesium, iron and manganese minerals of this group. Concerning the relative solubilities of these carbonates it may be added that smithsonite is perhaps most easily attacked, while magnesite presents a very marked resistance to the dilute common laboratory acids.

*Base*—The base (0001), well developed on the simple crystals of calcite from Patterdale, England, was easily etched by HCl and citric acids. The HCl was one-tenth strength and required immersion for fifteen seconds to produce distinct figures (fig. 18); these are regular triangular pyramidal pits with the three faces lying in the zone of the unit prism, rhombohedron and the base; the bounding lines of the figures are curved, but extend in the general direction of the intersections of the first order prism and base.

Hot concentrated citric acid if allowed to act for three minutes upon the base, produces well-defined figures, oriented as are the HCl forms, but the bounding lines are straight, with the three angles rounded,—otherwise they appear identical with the HCl figures. If, however, the

crystal is allowed to lie in the cold 25-percent citric acid for twenty minutes, the base is well etched with very distinct figures (fig. 18); these are very much like those produced by the hot citric acid, but differ by possessing sharp angles. The sides of the figures are very straight and oriented parallel to the edge  $0001/10\bar{1}0$ . Like the HCl figures they are regular, triangular pyramidal pits and by



their form and position indicate the three vertical planes of symmetry characteristic of the calcite type. Diagram B represents calcite as etched by citric acid.

Thus five of the seven possible forms of calcite have been etched with three or four different solvents,—sulphuric acid and acetic acid having been tried and found less desirable, and although there has been a great variation in the form of the figures produced, each shows with unerring accuracy the symmetry of the face upon which it occurs, and the symmetry requirements of a calcite crystal as determined geometrically have been fully met in the etch figure.

*Natural Etch Figures on Calcite.*

Natural etchings are quite often observed on the rhombohedrons, but well-defined figures upon the scalenohedron and prism of calcite are much less common; hence a brief description of the natural figures found on the Cumberland crystals may be of interest. Three forms are etched; the rhombohedron  $c$  ( $01\bar{1}2$ ), the scalenohedron  $v$  ( $21\bar{3}1$ ), and the unit prism ( $10\bar{1}0$ ). The figures occurring upon the rhombohedron are the simple triangular pits, frequently found on that form, but the figures of the scalenohedron are unique. They are blade-like and extend horizontally across the crystal face (see Dia. A). The figures are composed of two large faces, and a very small one; the larger faces lie in the same zone ( $v:r$ ); the upper face dips very abruptly to connect the lower one, which descends very gradually, producing a basal groove lying in the uppermost part of the figure. The lower face forms a very ragged intersection with the surface of the crystal. One end of the figure is pointed, the other occupied by a very small face, which dips abruptly to meet the basal groove. The figures reveal no planes of symmetry except through the middle edge of the scalenohedron.

The unit prism contains many elongated triangular forms, with curved contours; they are composed of three faces as are the artificial figures of the rhombohedron  $r$ . The figures are symmetrical to a vertical plane and indicate by their position the alternating  $c$  axis.

The etchings of the second-order prism are asymmetric quadrilateral forms, having straight margins, two of which extend approximately at right angles to the prism edge (see Dia. A). These etch figures reveal the asymmetrical character of the face.

Thus, it is readily observed that the etch figures as obtained naturally or artificially, upon the various forms of this series of minerals, are in perfect type and that the etching itself is of the greatest importance in the rôle which it plays, as a check upon the symmetry of crystals as derived geometrically.

ART. XV.—*The Occurrence of Cristobalite in California;*  
by AUSTIN F. ROGERS.

The high-temperature pseudo-isometric form of silica known as cristobalite is a rare mineral found at Cerro San Cristóbal near Pachuca, Mexico (the original locality); at Saint Vincent, Martinique (lava of 1902-3); at Mont-Dore, Plateau Central, France; at Olokele Canyon, Kauai (one of the Hawaiian Islands);<sup>1</sup> and at several localities in Rhenish Prussia.

While cristobalite has been reported from the Kendall County, Texas meteorite,<sup>2</sup> it has not been recorded from any of the terrestrial rocks of the United States. The writer has been fortunate enough to find this unusual and interesting mineral in specimens from two widely separated localities in California, *viz.* Tehama County and Tuolumne County. At the Tehama County locality the cristobalite occurs in definite, well-formed octahedral crystals plainly visible to the naked eye while the Tuolumne County occurrence is especially interesting in that the cristobalite proves to be paramorphous after tridymite.

1. *Cristobalite from Tuscan Springs, Tehama County, California.*

The cristobalite was found in a large boulder of a gray porphyritic igneous rock a few miles northeast of Tuscan Springs, Tehama County, by Mr. R. M. Wilke of Palo Alto, California, to whom the writer is indebted for the opportunity of describing this interesting occurrence. Mr. Wilke identified the mineral as cristobalite and the writer has confirmed his sight determination by physical and chemical tests.

*Cristobalite-bearing auganite.* The cristobalite-bearing rock is a porphyritic rock with labradorite and augite as the dominant minerals and since it contains no olivine, Winchell's useful name *auganite*<sup>3</sup> may be used for it. The plagioclase is a labradorite with approximately the composition  $Ab_1 An_2$ , which was determined by finding the maximum symmetrical extinction-angle in albite twins. The euhedral phenocrysts of labradorite are

<sup>1</sup> Cross, U. S. Geol. Surv., Prof. Paper 88, p. 11, 1915.

<sup>2</sup> Cohen, Meteoritenkunde, p. 260, 1903.

<sup>3</sup> Mining and Sci. Press, 105, 656, 1912. Auganite differs from basalt in the absence of olivine and from augite-andesite in having the plagioclase more calcic than  $Ab, An$ .

thick tabular parallel to (010). They show zonal structure, the exterior zone being more sodic than the interior as is generally the case.

The augite occurs in euhedral to subhedral phenocrysts of stout prismatic habit and square cross-section with (100), (010), and (110), the latter form being subordinate. Sections parallel to (100), which are recognized by the parallel extinction, are somewhat pleochroic from greenish to reddish while sections parallel to (010) are non-pleochroic. The maximum extinction-angle is about  $42^\circ$  and the maximum birefringence about 0.022.

Magnetite occurs in small euhedral to subhedral crystals. There are also a few large, almost opaque skeleton crystals which could not be identified.

Some glass is present in the groundmass and the rock as a whole is docrystalline and dopatic with seriate porphyritic texture or fabric.<sup>4</sup>

*Cristobalite in the rock.* The cristobalite is found for the most part in cavities of the auganite but it is also identified in thin sections as anhedra which, however, may be entire cavity fillings. These anhedra are weakly birefringent with a kind of mosaic structure, which is due to minute, roughly rectangular crystals. The parts of the mosaics usually extinguish together as a whole but vary in their birefringence. One imperfect euhedral crystal was observed in the thin section. It is about half of an octagon. A part of it extinguishes parallel (and perpendicular) to one edge of the octagon, while the other portion is almost dark between crossed nicols. These tests prove the existence of twinning in the original high-temperature cristobalite. The maximum double refraction of the cristobalite is about 0.0023. The value determined by Fenner<sup>5</sup> is 0.003.

*Euhedral cristobalite in cavities.* The euhedral cristobalite occurring in cavities of the auganite are opaque white to subtranslucent octahedra, usually  $\frac{1}{2}$  mm. to  $\frac{3}{4}$  mm. in diameter with a maximum size of 1 mm. The crystal edges are straight and some of the faces are smooth and plane but many of them are slightly concave, sometimes with symmetrical triangular depressions. A few contact spinel twins without reëntrant angles were noted and also a peculiar double contact and penetration

<sup>4</sup> These terms were introduced by Cross, Iddings, Pirsson, and Washington. (Jour. Geol., 14, 692-707, 1906.)

<sup>5</sup> This Journal (4) 36, 354, 1913.

spinel twin. The crystals have a peculiar enamel-like appearance, which is probably due to the fact that they consist of aggregates of *a*-cristobalite.

The cristobalite is infusible before the mouth blowpipe and is insoluble in hydrochloric acid and aqua regia. It scratches glass slightly.

The identification of the mineral as cristobalite, however, rests largely upon the optical properties. The index of refraction is  $1.483 \pm .003$ , which was determined by means of the immersion method. The liquids used were determined accurately to the fourth decimal place on the refractometer and were rechecked at the time of the determination. They had changed less than 0.001 in a year's time.

A little tridymite was found adhering to one of the cristobalite octahedrons. It was a typical penetration twin group with sharp edges and was clear and glassy in contrast with the subtranslucent cristobalite. It was positively identified by its index of refraction.

Hyalite opal and calcite are associated with the cristobalite in cavities and were formed later than the cristobalite. Opal also occurs in filaments which are probably pseudomorphous after acicular calcite crystals.

## 2. *Cristobalite from Jamestown, Tuolumne County, California.*

Cristobalite has also been identified in a porphyritic augite andesite found by the writer near Jamestown, Tuolumne County. This rock is a boulder from the coarse gravel found in the buried river channel beneath the Table Mountain latite flow described by Ransome.<sup>6</sup> The boulders had been exposed by drift mining for gold and were for the most part hornblende andesites. The andesite boulders have probably been derived from the andesite breccias to the northeast.

*The Cristobalite-bearing andesite.* This is a reddish-gray porphyritic rock containing andesine and augite as the dominant minerals. The andesine has approximately the composition  $Ab_{56} An_{44}$  which was determined by the maximum symmetrical extinction angles in albite twins. Many of the andesine crystals have a narrow opaque zone near the outer margin and beyond this a colorless rim. The probable explanation is that the feldspar was partially altered by magmatic gases and then at a later

<sup>6</sup> Bull. U. S. Geol. Surv., 89, 1898.



stage conditions were again favorable for the formation of the feldspar. The colorless rims in this case are more calcic than the interior.

The augite is much like that in the Tehama county auganite with the (100) section pleochroic from reddish to greenish. The maximum extinction-angle is about  $43^\circ$  and the maximum birefringence about 0.025. Some of the augite is altered to an aggregate of fibrous crystals with a maximum extinction angle of about  $23^\circ$ . This is probably a mineral of the amphibole group.

Magnetite occurs in small crystals and a small amount of apatite is also present. Elongate opaque crystals are red by reflected light and doubtless represent hematite pseudomorphs after some ferro-magnesian mineral, the most likely of which is hornblende. Red scales through the rock are probably specularite (crystalline  $\text{Fe}_2\text{O}_3$ ) crystals.

The rock is docrystalline and dopatic, and has a seriate porphyritic texture or fabric, some glass being present in the groundmass.

*Cristobalite in the rock.* A weakly birefringent mineral with rather high relief occurs as cavity fillings and also in patches in the thin section. With the sensitive-tint plate it exhibits a mosaic of rough squares. Some spots show a radial excentric structure. This is characteristic of tridymite but the mineral is identified as cristobalite for the index of refraction is greater than 1.480 (tridymite is less than 1.480)<sup>7</sup>. The explanation, as I shall presently show, is that the mineral is cristobalite with the form of tridymite.

*Cristobalite paramorphs after tridymite.* Cavities of the augite-andesite just described contain minute ( $\frac{1}{2}$ mm.) confused aggregates of translucent crystals. Many of these are well-formed six-sided tabular crystals but they are not clear and glassy like typical tridymite. Several distinct penetration twins of the form so characteristic of tridymite were noted. The form is that of tridymite but the index of refraction is  $1.483 \pm 0.003$ , which agrees well with that of cristobalite. The explanation is that the mineral is a paramorph of cristobalite after tridymite and so far as I can learn this is the first recorded instance of

<sup>7</sup> The work of Fenner (this Journal (4), 36, 351-356, 1913) of the Geophysical Laboratory of the Carnegie Institution of Washington enables us to positively distinguish cristobalite and tridymite by means of the refractive index.

the kind. One usually thinks of the chemical composition and crystal form taken together as being sufficient to determine any mineral, but on account of the possibility of paramorphism it is necessary to determine some physical property in addition. Of the various physical properties the index of refraction is in general (except for opaque minerals of course) the most useful one in determinative work.

Fragments of the cristobalite have weak birefringence and mottled interference colors. Some of the fragments, however, are minute crystals of hexagonal tabular form which remain dark between crossed nicols and suggest that they may be associated tridymite, but repeated trials show that the index of refraction is always greater than 1.480. These hexagonal crystals are perfectly clear and colorless without any hint of the mosaic effect and are probably single uniaxial (tetragonal?) crystals of  $\alpha$ -cristobalite which have retained the hexagonal form of the original tridymite from which they were formed. This probably involves only a slight change in the space-lattice.

The conversion of the tridymite into cristobalite was probably brought about by hot gases or mineralizers. According to Le Chatelier<sup>s</sup> rapid crystallization is responsible for the formation of cristobalite. As evidence of post-magmatic action the opaque zones in the andesine crystals, the fibrous alteration product of the augite and the opaque red hematite may be recalled.

Associated with the cristobalite aggregates in the cavities are very thin tabular six-sided crystals which prove to be kaolinite. They show several features out of the ordinary and will be described at another time. The kaolinite is later than the cristobalite (or original tridymite, at least) but the data are not sufficient to prove whether it is a hypogene or supergene mineral. Long acicular crystals of unknown identity occur in the cavities with the kaolinite.

#### *Summary.*

Cristobalite is described from two localities in California. Near Tuscan Springs in Tehama County it occurs as distinct octahedral crystals in an auganite. At Jamestown in Tuolumne County it occurs in an augite andesite and proves to be paramorphous after tridymite.

Dept. of Geology, Stanford University, California, Nov. 1917.

<sup>s</sup> Bull. Soc. Min., 40, 56, 1917.

ART. XVI.—*The Oxidimetric Determination of Thorium precipitated as the Oxalate*; by F. A. GOOCH and MATSUSUKE KOBAYASHI.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cexcix.]

There appears to be in the literature no account of an oxidimetric method for the determination of thorium, based upon the precipitation of that element as the oxalate, by procedure similar to that which is applicable in the case of many oxalates of definitely known constitution. In the well-known gravimetric method in which thorium is precipitated as oxalate and weighed as thorium dioxide the exact constitution of the precipitated oxalate is not a matter of moment since the final product will be definite whatever the form of the precipitated oxalate may be. It is necessary, however, that definiteness in the constitution of the precipitate shall be assured in order that the determination may be made to depend upon the oxidimetric measurement of the oxalate. The following account gives the results of a study made to fix the conditions under which an accurate determination of thorium may be made by estimating either the oxalate radical combined in thorium oxalate or the excess of oxalic acid remaining from a known amount of oxalic acid used to effect the precipitation of the thorium.

In the experiments to be described a solution of thorium nitrate was made by dissolving 10 grm. of that salt (hydrous) in a liter of cold water acidified with 1 cm<sup>3</sup> of concentrated sulphuric acid and this solution was standardized accurately by the gravimetric method in which thorium oxalate is precipitated by oxalic acid and ignited and the residue weighed as thorium dioxide, ThO<sub>2</sub>.

Potassium permanganate, made up in approximately N/10 solution, and standardized against pure sodium oxalate, was used as the oxidizing reagent and the solution of oxalic acid employed as the precipitant was standardized against the permanganate. In making use of these solutions, the burette readings were corrected for any change of temperature from that prevailing at the time of standardization.

In all the experiments the precipitation was brought about by the reaction of measured amounts of the standard oxalic acid with measured amounts of the solution

of thorium nitrate and the mixtures were allowed to stand on the steam bath for intervals varying from fifteen to thirty minutes. The precipitated oxalate was filtered off on asbestos in the perforated crucible and washed with cold water containing in every 25 cm<sup>3</sup> a drop of concentrated sulphuric acid. The oxalic acid in the filtrate and the thorium oxalate of the precipitate were oxidized separately, by the standard permanganate. In the former case the amount of permanganate measured directly the oxalic acid radical of precipitated oxalate; in the latter case the amount of permanganate used measured that part of the known amount of standard oxalic acid which remained uncombined, the difference between the amount of oxalic acid taken and that found in the filtrate representing also the combined oxalic acid radical.

In the treatment of the precipitate, the crucible and precipitate were put into a beaker containing 100 cm<sup>3</sup> of water, the whole was heated to a temperature of about 85°, sulphuric acid (5 cm<sup>3</sup> of the 1:1 acid) added, the measured permanganate solution run in until the larger part of the precipitate had been oxidized, the mixture again heated to facilitate the oxidation of the precipitate (retained by the cooling of the mixture during the titration) and the titration continued to an end-point (which is very sharp if the liquid is kept hot). The coloration was matched with that obtained by adding a definite amount of N/10 permanganate (0.02 cm<sup>3</sup> to 0.04 cm<sup>3</sup>) to an emulsion of asbestos in 100 cm<sup>3</sup> of water.

The filtrate from the precipitated thorium oxalate was diluted to a volume of 200 cm<sup>3</sup>, heated to about 85°, and sulphuric acid (10 cm<sup>3</sup> of the 1:1 acid) was added. The titration with permanganate was continued to the end-point, since in the titration of the soluble oxalic acid in the filtrate there is no need of reheating as is the case in the titration of the insoluble oxalate.

In the experiments of Series I, A, in which the oxalic acid was added to the hot solution of thorium nitrate, the results show a deficiency amounting in the average to 2.75% of the oxalate radical which should be in combination with thorium, upon the hypothesis that the precipitate is the normal oxalate  $\text{Th}(\text{C}_2\text{O}_4)_2$ .

The results of the experiments in Series I, B, in which the oxalic acid was added to the cold solution of the thorium salt, though more regular, point to a deviation of

SERIES I.

Precipitation by Addition of Oxalic Acid to Thorium Nitrate.

ThO <sub>2</sub> taken as nitrate gm.	ThO <sub>2</sub> found in treatment of precipitate gm.	ThO <sub>2</sub> found in treatment of filtrate gm.	Error in treatment of precipitate gm.	Error in treatment of filtrate gm.
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A.

Precipitation in hot solution.

0.0216	0.0213	0.0210	-0.0003	-0.0006
0.0430	0.0425	0.0418	-0.0005	-0.0012
0.1074	0.1043	0.1040	-0.0031	-0.0034
0.1721	0.1670	0.1669	-0.0051	-0.0052

B.

Precipitation in cold solution.

0.0237	0.0235	0.0234	-0.0002	-0.0003
0.0242	0.0241	0.0236	-0.0001	-0.0006
0.0474	0.0471	0.0471	-0.0003	-0.0003
0.0474	0.0467	0.0470	-0.0007	-0.0004

the precipitated oxalate from the normal form amounting to about 1%.

In the experiments of Series II, the order of addition was reversed and the thorium nitrate solution was added gradually to the oxalic acid with the intent to keep the latter reagent in excess during the precipitation. The mean error of the results shown in the experiments of section B in which the precipitation was made in cold solution amounts to about 0.1% while that of the experiments of section A, made in hot solution, is practically negligible.

SERIES II.

Precipitation by Addition of Thorium Nitrate to Oxalic Acid.

ThO <sub>2</sub> taken as nitrate gm.	ThO <sub>2</sub> found in treatment of precipitate gm.	ThO <sub>2</sub> found in treatment of filtrate gm.	Error in treatment of precipitate gm.	Error in treatment of filtrate gm.
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A.

Precipitation in hot solution.

0.0216	0.0217	0.0212	+0.0001	-0.0004
0.0431	0.0432	0.0428	+0.0001	-0.0003
0.0646	0.0646	0.0643	0.0000	-0.0003
0.0860	0.0861	0.0858	+0.0001	-0.0002
0.1075	0.1074	0.1075	-0.0001	0.0000

*A. (Continued).*

## Precipitation in hot solution.

ThO <sub>2</sub> taken as nitrate grm.	ThO <sub>2</sub> found in treatment of precipitate grm.	ThO <sub>2</sub> found in treatment of filtrate grm.	Error in treatment of precipitate grm.	Error in treatment of filtrate grm.
0.1290	0.1291	0.1290	+0.0001	0.0000
0.1506	0.1505	0.1504	-0.0001	-0.0002
0.1722	0.1723	0.1720	+0.0001	-0.0002
0.1937	0.1944	0.1937	+0.0007	0.0000
0.2151	0.2153	0.2151	+0.0002	0.0000

*B.*

## Precipitation in cold solution.

0.0238	0.0236	0.0236	-0.0002	-0.0002
0.0474	0.0475	0.0472	+0.0001	-0.0002
0.0711	0.0707	0.0709	-0.0004	-0.0002
0.0711	0.0710	0.0711	-0.0001	0.0000
0.0947	0.0946	0.0945	-0.0001	-0.0002
0.1183	0.1180	0.1184	-0.0003	+0.0001
0.1419	0.1417	0.1416	-0.0002	-0.0003
0.1658	0.1654	0.1658	-0.0004	0.0000
0.1895	0.1888	0.1890	-0.0007	-0.0005
0.2130	0.2128	0.2133	-0.0002	+0.0003
0.2366	0.2365	0.2368	-0.0001	+0.0002

The work described shows that thorium may be estimated by an oxidimetric titration based upon the precipitation of thorium oxalate, provided that the precaution is taken to add the thorium salt gradually during the process of precipitation to an excess of oxalic acid. In the reverse procedure the tendency of thorium oxalate to fall as a basic salt is manifest and this tendency is especially marked in hot solutions. An accurate determination may be made either by the direct oxidation of the precipitated thorium salt, Th(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>, or by determining the excess remaining in solution from a known amount of oxalic acid, after filtering and washing the precipitate.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *The Recovery of Potash and Other Constituents from Sea-Water Bittern.*—JOEL H. HILDEBRAND states that the total production of potash in this country, calculated on the basis of  $K_2O$ , was about 14,000 tons during the first half of the year 1917, an amount equal to only about 10 per cent of the normal amount used before the war. He states that about 140,000 tons of common salt are produced annually from sea-water in the region of San Francisco Bay, and that if the potash in the mother-liquor or "bittern" from this salt could be saved it would add about 10 per cent to the present production of the country, while a much greater yield might be obtained by utilizing also the bitterns from other regions on the Pacific Coast. Professor Hildebrand has presented a very good review of the elaborate scientific study by Van't Hoff and his co-workers of the relationships of the simple and double salts in deposits from ocean waters, in order to make these principles easily accessible for use in solving this problem. He has also worked out from laboratory experiments a proposed process, the outline of which is as follows:

"Evaporate bittern till boiling point becomes about  $120^\circ$ , and density (hot) 1.35. Separate solid and liquid while hot (settling tank and centrifuge).

A. Solid.  $NaCl$  and  $MgSO_4 \cdot H_2O$ .

Dissolve out  $NaCl$  with cold water (containing some  $MgCl_2$ ?); dissolve residue in hot water and cool with ice machine, getting  $MgSO_4 \cdot 7H_2O$ .

B. Liquid. Cool.

I. Solid carnallite ( $KMgCl_3 \cdot 6H_2O$ )

Extract with minimum amount of cold water leaving.

1. Solid  $KCl$ .

2. Solution. Evaporate partly. Cool.

a. Solid carnallite. Add to I.

b. Solution of  $MgCl_2$ . Add to II.

II. Solution, mainly  $MgCl_2$ . Bleach with  $Cl_2$  and remove  $Br_2$ . Evaporate, cool and recover  $MgCl_2 \cdot 6H_2O$ ."

The process appears to be well planned, and it agrees in some important features with the methods used in the German potash industry. It is a question whether the large amounts of magnesium salts that might be produced would be marketable, and it is suggested that hydrochloric acid and the oxide

might be manufactured by igniting the magnesium chloride in the presence of steam.—*Jour. Indust. Engr. Chem.*, 10, 96.

H. L. W.

2. *Potash from Cement Mills.*—Much attention has been paid recently to the dust from cement kilns as a source of potash, both under the usual conditions and with the suggestion that material such as feldspar richer in potash than that ordinarily employed, should be used in the operation.

ALBERT R. MERZ, of the U. S. Bureau of Soils, states that dust precipitated by the Cottrell process at a works in California where oil was used for fuel in the kilns, had 92 per cent of its potash in a water-soluble condition, while at two Eastern works where powdered coal was blown in as the fuel only 60 and 42 per cent of the potash could be dissolved in water. Merz appears to have found a remedy for this serious difficulty, as he found that when the Eastern dusts were heated at temperatures of from 600 to 1100° for a short time the greater part of the potash became soluble in water, apparently on account of the action of the lime present in the dust upon insoluble silicates.

Another aspect of this matter has been presented by N. S. PORTER, Jr., and R. D. CHEESMAN, of a Portland Cement Company in Michigan. They have found that the content of potash in coal ashes is considerable, amounting in several cases to about 5 per cent, and since it appears that most of this ash, under the conditions employed, passes into the dust, they believe that this is the chief source of the insoluble potash. They do not believe, as Merz has suggested, that the coal ash combines with the volatilized potash from the change and renders it insoluble. They make no suggestion as to a remedy for the difficulty, such as plowing in a little dry slacked lime with the coal, but it is to be hoped that the method of Merz or some other device will make this source of potash available.—*Jour. Indust. Eng. Chem.*, 10, 109.

H. L. W.

3. *The Preparation of Very Dilute Permanganate Solutions.*—J. O. HALVERSON and OLAF BERGEIM have found that particular precautions are necessary in the preparation of these solutions where the strength is about 1/100 normal. They state that when such solutions are made up by diluting stronger ones, as is frequently done, there is enough organic matter in the distilled water used for dilution to seriously affect the strength, even if the diluted solutions are used almost immediately. Even when the water used for diluting had been distilled from both acid and alkaline permanganate, there was still a serious deterioration of the solutions. They recommend, therefore, the dissolving of 0.40 g of pure potassium permanganate crystals in a liter of redistilled water, in a very carefully cleaned flask, then digesting the solution for 36 hours at near the boiling point, cooling, allowing to stand over night, and without disturbing the



sediment, filtering through ignited asbestos into a perfectly clean bottle. This solution when kept in the dark is stable for a long time, and it should be standardized with a 1/50 normal solution of oxalic acid which has been acidified with 10 cc. of 10 per cent sulphuric acid, which in turn has been treated with just enough permanganate solution to give it a faint pink color. The standardization is made after heating the oxalic acid solution to 65° in a water bath.—*Jour. Indust. Engr. Chem.*, 10, 119.

H. L. W.

4. *An Elementary Study of Chemistry*; by MCPHERSON and HENDERSON. Second Revised Edition. 12mo, pp. 576. Boston, 1917 (Ginn and Company).—This is the smaller and more elementary of two text-books on general chemistry by these authors, both of which books appear to have met with much favor among teachers. The fact is evidently appreciated that the book under consideration gives more attention to fundamental principles, and is more comprehensive in other respects than is frequently the case with books intended for the same grade of instruction. The present edition has been revised to meet the advances in chemistry during the past decade, some changes have been made in the arrangement of the matter, and a little more space has been given to the compounds of carbon. The last change seems well justified, for, as the authors argue, many students take no more than one year of chemical study, and it seems unreasonable that these should have no knowledge of the organic compounds that are met with in everyday life far oftener than the majority of inorganic compounds. It seems to the reviewer that this improvement might well have been carried still farther by including a few structural formulas explaining the very important matter of isomerism in organic substances. However, it is difficult to decide upon the things to be included and omitted in a text-book of limited scope, like this one, and it may be said that the book has many very excellent features, and that it appears to be, on the whole, an unusually satisfactory one.

H. L. W.

5. *A Class-Book of Organic Chemistry*; by J. B. COHEN. 12mo, pp. 344. London, 1917 (Macmillan and Co., Limited).—This text-book is intended for the use of first year medical students and for senior science students in schools. The theoretical and practical sides of the subject are treated concurrently, so that the book serves the double purpose of text-book and laboratory manual. It appears that this combination has been effected in a very satisfactory manner, so that the bearings of the two sides of the subject, as it is studied, are kept very clearly in view. The topics are very well selected for the purpose of giving a good general knowledge of this vast subject. The course is divided into three parts. In the first part the general principles underlying determinations of purity, empirical and molec-

ular formulas and structure are explained and illustrated by a careful study of derivatives of methyl and ethyl alcohols. In the second part the aliphatic compounds are described more systematically, while the third part is devoted to a brief treatment of the more important members of the aromatic series.

The book appears to be an excellent one for the purpose in view. The explanations are clear, the laboratory experiments are well selected, and each chapter, of which there are twenty-six, is supplied with a list of questions, while there are, at the end of the book, some general questions, as well as some very instructive problems upon the calculation of formulas from such data as are usually obtained in practical research.

H. L. W.

6. *Electric Discharge in Gases and Vapors.*—The facts recorded below are derived from a recent paper by R. J. STRUTT. The first part of the investigation relates to the phenomena presented by luminous jets at low pressures in a transverse electric field. The gas was excited to luminosity during its passage through a glass bulb of about 16 cm. diameter. The anode consisted of an iron disc which was soldered into the end of a brass tube. The disc was perforated at the center by a hole 1 mm. in diameter. The brass tube formed the prolongation of a small lateral glass tube which was blown on the wall of the spherical bulb. This outlet tube was diametrically opposite to, and coaxial with, the inlet tube. The cathode was fixed close to the inner wall of the bulb at 90° from the openings of the coaxial glass tubes. The current was produced by three high-tension magneto generators arranged in series and direct driven by a motor. The maximum output of this system was 10 milliamperes at 5000 volts. The variation of the current from a constant value did not exceed  $\pm 0.22$  per cent. After passing through the hole in the anode the gas escaped as a jet into a large cylindrical glass tube the axis of which was perpendicular to the common axis of the brass and glass tubes mentioned above. The transverse glass tube contained two condenser plates the planes of which were parallel to the axis of the jet. This tube was closed at one end by a plate glass window through which the light from the jet passed to the camera lens. The gas finally escaped through a lateral tube to a molecular pump. The condenser plates were 13 mm. apart and they usually had a difference of potential of 160 volts. The luminosity of the jets was too low for visual observation so that the photographic method could not be avoided. The pressures were not measured directly but were controlled by the length of the negative dark space.

The gases investigated with this apparatus were hydrogen, oxygen, nitrogen, carbon dioxide, and mercury vapor. With hydrogen at a pressure corresponding to a dark space of 6 mm. the bulk of the luminous particles were attracted to the positive

plate and hence they were negatively electrified. Only a few of the particles pursued an undeviated course and were accordingly neutral. With hydrogen at 13 mm. dark space the luminous particles were practically all negative, the neutral particles having disappeared. With the same gas at 25 mm. dark space a few positive particles made their appearance. When the dark space was 51 mm. in hydrogen (the lowest pressure practicable with the apparatus) the number of positive particles had increased markedly, but the negative ones still predominated. With oxygen at 6 mm. dark space the negative particles were somewhat more conspicuous than the positive particles, whereas at 13 mm. and 25 mm. the positive and negative centers produced about equal photographic impressions. With carbon dioxide at 25 mm. the two kinds of charged particles were equally conspicuous. In the case of nitrogen at 25 mm. the positive particles slightly exceeded the negative ones in luminous effect. Mercury vapor at 19 mm. gave negative centers only. At 32 mm. dark space this vapor showed also a trace of positive particles. At 38 mm. the proportion of positive particles had increased noticeably. The final explanation of these phenomena has not been found, but Strutt favors the opinion that the luminosity must have been stimulated in the particles before they entered the electrostatic field and therefore the luminosity of the deflected streams cannot be due to ionization by recombination.

The next experiments described correspond to relatively high pressures and a different form of apparatus. A spark was passed, in the gas under investigation, between iron wires the ends of which were 1 cm. apart. These wires ran along the axis of a silica tube of 1.5 mm. inside diameter. A hole of about 0.7 mm. diameter was pierced in the wall of this tube opposite the middle of the spark gap. The silica tube passed eccentrically across a right section of a larger cylinder having a transparent window at one end, etc. Hydrogen gave far more striking effects with the condensed than with the uncondensed discharge. The best results were obtained with a pressure of 17 cm. in the silica tube and 2 or 3 mm. in the outer cylinder. "In this case a tongue of flame of a beautiful rosy colour, and about 9 mm. long, was seen issuing from the hole." The spectrum of this jet shows the Balmer series lines without the usual background of the band spectrum. Strutt was able to photograph the first ten series lines. He also found that the width of the spectral lines was much less in the jet than in the condensed spark where the luminosity had been excited. Stark has given reasons for believing that the broadening of spectral lines is due to the electric fields of neighboring atoms. "It is, therefore, not surprising that the removal of these to a greater mean distance, when the gas issues from the hole and expands, should cause the lines to become narrow."

With the second form of apparatus extremely interesting phenomena were obtained with nitrogen, when the pressures inside and outside the silica tube were 155 mm. and 7 mm., respectively. In this case, however, the simple induction coil discharge without a condenser gave the best results. Both the jet and spark had a reddish-orange color and the jet could be traced for a distance of 5 cm. from the orifice. "The most striking features of this jet, both visually and photographically, are the alternations of light and comparative darkness which may be seen along its length. Five or six of these can easily be counted, but they become less distinct the farther out we go from the orifice. They remain absolutely steady in position in spite of any irregularity in the working of the induction coil." Strutt shows that the variations in luminous intensity are of purely hydrodynamic origin, changes in density giving rise to corresponding alterations in intrinsic brightness. By using Emden's empirical formula for the wave-length of the periodic structure and *extrapolating*, a length of 2 mm. is obtained. Strutt's photographs show that the wave-length is 1.8 mm. Under the circumstances, the agreement may be considered quite satisfactory. The last part of the paper deals with the spectrum of the nitrogen jet. The spectrum consists of the bands known as the first, second, and third positive nitrogen groups. This spectrum is entirely different from that of the "active modification" of nitrogen. The luminosity of the jet lasts for about 1/6000 of a second whereas that of the active modification often persists for several seconds, or even minutes.—*Proc. Roy. Soc.*, 94 A, 88, 1917.

H. S. U.

7. *Magnetic Tables and Magnetic Charts for 1915*; by DANIEL L. HAZARD. Pp. 256; numerous tables, 5 charts. Special Publication No. 44. U. S. Coast and Geodetic Survey. E. LESTER JONES, Superintendent.—The introductory chapter (pages 5 to 15) is historical and explanatory. Pages 16 to 94 give, in tabular form, the secular change data derived from observations at repeat stations. Secular change tables, that is, tables for reducing the values of the declination, inclination, and horizontal intensity to Jan. 1, 1915, occupy pages 95 to 99. The observed magnetic elements ( $D$ ,  $I$ ,  $H$ ) and the corresponding values reduced to 1915.0 are tabulated on pages 100 to 226. These tables refer not only to the United States but also to Canada, Mexico, the West Indies, Central America, Colombia, Guiana, Venezuela, the Gulf of Mexico, the Caribbean Sea, and certain portions of the Atlantic and Pacific Oceans. The rest of the volume comprises tables of the magnetic elements and magnetic components for each degree of latitude and longitude. Five loose charts, each on a scale of 0.9 inch to 100 statute miles, are contained in a pocket attached to the back cover. These give respectively, lines of equal declination and equal annual

change, lines of equal inclination and equal annual change, lines of equal horizontal intensity and equal annual change, lines of equal vertical intensity, and lines of equal total intensity.

H. S. U.

8. *Plane Trigonometry*; by EUGENE HENRY BARKER. Pp. vii, 172, with 86 figures. Philadelphia, 1917 (P. Blakiston's Son and Co.).—"The author believes that in a text-book of this sort the things on which the greatest stress should be laid are thorough familiarity with trigonometric functionality, acquaintance with the interdependence of the functions, a knowledge of the methods of trigonometric analysis, power of initiative in the development of formulas, and a certain definite resolute skill in their application to the solution of practical problems." Although a final opinion of the true value of a text-book can be formed only after it has been subjected to searching tests in the class room, nevertheless the writer of this brief notice has reached the tentative conclusion that the present volume is one of the best books of its grade and scope which has come under his observation for a number of years. The subject matter is carefully graded, clearly presented, logically arranged, and well balanced. The volume seems to contain just the right amount of material for practical purposes. The diagrams are drawn in bold lines, and the theorems and fundamental formulae are emphasized by italic and full-faced type respectively. In short, the text is characterized by appropriate contrast and perspective. The six trigonometric functions are defined as ratios and the entirely unnecessary representation of these functions by segments of lines associated with a circumference of unit radius (so often found in elementary texts) has been completely ignored. The book contains 524 examples and problems for solution by the student. The volume closes with carefully arranged five-place logarithmic tables and four-place tables of the natural functions.

On the other hand, the book is not entirely free from imperfections. For example, the paper is thin and very translucent so that the diagrams and type show through from one page to the next with annoying clearness. A few of the typographical errors may be confusing to the student. On page 42, the *heading* of article 29 contains, at the end, the superfluous factor  $\tan(A + B)$ . In chapter X the "Exercises" after the fifth are numbered 5, 6, 7, and 8 instead of 6, 7, 8, and 9. Since the answers to the examples in the exercises are given (pages 100 to 106), the slip just mentioned has led to the omission of all the answers to the sixth set of the tenth chapter.

H. S. U.

9. *Telegraph Practice*; by JOHN LEE. Pp. ix, 102. London, 1917 (Longmans, Green and Co.).—"This little book is an attempt to outline the fundamentals of telegraph practice in such a way as to indicate differences in method as adopted by

different administrations." It deals almost exclusively with British practice. The engineering and theoretical aspects of the subject are not dealt with explicitly so that the volume contains nothing of scientific interest for the physicist or electrician. On the other hand, the text will doubtless appeal to administrators and economists who are interested in the numerous complex problems which arise in connection with the development and efficient maintenance of large telegraph systems. A fairly precise idea of the general plan of the book may be derived from the following list of titles: The Acceptance of Telegrams from the Public, The Centralising of Telegraph Traffic, Telegraph Instrument Rooms, Telegraph Instruments, The Telegraph Organism, The Delivery of Telegrams, Press Telegrams, Telegraph Tariffs, and The Future of Telegraph Practice. H. S. U.

## II. GEOLOGY.

1. *Chemical Analyses of Igneous Rocks*; by H. S. WASHINGTON; U. S. Geol. Surv.; Prof. Paper 99, 4°, pp. 1201. (Washington, 1917.)—This is a new edition, a revision and extension, of Professional Paper 14 by the same author, published in 1903 and noticed in this Journal (16, 396, 1903). The first edition contained 2881 analyses from 1884-1900 inclusive; the present work carries them down to 1913 inclusive, and contains a number made in years 1884-1900 which were not in the first paper. It presents, therefore, nearly all analyses published which are of any value from 1884-1914. The total number listed is 8602.

It may also be recalled that in Professional Paper 28\* the author has given us a selection of the best and usable analyses from Roth's Tabellen covering the years 1869-1884, so that in conjunction with the present work we now have all the useful analyses of igneous rocks from 1869 down to 1914 in convenient form for ready reference.

Washington's Tables have become so well known, and are used so generally by petrologists, geologists, and chemists, that it seems unnecessary to give a detailed account of them. However, it may be said that the general plan and scope of the work remains the same. It opens with a discussion of the making, use and value of analyses of rocks; then come the listed analyses. These are given under four headings; Part I, Superior Analyses of Fresh Rocks; of these there are 4980 and they are arranged according to the Quantitative Classification, and the calculated norm of each is given; Part II, Incomplete Analyses of Fresh Rocks; Part III, Superior Analyses of Altered Rocks and Tuffs; Part IV, Inferior Analyses. The last three are arranged under the ordinary qualitative modal names. An appendix, containing

\*Noticed in this Journal, 18, 237, 1904.

an account of the Quantitative Classification, and a discussion and list of magmatic normative names, closes the volume. It is well indexed by several methods, so that analyses may be readily found.

The search for the material through the literature, its collation, the calculation of the norms, the preparation of the manuscript and the proof reading of this work, evince the expenditure of a vast amount of time and a patient industry in the performance of a great and tiresome task for which those who use the volume can feel only admiration and gratitude. Its appearance may be said to mark an epoch in chemical petrology.

L. V. P.

2 *Nickel Deposits of the World*; by WILLET G. MILLER and CYRIL W. KNIGHT. Reprinted from the Report of the Royal Ontario Nickel Commission, 1917. Toronto. Pp. 285, with many illustrations, diagrams, maps, plans, etc.—This book presents, after a general introduction concerning the ores of nickel, etc., a complete and detailed account of the nickel deposits of the Sudbury, Ontario, district. This includes a description of the geology, the theories as to the origin of the ores and descriptions with plans and diagrams of the different important ore bodies. A section is also devoted to the Sudbury methods of mining. In the latter part of the book the nickel deposits found elsewhere in the world are more briefly described, the important deposit in New Caledonia being treated however at some length. The volume will become an important reference book concerning the past and present conditions of the nickel mining industry.

W. E. F.

3. *Annual Report of the Board of Scientific Advice for India for the year 1915-16*. Pp. 204. Calcutta, 1917.—The Board of Scientific Advice for India includes eleven gentlemen, with Mr. R. A. MANT, Secretary to the Government, as *ex-officio* president. There are six sub-committees and the subjects treated briefly in this, as in earlier, volumes of the series, extend over the entire range of science from chemistry to medicine. The great variety of topics discussed, and the economic importance of many of them, gives the volume an especial interest. This is perhaps especially true in geology, where the director of the Geological Survey, Dr. H. H. Hayden, gives some important notes in regard to the occurrence of metals particularly valuable under existing conditions. In mineralogy, an analysis may be noted by A. K. Banerji of the highly pleochroic manganese variety of pyroxene named blandfordite (1906). The specimen analyzed came from the Kachi Dhana mine and the results obtained are here noted:  $\text{SiO}_2$  52.18,  $\text{Fe}_2\text{O}_3$  20.26,  $\text{Al}_2\text{O}_3$  5.89,  $\text{MnO}$  3.60,  $\text{CaO}$  4.37,  $\text{MgO}$  3.25,  $\text{Na}_2\text{O}$  10.12 = 99.57.

## III MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Animal Mind; A Text-book of Comparative Psychology*; by MARGARET FLOY WASHBURN. Second edition. Pp. xii, 386. New York, 1917 (The Macmillan Co.).—In the nine years that have elapsed since the publication of the first edition of this widely used text-book, the science has made such progress as to demand a revision of the whole book and the rewriting of more than half of it. The book consists of a general survey of the field of Comparative Psychology, including a discussion of the evidences of mind, the mind of the simplest animals, sensory discrimination, specially determined reactions, modification of conscious processes by individual experience, and aspects of attention. The subject is well considered and logically presented.

W. R. C.

2. *Comparative Anatomy of Vertebrates*; by J. S. KINGSLEY. Second edition, revised. Pp. x, 449, with 406 figures. Philadelphia, 1917 (P. Blakiston's Son & Co.).—The first edition of this book has been generally recognized as the standard American text-book on Comparative Anatomy. This new edition has been thoroughly revised and several sections entirely rewritten, bringing the whole subject matter into harmony with the results of the most recent investigations. About sixty new illustrations have been added and several others redrawn. In addition to the glossary of systematic names included in the earlier edition an extensive list of Greek and Latin roots has been added to aid the student in remembering the meaning of the technical terms used by understanding their origin. The elimination of many unnecessary technical terms, some of which are rarely used by other authors, would have been of even greater advantage both to the student and to the teacher. For the aim of the book is to teach the facts rather than the terminology of the subject, and in this respect it stands first in its field.

W. R. C.

3. *A Short History of Science*; by W. T. SEDGWICK and H. W. TYLER. Pp. xv, 474. New York, 1917 (The Macmillan Company).—For nearly thirty years the students of the Massachusetts Institute of Technology have had the benefit of a lecture course on the history of science designed to present to them a broad general view of its evolution and thus to increase their interest in their scientific studies. The present volume is stated to be an outgrowth of this lecture course and “aims to furnish the student and the general reader with a concise account of the origin of that scientific knowledge and that scientific method which, especially within the last century, have come to have so important a share in shaping the conditions and directing the activities of human life.”

It is hardly necessary to state that the work of the authors



has been admirably done and presents a full and interesting account of the early beginnings of science and its development to recent times. It might well be studied carefully by every intelligent student. The reader will be again impressed with the remarkable acuteness of the great minds of the past in developing mathematical principles and their application to mechanics and astronomy. At the same time, of the science of the natural world but little was learned beyond the accumulation of certain obvious facts and observations. Even a mind so keen and original as that of Aristotle failed to realize what could be obtained from experience and as remarked by Bacon, "he first settled his system to his will and then twisted experience around and made her bend to his system."

This early history of science occupies the first two hundred pages, then follows the discussion of the birth of the new astronomy and the beginnings of modern natural science with the end of the fifteenth and beginning of the sixteenth centuries. The reader thus passes on to the period of the eighteenth century when the foundations of much of our present science were laid. The marvelous developments of the nineteenth century are so recent and so definitely involved in all study of science that the authors have naturally allotted only a single brief chapter to this part of the subject. A series of appendices present some definite matters of particular interest and the work closes with a convenient classified list of books of reference; this is highly valuable, although its value would have been increased by the addition of the date of publication in each case.

4. *The Mastery of Nervousness, based upon the Re-education of Self*; by ROBERT S. CARROLL, M.D. Pp. 346. New York, 1917 (The Macmillan Co.).—This book, recommended to persons suffering from nervous debility as "a practical help in the way back to health," is evidently an attempt to express in the guise of scientific truths a variety of experiences gained by a physician in an empirical way in the management of patients. The author exhibits an unusual facility in turning phrases; and it must be admitted that there are many grains of approved scientific wisdom hidden in the midst of semi-scientific platitudes. As a characteristic illustration of the verbosity the following will suffice: "What is the effect of such masses of high potency foods in the undeveloped digestive organism of the brain-working girl but to waste digestive force, to clog the organs of elimination, to slowly but surely corrode the vital machinery?" (p. 83). The author's psychological tenets may be questioned in more than one place by an expert in mental science; yet there are many clever suggestions in the volume. It may be doubted whether a truly nervous person could ever acquire the mastery to absorb the prolixity represented in these chapters.

L. B. M.

5. *An Introduction to the Chemistry of Plant Products*; by P. HAAS and T. G. HILL. Second edition; pp. xii, 411, 1917. New York (Longmans, Green and Co.).—The recent researches of Willstätter and his pupils, which have supplied exact and detailed information concerning the chemistry of chlorophyll and other plant pigments, more especially the anthocyanins, have been the occasion for the publication of a second edition of the *Chemistry of Plants Products* by Haas and Hill. The appearance of this revised and enlarged edition will be welcome to both botanists and chemists, but particularly to biochemists and plant physiologists who are now awake to the importance of plant chemistry and to many of whom this book has already proved indispensable. The chapter on pigments has been rewritten for the most part and numerous minor amplifications have been made, among which may be noted a description of Benedict's solution for the estimation of glucose. It is to be regretted that this opportunity was not taken to revise the treatment of the polysaccharides and particularly of the "compound celluloses." A reclassification of these substances based more strictly on chemical structure would do much to clear up the confusion occasioned by adherence to the traditional scheme derived from histological considerations. The hemi-celluloses, for example, are chemically more closely related to mannane and galactane than to cellulose. It is to be hoped that in a subsequent edition space will be found for a chapter on terpenes and essential oils, which constitutes the only serious omission from this admirable handbook.

HENRY D. HOOKER, JR.

6. *The Botany of Crop Plants*; by WILFRED W. ROBBINS. Pp. xix, 681, with 263 text figures. Philadelphia, 1917 (P. Blakiston's Son & Co.).—The strong emphasis now being laid on the economic aspects of botany, in the teaching of the subject, is exemplified by the present volume. It is divided into two parts. The first part, consisting of only 67 pages, is general in character and gives a condensed but excellent account of the organs and tissues of plants. The second part, occupying over 600 pages, is devoted to a more detailed consideration of the plant families of economic importance, especially those which have cultivated representatives in northern and temperate regions. Much information is included, relating not only to the botanical features of the plants discussed but also to the products which they yield—their nature, methods of preparation, and uses. A welcome feature of the book is found in the full citations of the literature, many very recent titles being included.

A. W. E.

7. *French Academy of Sciences*.—Dr. Charles D. Walcott, Secretary of the Smithsonian Institution, has recently been elected corresponding member of the French Academy.

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*“ Au savant Auteur des Traités de Physique et de Minéralogie ”*





THE

# AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XVII.—*The Failure of Cavities in Crystals and Rocks under Pressure*; by P. W. BRIDGMAN.

It is a matter of geological importance to know at what depth in the earth's crust to expect open cavities. The problem is one of some difficulty, involving the complicated interplay of a number of factors. The character of the stress, the nature of the material, the effect of temperature and the element of time all must be considered. An experimental study of the problem must begin, therefore, under as simple and well-defined conditions as possible. The best known experimental work has been by Adams,<sup>1</sup> who subjected several minerals in the form of blocks pierced with holes to high pressures exerted by a steel plunger, and observed the pressure at which the hole collapsed. The most obvious criticism of these experiments is that the manner of applying stress is such that its character cannot be at all precisely specified, since the blocks were enclosed in shrunk-on jackets of mild steel, which yielded as the block was distorted. In an attempt to avoid this element of ambiguity I repeated the experiment of Adams under conditions such that the stress could be precisely specified. The cylinders of rock containing a cavity were directly immersed in a liquid, and stress applied by subjecting the liquid to a high hydrostatic pressure. The collapsing stress so obtained was considerably lower than that of Adams. These results are not yet published, and will be briefly described in the latter part of this paper. Their charac-

<sup>1</sup> F. D. Adams, *J. Geol.*, 20, 97-118, 1912.

ter was not just what I had expected, and indicated that a systematic examination of the whole subject was necessary. Among other things, it was evident that a rock is too complicated a structure to give information on the various elements of the problem. The first experiments should obviously be performed on the homogeneous materials of which a rock is composed, that is, on individual crystals. But the preparation of individual crystals was at that time beyond my resources, and I allowed the matter to drop.

The whole problem was again forced on my attention by Dr. George F. Becker, who had for some time recognized its importance and had published results obtained by quite a different method. Dr. Becker's interest in the problem was so great that he was willing to undertake all the arduous work of superintending the preparation of the specimens, leaving to me the easy task of making the actual experiments. He procured an appropriation from the National Academy of Sciences, which, with the kind coöperation of Dr. Stratton, made it possible to secure the services of the optician of the Bureau of Standards, Mr. Clacey. He personally selected many of the specimens from the resources of the National Museum, which were at his disposal; specimens both of single crystals and of several rocks were prepared. Without his interest and assistance this paper would not have been possible.

This paper presents, then, results on the crushing of hollow cylinders of single crystals and rocks by the application of hydrostatic pressure to the external surface. The results are not of immediate geological applicability, because the conditions of the experiment are not duplicated in the field, but they suggest the nature of the effects to be expected under actual conditions. Apart from their geological interest, the results have an intrinsic interest from the points of view both of theory of elasticity and of the structure of crystals. Very few experiments have ever been made on the rupture of crystals; in fact the nature of the symmetry relations has not yet been worked out. From the point of view of the mathematical theory of elasticity the problem of the stress-strain relations in a crystalline cylinder under the conditions of the experiments seems never to have been discussed. I have been able to obtain the solution in several of the simpler

cases. The general nature of these results will be used in this paper but the detailed solution is reserved for the following paper.

This paper also contains measurements on the density of several powdered minerals (quartz, feldspar, and tale) after subjection to 30,000 kg/cm<sup>2</sup>. These measurements were directly suggested by the experiments on collapse of

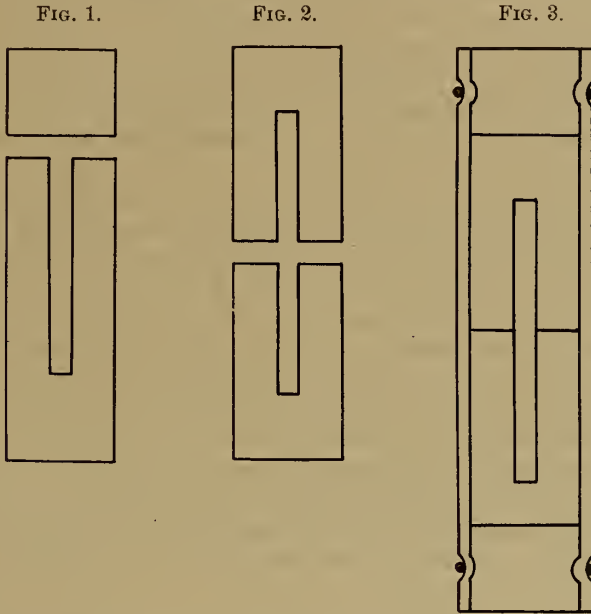


FIG. 1. Section of one form of specimen.

FIG. 2. Section of another form of specimen.

FIG. 3. Cylinder mounted in rubber tube with brass end pieces, ready for immersion in liquid and subjection to pressure.

cavities, and should allow a more significant geological interpretation to be attached to those results.

#### *Details of Experiment.*

The specimens were made in one of the two forms showed in figs. 1 and 2. The two parts were cut from contiguous parts of the same original crystal or rock. The two flat surfaces on which the two parts abut were made optically plane so that there should be as little distortion as possible when the two parts were pressed together.

This ensured that the stress conditions in a single uncut cylinder with an axial hole were reproduced as exactly as possible. The orientation of the two parts with respect to the original crystal was marked, and the two pieces were always, except at the very first, fitted together in the original orientation. This is an important point to which I will return. The outside surfaces of the cylinders were very nearly circular, and were polished. The inner holes were nearly but not quite coaxial with the outer surface, and were nearly but not quite round. During the test the inner hole contained only air at atmospheric pressure, except for a small device to be described later. The outer ends of the cylinder were ground flat, but were not polished.

A piece of soft rubber tubing was slipped over the outside of the cylinders and was tied to brass end pieces as shown in fig 3. Between the brass end pieces and the crystal was a thin piece of hard rubber or red fiber, to equalize any slight inequalities in the surface of the brass. The combination was then immersed in a liquid in a heavy steel cylinder and stress applied by producing hydrostatic pressure to any desired amount in the liquid. The function of the soft rubber tubing was to freely transmit pressure to the specimen and at the same time to keep the liquid from the surface of separation of the two cylinders. It is evident that under these conditions the entire outer surface of the cylinders is exposed to the same hydrostatic pressure.

The cylinder in which pressure was produced was of chrome-nickel steel, 8 inches outside diameter and  $1\frac{1}{8}$  inches inside diameter. Pressure could be raised to 12,000 kg/cm<sup>2</sup> with this apparatus. The details of construction and methods of measuring pressure have been previously described.<sup>2</sup> A smaller cylinder in which a few tests were made permitted a maximum of 24,000 kg/cm<sup>2</sup>.

The following measurements were made. The outside diameter of each piece at the two ends and the middle and at angular intervals of 30° was measured to 0.0001 inch with a micrometer. Six measurements of the outside length were also made with the same micrometer. The depth of the hole was measured with a depth gauge to 0.0001 inch; this measurement was always somewhat unsatisfactory because the bottom of the hole might be

<sup>2</sup> P. W. Bridgman, Proc. Amer. Acad., 49, 626-643, 1914.

irregular. The average diameter of the hole was measured by weighing the mercury which exactly filled it. By using the optically plane surface of the other piece of the crystal to rub off any mercury which might rise in the meniscus above the surface, it was particularly easy to get the hole always exactly full. All of these measurements were made at atmospheric pressure, after each exposure to pressure. The procedure was to expose the cylinder to a known pressure for a known time, take the apparatus apart, make all the measurements above, and set the apparatus up again and expose to a higher pressure. These measurements simply show, therefore, whether there has been any permanent deformation produced by the pressure. It would have been most desirable also to have made all these measurements while pressure was applied, and so obtain the strain for a given stress. But to do this would have been of excessive difficulty. By the use of a simple device it was possible, however, to obtain rough measurements of the diameter of the hole while under pressure. A little disc of solder mounted on a brass rod to facilitate handling and to keep it in position was turned in the lathe so as to be initially a push fit for the hole. This was placed in the hole during the application of pressure. The effect of pressure is of course to diminish the size of the hole. The solder disc offers inappreciable resistance, and because of its low elastic limit is permanently deformed to very nearly the minimum diameter reached by the hole. After application of pressure the disc may be removed and the minimum diameter obtained by direct measurements.

Collapsing tests of this kind were made on two specimens of quartz, two of tourmaline, and one each of calcite, barite, feldspar, andesite, porphyry and glass. Negative crystals of quartz were also tried. These experiments will now be described in detail.

*Quartz.*—The first specimen was in the shape of fig. 1, a long hollow cylinder with a shorter solid cap. The dimensions were: Outside length of hollow part 4.5 cm., external diameter 2.0 cm., inside diameter 0.36 cm. This cylinder was subjected to ten applications of pressure, beginning at 2000 kg/cm<sup>2</sup>, and continuing at approximately equal intervals to 11,500 kg. Each application was for ten minutes. The first noticeable effect of pressure was at 3000 kg. and was a chipping off of slivers from the

outside surface where the two pieces join. This was due to failure to orient the two pieces in their natural position. The proper orientation was found after a few trials, and after this the chipping almost entirely ceased, even up to the maximum pressure. The mathematical discussion shows that plane cross sections of the crystal warp under pressure, and explains therefore, the necessity for observing the original orientation. All later specimens were marked when cut from the original crystal so as to allow the correct orientation, but this precaution was not taken with the first specimen.

At higher pressures, beginning at about 6000, signs of failure at the interior appeared, increasing in intensity up to final complete rupture. These signs of failure were of two kinds. In the first place, there was a system of fissures in both the hollow piece and the cap. In the hollow piece these began as a set of cracks near the inner mouth of the hole, separated by an angular interval of  $120^\circ$ , corresponding to the symmetry of the crystal, and penetrating a short distance into the body of the crystal at right angles to the surface. At higher pressures these cracks became more numerous and penetrated to a greater depth, inclining toward the axis at the greater depths. This system of cracks had its counterpart in the solid cap, but the penetration here was always to only a slight depth. The cap also showed cleavage in the interior on surfaces at right angles to the axis, a phenomenon for which there was no counterpart in the hollow piece. These systems of cleavage planes are apparently connected in some way with end effects due to imperfect matching together of the two pieces. A mathematical discussion of these end effects is too difficult to be attempted.

Final failure of the crystal took place in a way entirely unconnected with these cleavage planes. At pressures of 7500 and higher minute flakes scaled off the inner surface, leaving it rough. This flaking proceeded at an accelerated rate at higher pressures, at 10,500 amounting to an enlargement of 3% of the volume. On the next application of pressure, to 11,500, however, the flaking off was so extensive that the upper end of the hole was eroded away to three times its original diameter, and the entire hole was tightly packed with a very fine quartz sand. The density of this sand was of course much less than that of the original solid quartz; so that when the hole had

become sufficiently large, the sand was in a position to exert pressure on the interior walls, and in this way prevented further disintegrating action. The eroded cavity was very irregular in outline; for the greater part of its depth it was entirely unsymmetrical, being merely an angular extension on one side of the original circular cavity. This is as one would expect; an angle once formed at any part of the surface would be relatively unstable, and erosion would proceed more rapidly here. There was no apparent relation between the axis of the eroded cavity and the three systems of cleavage planes mentioned.

The outside of the cylinder was entirely unaffected by the erosion of the interior; there was no perceptible change of dimensions, either diameter or length, and the cracks were entirely confined to the interior. This is true of many of the other specimens tried. A photograph of this cylinder is shown in fig. 4.

The second specimen of quartz was cut in two symmetrical pieces as in fig. 2. The two parts were always so put together as to observe the original orientation in the crystal. It was subjected to pressures of 4000, 6000, 8000, 10,000, and 12,000 for 10 minutes each, experience with the first crystal having shown that applications of pressure at 1000 kg. intervals was not necessary. The results were very similar to those with the first specimen. The same system of funnel-shaped cracks separated by  $120^\circ$  was observed, but they were not so prominent, indicating that the fitting together was better, and the end effects, therefore, not so important. The same flaking-off of the inner surface was observed, first noticeable at 8000, and resulting in complete disintegration of the interior at 12,000. A photograph of one of these cylinders is shown in fig. 5. There was no permanent change of outside dimensions, no evidence whatever for flow, and the cracks did not reach to the outside. The density of the sand which packed the cavity was 1.43 against 2.65 of the original quartz; the interstitial space was therefore nearly 50%.

The stress required to produce rupture of these crystals is much higher than might be expected, and the manner of rupture is apparently not like that contemplated in any theory of rupture, nor is it such as would be suggested by the elastic deformation before rupture. I have worked out mathematically the nature of the stress-strain relation,

FIG. 4.



FIG. 5a.

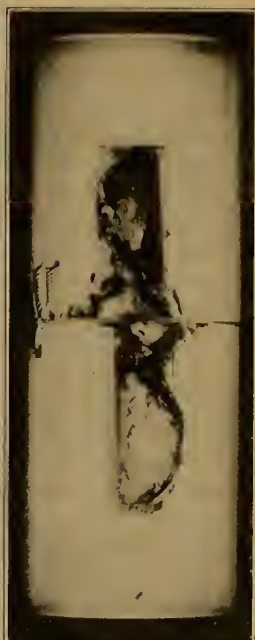


FIG. 5b.



FIG. 5c.

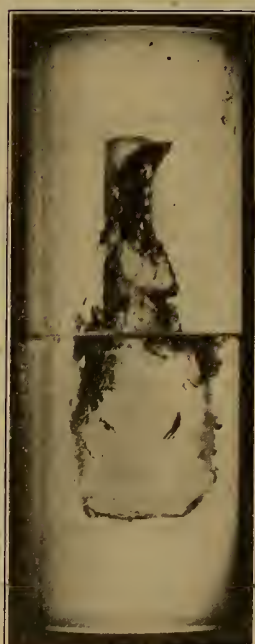


FIG. 4. The first quartz cylinder after failure under 12,000 kg.  
FIG. 5 a, b, c. Three views of the second quartz cylinder after failure under 12,000 kg.



and shall assume here the results of the analysis, which will be given in detail in the following paper. Let us consider the ideal case of an infinitely long hollow cylinder subjected to hydrostatic pressure over its external surface. If the material is isotropic the system of stresses and strains is well known, and is very simple. Every plane cross section of the cylinder remains plane, and the distortion consists merely of a shortening of every radius without any change in the angle between any two radii. The most intense stress and strain are both at the inner surface. The stress at the interior is a compression on planes including the axis and the radius, amounting to approximately twice the external hydrostatic pressure. The amount of strain depends of course on the elastic constants; its nature is an elongation of the fibers along the radius at the inner surface (a paradoxical result) and a numerically much greater shortening of the circumferential fibers.

The elastic deformation in a crystal of quartz is much more complicated. The most important difference compared with the isotropic case is that plane cross sections do not remain plane, but become warped, the warping of course satisfying the conditions of symmetry and repeating itself every  $120^\circ$ . The warping with cylinders of the dimensions above, the inside diameter of which was 3.6 mm. and the outside diameter 2.0 cm., is a maximum at about 2.7 mm. from the axis. The shearing strain due to the warping is a maximum at the inner surface, however, and may amount to 35% of the maximum circumferential compression. In addition to the warping there are further distortions in the plane perpendicular to the axis. The radial displacement is not independent of the orientation in the crystal, but fluctuates with a period of  $60^\circ$ . The strain resulting from this fluctuation is only 4% of the maximum. Furthermore, there is a displacement along the circumference with a period of  $60^\circ$ , the resulting strain being only about 1% of the maximum. This complicated set of displacements results in a much more complicated system of stresses than in an isotropic solid. The most important of these additional stresses is a shearing stress along the axis in planes containing the axis and radius, rising at the inner surface to a maximum of 47% of the external pressure.

Numerical computation shows that with quartz of the dimensions above (inside diameter equal 1, outside diam-

eter equal 5.5) using the values of the constants found by Voigt (see Love's *Elasticity*, page 157), the displacements, stresses and strains at the inner surface under an external pressure of 12,000 kg. are as follows: radial displacement 2.9% of the original radius, circumferential pressure 25,000 kg/cm<sup>2</sup>, axial shearing stress 5700 kg., radial elongation 0.5%, circumferential compression 2.9%, shearing strain between radius and axis 0.97%. The inapplicability of the ordinary criteria of rupture is obvious. Under ordinary conditions of tests in one-sided compression, the crushing strength of quartz is about 1200 kg/cm<sup>2</sup>. A stress 20 times as great, with corresponding larger values of shearing stresses and strains, was supported by the crystal above, and then rupture took place in a manner different from that to be expected.

The measurements of the change in internal dimensions already mentioned were not in conflict with what is to be expected from the mathematical analysis. The measurements were only rough, giving the order of the effect. Those on the second cylinder were much more consistent than those on the first, and gave a radial displacement of 2.7% under 12,000 kg. against 2.9% calculated above. The agreement is much better than could be expected. The accuracy of the measurements was of course not great enough to permit detection of the small oscillating effect superposed on the average radial displacement. The measurements of radial displacement furthermore showed that the relation between displacement and stress remains linear up to the point of complete rupture, thus justifying the use of the ordinary mathematical analysis of elasticity. This is of course only what is to be expected from a substance of such small viscosity as to show no flow under these very high stresses.

*Tourmaline.*—Both specimens were of approximately the dimensions of the second quartz specimen. They were cut perpendicularly to the axis. The first specimen was colored, ranging from light green through purple to dark brown, but was sufficiently transparent so that all the inner defects could be seen. The crystal was full of small striae parallel to the axis, and also contained many surfaces of internal reflection, which were probably minute cracks. These were scattered at random through-

out the crystal. This specimen was exposed to 3000, 5000, 7000, 10,000 and 12,000 kg. for 10 minutes each. At 12,000 there was appreciable flaking-off of the inner surface, similar to that of quartz at lower pressures. But there was no extensive erosion, so that tourmaline appears as a much stronger crystal than quartz. At 7000 and 10,000 minute longitudinal splinters were separated from the inner surface, but this ceased at 12,000. Very minute cracks were formed in the polished faces at the ends of some of the striæ. At 12,000 cracks at an angular separation of  $120^\circ$  had started, like those formed in quartz at 6000, but they were small, and there was none of the funnel-shaped appearance of the quartz. It was a surprise that there was no connection between the new cracks which appeared and the original flaws. There was also a system of cracks unlike those of quartz, cracks in planes perpendicular to the axis, reaching in some cases to the outer surface. One such crack was situated diametrically below the end of the hole. No phenomena of flow could be detected.

The behavior of this cylinder, as well as that of the quartz cylinder, was peculiar when compared with ordinary substances. Iron and copper, for example, when in the form of cylinders like this,<sup>3</sup> will also stand a much higher stress than indicated by ordinary compression tests, but they do it by a process of accommodation. Under stress they flow viscously until the grains have become properly arranged to stand a higher stress. But the quartz and tourmaline cylinders show no flow, and the only analogy to accommodation is flaking-off. I found it most difficult to see how flaking-off of the inner surface could result in enhanced resistance to rupture, and could think of no explanation except that the effect of time had been neglected. The same cylinders of tourmaline were therefore exposed again to 12,000 kg., this time for two hours. If tourmaline were like an ordinary metal, no effect would be produced by the second application of the maximum stress; there would be no further cracking or flaking-off, because the elastic limit had been raised by the previous application of pressure. But the effect was the exact opposite. Under the longer duration of stress the cylinder failed completely, being packed tightly full with an impalpable sand. The region of erosion of

<sup>3</sup> P. W. Bridgman, Proc. Amer. Acad., loc. cit.; Phys. Rev., 34, 1-24, 1912.

one of the cylinders, which was in form an elongated ellipse with pointed ends, extended entirely across the cylinder. The outer surface of this piece had in places been displaced bodily into the cavity. In the other piece, however, the erosion was much less extensive, and the outer surface had received no permanent change. In this second piece the most extensive erosion was not at the mouth of the hole but was nearer the bottom, showing that the flaking-off is not an end effect. This remark is confirmed by many other observations; the flaking-off has no relation to the end effect, and may take place at any point on the interior surface.

The second specimen of tourmaline was entirely opaque, so that no intimation could be obtained as to its internal structure; there were no flaws apparent in the original piece. The tests on this specimen were especially designed to find the effect of the element of time. It was exposed to 5100 kg. for  $28\frac{1}{2}$  hours, to 6630 for  $46\frac{1}{2}$  hours, to 8170 for  $38\frac{1}{2}$  hours, to 9500 for  $38\frac{1}{2}$  hours, and to 12,200 for  $40\frac{1}{4}$  hours. This specimen was much stronger than the first. Up to and including 9570 there was practically no effect. The edges of the mouths of the holes splintered a little, as they always do, because of imperfect register of the two parts, and there were a few barely perceptible flakes from the inside. At 12,200, however, the failure of the interior was complete, as it had been for the other specimen. There was no flow or permanent alteration of the outside. The average density of the sand with which the eroded cavity was packed was 2.15, against 3.09 for the original crystal. The interstitial space in the sand was therefore about 30%.

The change in internal dimensions of the cavity, found from measurements on the solder plugs, was at the rate of 0.65% per 12,000 kg. for the first, and 0.74% for the second specimen. Using Voigt's values for the elastic constants of tourmaline (see Love, page 157) the theoretical value is, about 0.90%. Tourmaline varies greatly in its properties; the discrepancy may therefore be due to difference in the specimens. Here again, as for quartz, the relation between distortion and stress remained linear within the errors of measurement, which were large.

*Calcite.*—The interest in this material lies in its extraordinarily easily developed planes of cleavage, whereas both quartz and tourmaline show practically no such

planes. One might expect the cleavage planes of calcite to bear some especial relation to its manner of rupture.

The specimen was in the form of a single cylinder with a cap, of the same dimensions as the first specimen of quartz. The axis of the cylinder was supposed to be parallel to the trigonal axis, as were quartz and tourmaline, but subsequent examination showed that the axis of the cylinder was inclined at about  $7^\circ$  to the axis of the crystal. The cleavage planes in the original piece were so strongly developed that at first it seemed of little use to attempt the experiment, but the results only confirmed the results with other specimens that original flaws have no effect on the manner of rupture under these special conditions. Apparently the friction produced by the high pressure is sufficient to prevent any slipping on original planes of fracture.

Three applications of pressure were made, to 500, 1000, and 1500 kg. for 10 minutes each. The most marked effect of pressure was a great increase in the number of internal cleavage planes. The increase was so great as to make the substance partially translucent instead of transparent. The development of cracks put an end to the experiment, the crystal falling apart in handling at atmospheric pressure while preparing for the next test at 2000 kg. The effect of stress on the cavity was not marked, but after 1500 there was unquestionably some flaking-off of the interior, just as for quartz and tourmaline at higher pressures. The material also showed a tendency to slip into the cavity along cleavage planes, but full accomplishment of this tendency was prevented by the geometrical configuration, the parts affording each other mutual support. The inner surface of the wall of the cavity, to a depth of several millimeters, was rendered entirely opaque, evidently because of the grinding together of the material as it was carried toward the center on convergent cleavage planes. The slip produced a definite figure on the plane surface, as shown in figure 6. Within the triangle the development of cleavage planes was much more pronounced than outside of it.

Slip was accompanied by permanent change of dimensions, one of the few examples of it found. The outer diameter decreased from 0.7331 to 0.7310 inches, and the inner diameter by 2.3%. The slipping was in such a direction as to produce an increase of external length from

1.5894 to 1.6032 inches. The effect of slip on length was irregular, however, at 1000, there being a slight decrease instead of an increase. At 1000 the diameter was little changed, nearly all the effect coming between 1000 and 1500.

It was not possible to make measurements of the internal diameter under pressure with the solder plugs, the effect being too small. In spite of its easy cleavage and

FIG. 6.

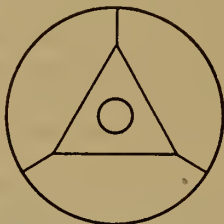


FIG. 6. Slip figure on plane face of calcite cylinder after exposure to 1500 kg.

mechanical softness, the elastic constants of calcite are high, its cubic compressibility, for example, being the same as that of quartz.

Apart from cleavage effects, these results show that in calcite there is present the same mechanism of rupture by flaking-off as was shown by quartz and by tourmaline.

*Feldspar*.—This was a white microcline feldspar, prepared in the same form and dimensions as the second specimen of quartz. Feldspar crystallizes in the triclinic system; quartz, tourmaline, and calcite are all trigonal. This material is of course opaque, but there were no evident flaws in it.

It was exposed to 3000 kg. for 40½ hours, to 5000 for 4 hours, and to 3000 again for 15½ hours. There was no noticeable change of appearance after the first application of 3000; no fissures appeared, and there was no change of dimensions, but a very minute quantity of fine dust had flaked off from the inner surface. After exposure to 5000 the disintegration of the interior was complete, the hole being packed with fine sand, as we have come to expect. The average density of this sand was 1.77 against 2.57 of the original crystal. The shape of the eroded region was more symmetrical than usual,

being a well-marked rhombus in section, with evidently some connection with the crystalline system. The long axis of the rhombus was parallel to the direction of the white streaks in the original crystal. This substance is unusual in that no fissures whatever accompanied the erosion. Apparently, therefore, the mechanism of rupture by flaking-off is entirely independent of the mechanism of formation of cracks. As usual there was no change of external dimensions.

After exposure to 5000 it was exposed again to 3000, to see whether the flaking-off would continue at a lower pressure after having started at a higher pressure, and also to find whether loss of circular cross section in the cavity would result in easier rupture. There was practically no effect from the second application of 3000; a slight quantity of dust had flaked off the inner surface, but no more than on the first trial.

The change of internal diameter as measured by the solder plugs was 0.2% per 1000 kg., which is of the same order as for quartz. Apparently the elastic constants of feldspar have not been measured, so there is no chance to compare this value with calculated values.

*Barite.*—This was a translucent specimen with numerous flaws, which however did not affect the behavior under pressure. The specimen was of the form and dimensions of the second specimen of quartz. This was exposed to 1000 kg. for 4 hours, to 2000 for 17 hours, to 3300 for 6 hours, and to 11,400 for 39 hours.

The first two applications of pressure had no perceptible effect. At 3300, however, the cavity was partly disintegrated in the usual fashion, but not tightly packed with sand. The eroded region was a rhombus in section, rather more nearly square than for feldspar, and around this was another rhomboidal region, equal to the diameter in width, within which the original translucent material had changed to an opaque white like marble, evidently due to internal slip. There was no change of external dimensions.

It was evident that a pressure only slightly above 3300 would produce the usual complete disintegration, and occasion was therefore taken to answer a question suggested by much of the previous work, namely, what happens to the sand in the cavity when pressure is raised very far above the disintegrating pressure? It is hardly

conceivable that interstitial spaces as large as 50 or 30% will persist, but on the other hand, will the powder fuse to a compact mass? The conditions here were exceptionally favorable for getting some idea of the answer to this question since pressure could be raised in the available apparatus to more than three times the disintegrating pressure. If fusing by pressure alone is ever to be expected, there is a good chance to find it here. For it is to be considered that the manner of formation of the sand, by automatic flaking-off of the solid material inside a closed cavity, ensures that the grains shall be clean. This is an important point, and one that is most difficult to obtain under ordinary conditions of experiment.

In an attempt to produce fusion of the powder, pressure was maintained at 11,400 for 39 hours. The crystal was thereby changed in appearance throughout the entire mass to the opaque white of marble, showing that slip had spread throughout the entire substance. At the inside there was a core of fine sand which had not fused together, but could readily be picked out with a wire. The average density of the entire cylinder was decreased somewhat, as had also the external diameter. In the marbleized region, there were no cracks except a few fine fissures near the core itself. Obviously, then, this material may suffer flow without losing its mechanical coherence, but if the particles have ever been separated too much, as when the grains of sand are formed, even a relatively high pressure will not cause them to fuse together. The core of sand had lost all rhomboidal shape, and was now ellipsoidal with angular ends. Small fissures radiated from the ends, in appearance extremely like lines of force about a bar magnet.

In spite of this experiment, the conviction is hard to escape that it must be possible to weld together the fragments of a solid merely by bringing them into contact, provided they are perfectly clean. In this connection Langmuir's<sup>4</sup> recent work on the significance of the rôle played by adsorbed layers of a gas only one molecule deep is most suggestive. The particles of sand formed from the barite appeared by microscopic analysis to be of the order of 0.001 mm. in diameter. A very rough calculation shows that the air originally in the cavity was much more than sufficient to cover all the grains of sand

<sup>4</sup> I. Langmuir, *J. Amer. Chem. Soc.*, 38, 1145, 1916.



with molecules one layer deep. As far as any present evidence goes, it is not unreasonable to suppose that the sand formed by stress in a cavity originally entirely free from gas would ultimately be fused together again to a coherent mass.

This completes the experiments on single crystals. As being of geological interest, several experiments were made on rocks and other substances.

*Porphyry.*—The two cylinders of this material were of approximately the same shape and dimensions as the second quartz. They were exposed to 1000, 2000, 3000, 4000, 6000, and 7000 kg. for 10 minutes each. Up to 4000 there was no perceptible effect; at 6000 a slight flaking off was perceptible at the mouth of the hole, and at 7000 failure was complete by flaking-off. The eroded regions were roughly triangular prisms, the prism in one piece being a prolongation of that in the other. There was no viscous flow of the outside of as much as 0.0001 cm. and no cracks whatever in the solid mass, even in the neighborhood of the eroded region. The mean density of the sand was only 0.31. Doubtless if the pressure had been continued longer, the sand would have become more tightly packed.

The elastic decrease of diameter of the inner hole was at the rate of 0.14% for 1000 kg. This is considerably less than that of quartz, showing that probably the mean elastic constants are considerably higher. Failure by erosion occurred at a lower stress than for quartz, however. Of course this is just as one would expect; a rock would have elements of weakness not possessed by an individual crystal.

The stress at the inside at the rupture point may be computed for an isotropic substance without knowing the elastic constants, and was approximately 14,000 kg/cm<sup>2</sup>. Engineering tests on porphyry give a compressive strength under ordinary one-sided crushing tests varying from 1000 to 2600 kg/cm<sup>2</sup>. The excess above the value computed from ordinary tests is therefore high, although not so extreme as for quartz.

*Andesite.*—This was a very fine-grained and perfect specimen, of the form and dimensions of the second specimen of quartz. Dr. Becker remarked that the results would be of particular significance because the composition of this rock is the mean composition of the crust of the earth.

Andesite was exposed to 1000, 2000, 3000, 4000, 6000, and 7000 kg. for 30 minutes each, then to 7000 again for 9 hours, and then to 8000 for 5½ hours. At 6000 the flaking-off of the interior was just perceptible. A most interesting effect in connection with this flaking-off was observed. The brass rod supporting the solder disc inside the cavity assumed a curious whitish appearance, suggesting chemical action with gaseous fumes. Examination with a high-power microscope showed, however, that the whitish coating was a covering of minute splinters of the rock, which had been projected with such violence when they had flaked off as to penetrate some distance into the solid brass and stick themselves in position.

Under the first application of 7000 the flaking-off was greater than at 6000, but still only slight. The brass rod was peppered with splinters as before. The second application of 7000 produced still more flaking-off, but not nearly as much as I had expected from the longer time interval. At 8000 the disintegration of the interior was complete. The eroded region was much larger than in porphyry, and was in shape an irregular pointed ellipse. There was no flow whatever of the outside, and no cracks in the solid mass, even in the immediate neighborhood of the hole. The average density of the sand was 1.14 against 2.69 of the original rock. The interstitial space was therefore more than 50%.

Microscopic examination of the sand showed that the pieces were most irregular in shape and of great range of size. Furthermore, coincidence in one piece of the light and dark material of which the rock is composed is extremely common, showing no tendency for each flake to be all of the same composition. It is evident, therefore, that the flaking-off is something which has no particular connection with structure, at least when it is on as fine a scale as in this rock. The same remarks apply to porphyry.

The compressive strength of basalt, which is closely allied to this fine-grained andesite, is given in engineering works as varying from 1000 to 3200 kg/cm<sup>2</sup>. The compressive stress at the interior of this specimen when failure took place was 16,000 kg.

*Granite and Limestone.*—These materials formed the subject of the preliminary experiments mentioned in the introduction; they were much rougher in character than

those just described. Both of these specimens were obtained for me by Professor R. A. Daly, who first aroused my interest in this subject.

The granite was gray granite, cylindrical in form, 2 inches long, 1 inch outside diameter, pierced for its entire length with a  $\frac{1}{4}$ -inch hole. The ends were closed with flat caps of hardened steel, a rubber tube was slipped over the whole, and it was completely immersed in a liquid and exposed to a pressure of 5000 kg. for 1 hour. The cavity was completely disintegrated into a closely packed sand, just as the other specimens already described. The outline of the eroded region was that of a pointed ellipse. The outside had also become slightly elliptical, thus showing some slight flow. There were no cracks in the non-eroded region.

The cylinder of limestone was of the same dimensions as the granite, and the manner of treatment and the results were the same. These two experiments, of course, gave no idea of the minimum pressure at which the cavity would close, but did show conclusively that Adam's value of 11,000 kg. for the pressure of collapse of granite is too high.

*Negative Quartz Crystals.*—One of the questions raised by these experiments is as to the effect of the plane of separation of the two parts of the specimen. It is not possible by any perfection of workmanship to secure such precise register of the cavities in the two parts of the specimen that one is exactly a continuation of the other, and disturbing effects at the surface are therefore to be expected. The mathematical solution would indicate infinite stresses and strains, that is rupture, in the neighborhood of any abrupt discontinuity, no matter how minute, and as a matter of experiment, the mouths of the cavities did always splinter somewhat. If experiments could be made with the natural cavities which occur in some minerals this objection would not be present.

Dr. Becker placed at my disposal a number of singularly perfect negative crystals of quartz, which he had selected with considerable labor from the resources of the National Museum. Some of these contained bubbles of gas, and were therefore adapted to this purpose. Two of these were exposed to 18,000 kg. under kerosene for  $4\frac{1}{2}$  hours. No effect whatever was observable in the neighborhood of the negative crystals, and there was no dimi-

nution in the size of the bubble, indicating that there had been no permanent change of dimensions. A disturbing question naturally arises here: did not the liquid in the cavity afford important support to the walls from the inside, after the external pressure had slightly decreased the size of the cavity? But such cavities are usually filled with  $\text{CO}_2$ , and in this case the support would be quite inappreciable, because of the high compressibility of this gas. However, even if the cavity had been initially entirely filled with water, a simple computation shows that the maximum internal pressure would have been of the order of 1000 kg., which may be neglected in comparison with 18,000.

Some parts of the original quartz crystals remote from the negative crystals were smoky in appearance, and under the microscope, before the application of pressure, were seen to contain minute bubbles of quite irregular shape. In these regions a positive effect was produced by pressure, the appearance being that the interior of the bubbles had been eroded and tightly packed with sand, exactly as had the larger cavities in the cylindrical specimens. The same effect had been previously observed in a small region in the end of the second quartz specimen.

The conclusion must not be drawn that the flaking-off process is an end-effect connected with the unavoidable surface of separation, for this flaking-off was repeatedly observed at all points of the cavity, irrespective of the distance from the mouth. For instance, the fine splinters referred to in the experiment on andesite were distributed quite uniformly over the entire length of the brass wire. The cracks, however, which frequently appear, and are usually especially prominent near the surface of separation, may in the majority of cases be intimately connected with imperfect joining.

With respect to flaking-off, the conclusion seems to be that the state of polish of the surface is an important factor; if the polish is complete down to molecular dimensions, as it was for the negative crystals, the tendency to flake off is much less than if there are grosser irregularities in the surface structure. The polish must be very complete indeed to produce an appreciable effect; no artificial polish that could be applied to the interior of the specimens above had any effect. The first specimens were left rough after drilling the hole, but the later ones were polished.

*Glass.*—I have already referred to former experiments in which a sealed glass capillary had been exposed to 24,000 kg. without effect, while cavities in copper have been squeezed out of existence by 10,000 kg. Some essential difference between crystalline and non-crystalline materials suggested itself, which it was the partial purpose of these experiments to examine. A control specimen was therefore made of optical glass, exactly like the second specimen of quartz, and it was subjected to the same sort of treatment. It was first exposed to 5100 kg. and pressure immediately released, with no effect whatever. This confirmed the result with the capillary tube, that stresses much higher than those reached in ordinary compression could be sustained if the material is so arranged as to afford itself mutual support. After this test at 5100 it was a serious question how to proceed. Previous experience had shown that glass is exceedingly likely to receive some sort of internal strain under pressure so that on the second application of pressure it is much more likely to rupture than on the first. If a complete series of tests were made, as with quartz, there was danger that this effect would obscure the results, whereas if pressure were at once raised to the maximum and rupture found to have been produced, there would be no way of telling at what pressure rupture had occurred. I optimistically chose the second method and lost.

Pressure was raised to 12,000 kg. and immediately released. Rupture was complete. Failure to reproduce the result found with the capillary was doubtless due to incomplete alignment of the two halves. The results were nevertheless instructive in that the manner of rupture was entirely different from that of quartz. The entire mass of glass was filled with haphazard cracks, many of them running through to the outside. Each crack was curved and changed direction many times in a complicated fashion, quite unlike the simple cracks in the crystals. These cracks were more numerous at the inner wall, where they interpenetrated each other so extensively as to produce an apparent erosion of the interior like that of the minerals. But the eroded fragments were large instead of an impalpable powder, and in places the original polish of the walls of the cavity was still intact. It is therefore probable that the mechanism of rupture by flaking off was entirely absent in this specimen of glass.

*Density of Compressed Sand.*

The results already described show that in all probability large cavities cannot exist at considerable depths in the earth's crust, but the walls will disintegrate, packing the cavity with fine sand. The question as to the existence of microscopic cavities in this sand and the average density of material which has been ruptured was still untouched, and I therefore made a few further simple experiments in an attempt to partially answer' this question.

Quartz, orthoclase feldspar, and talc were experimented on. These were reduced to sand in a mortar, and the quartz and feldspar were separated into various sizes with sieves of 40, 60, 80, and 120 meshes to the inch, and then cleaned by washing them with HCl and distilled water and dried by moderate heating in the air. The powder was placed in thin cylindrical copper boxes with copper covers, 1.5 cm. diameter and 1.5 cm. high, and subjected to compression between pistons of hardened steel in a hydraulic press. Lateral expansion was prevented by a very heavy ring of chrome-vanadium steel. The intensity of pressure in these experiments was 30,000 kg/cm<sup>2</sup>. The pressure was not strictly hydrostatic, but this was no objection in view of the negative nature of the results. Under the conditions there must have been considerable grinding past each other of the grains, which is more conducive to fusion than pure normal pressure.

As far as fusion goes, the results were entirely negative. Talc, as well as quartz and feldspar of different sizes, pure and mingled together could not be fused to a homogeneous mass. All of these materials, however, could be pressed together into a cake coherent enough to handle; it was a surprise that the cake of talc was not especially more coherent than that of quartz. The average density of the cake was determined in the standard way by weighing under water, and is of some significance. The quartz ranged in density from 2.572 to 2.584, the original material being 2.65. There was a tendency for the cakes formed from originally larger grains to be of higher density, probably because a larger proportion of the total volume was occupied by unfractured material. The smallest density of all, 2.572, was that from a mixture of two sizes of sand, one passing through 40 but not 60, and the other through 120. The fragments into which

the sand was reduced after compression were entirely irregular and of all sizes from a few hundredths to fractions of a thousandth of a millimeter. It is therefore obvious that any calculation of the density to be expected from the average density of closely piled spheres is inappropriate.

A single experiment on pure feldspar gave a density of 2.47, on pure talc 2.616, and on a mixture of equal parts by weight of quartz and feldspar sand, 2.520. The initial densities of feldspar and talc were 2.57 and 2.76. The average interstitial spaces were, therefore, 2.6, 3.9, and 5.2% in quartz, feldspar, and talc respectively. The high value for talc was a surprise, but it receives possible explanation from the remarks of the next paragraph.

The powder after compression has been referred to as in the form of coherent cakes; this requires considerable qualification. It was never possible to obtain a single coherent button of the dimensions of the containing box, but this button always broke up spontaneously into laminae, slightly cupped, the faces of the laminae at right angles to the direction of pressure. These laminae varied from small scales a few tenths of a millimeter thick to comparatively large plates 2 mm. thick and nearly 1.5 cm. in diameter. Density determinations were made on the largest coherent pieces. Spontaneous break-up of the buttons into laminae was always a comparatively slow affair, and might occupy 10 or 15 minutes, the button slowly puffing up with a crawling simulation of life. The force involved in this break-up was considerable, and was frequently sufficient to pull apart the copper box.

This phenomenon is not what one would at first expect, elastic recovery from stress being immediate, and it seems to me of considerable importance for an interpretation of the other results. A plausible explanation seems to me as follows: Under the intense stress, comminution into minute fragments proceeds so far that there are few actual voids left, but many spaces that would be void under no stress are closed by the elastic deformation of the walls. The majority of such spaces are probably lens-shaped, like the erosion cavities in the crystals above, and these are squeezed flat by the pressure. But on the surface of each grain there is a film of adsorbed air, which is squeezed extremely thin by the pressure, but nevertheless keeps the walls of the cavities from actual molecular

contact, for otherwise there would be welding of the grains. When pressure is released, the lens-shaped cavities tend elastically to recover their form, but are prevented by the air films, which in such excessively thin layers will act like an extremely sticky and viscous glue. The slow viscous yield of these thin films of air accounts for the visibly slow break-up into laminae.

This explanation suggests that the figures given above for the densities of compressed powders must be considerably less than the density when actually under pressure, and that for example the interstitial space in quartz sand under high pressure may possibly be considerably less than 2.6%. It is certain that 2.6% represents an upper limit. I made an attempt to find the actual volume of the sand while under pressure from the dimensions of the copper box, but unsuccessfully.

When these considerations are applied to geology, there are further complicating elements. In a cavity surrounded by solid walls the process of erosion by flaking-off may well be stopped long before the sand has acquired the mean pressure of the surrounding rock; this would allow a larger interstitial space than might be computed from the mean pressure.

#### *Discussion and Summary.*

Cavities in the materials dealt with in this paper, which may be broadly characterized by the property of brittleness, exhibit a method of failure under high compressive stresses not shown by ductile materials like the metals. This method consists in the shooting-off of minute fragments with considerable violence from the walls of the cavity. The frequency, and probably the velocity, of projection varies with the pressure, the rapidity of disintegration becoming greater at higher pressures. This mode of disintegration is shown both by rocks and by single crystals; in rocks the splinters show no relation to the boundaries between chemically homogeneous parts of the mixture, and in the crystals there is no obvious connection with the crystalline symmetry. The rate of change of speed of disintegration with pressure may vary greatly from substance to substance, being comparatively small for quartz and high for tourmaline and andesite.



The phenomenon of rupture by flaking-off is independent of other phenomena accompanying high stress. Some substances develop cracks at the same time that they erode; the number of cracks may be great as in calcite, or small as in quartz. Or the erosion may be accompanied by no cracks whatever, as in feldspar, porphyry and andesite. The substance may show no viscous flow during erosion, or it may flow like granite and baryte. The formation of cracks was never in these tests the cause of final rupture, except with glass. Cracks are probably in many cases due to the attempt of the solid to slip bodily into the cavity, but such slip can never go far before it is stopped by the mutual supporting action of the walls. Such slip may be prominent in a substance with easy cleavage, or slight as in quartz. It is probable that the cracks in quartz and calcite were essentially the same in character, one being merely more prominently developed than the other.

Flaws in the original specimen are apparently so tightly closed by pressure that they play no part in fracture.

Rupture by flaking-off is not even suggested by any mathematical theory of rupture, and probably cannot be in the nature of things. Mathematical theory treats the material as mathematically homogeneous, whereas we probably have to do here with a phenomenon of molecular agitation. All the observations are consistent with the view that a microscopic splinter flies off when its kinetic energy of temperature agitation has by chance become sufficiently higher than the average. The tendency to fly off will evidently be higher when the stress is high, and if the stress is high enough the process of disintegration will become rapid enough to be appreciable. Thermodynamics is familiar with something similar when the vapor pressure of a liquid is increased by an increase of pressure acting on the liquid phase. One expects that there will be no sharp point at which spontaneous disintegration suddenly begins, but that the effect continues over a range of pressure. This is confirmed by the experiments above. On the other hand, as with all such effects, there must be a pressure at which the effect practically ceases, so that at low pressures the chance of disintegration is of the same order, for example, as the chance that a pail of water will freeze on a red hot stove.

Consistently with this view one would expect the character of the surface to have an important effect. If the surface is perfectly smooth, as in the negative quartz crystals, or if as in glass there is a protecting covering of water 200 molecules deep like a jelly in which there may be surface tension effects, one expects very slight disintegrating tendency. Any artificial cavities, on the other hand, must contain large irregularities and be favorable to the effect.

This paper mentions the results of a new mathematical analysis of the effect in crystals of hydrostatic pressure applied as in these experiments. It appears that the new phenomena introduced by crystalline structure are not prominent enough to lead one to expect rupture because of them, and that in most cases an approximate solution may be obtained by treating the crystal as isotropic with mean values of the elastic constants.

The stresses which these brittle materials stand are many times higher than would be predicted by ordinary compression tests. If one neglects the flaking-off effect, which is entirely un contemplated in mathematical theory, stresses at least 20 times higher than those of ordinary compression tests may be reached without rupture. At the same time the possible stresses are very appreciably lower than those found by Adams. His results were affected by the unknown action of shrunk-on steel jackets.

Attempts to weld together finely powdered quartz, feldspar, and talc failed up to 30,000 kg/cm<sup>2</sup>. There is, however, no evidence that such welding would not take place if the adherent film of air could be entirely removed; this is a matter of extreme experimental difficulty. The amount of interstitial space in compressed powders has been measured, but caution must be used in inferring from these figures the density of a compressed sand while actually under pressure. The results of these collapsing tests makes it extremely probable, however, that minute crevices, at least large enough for the percolation of liquids, exist in the stronger rocks at depths corresponding to 6000 or 7000 kg/cm<sup>2</sup>, and possibly more.

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ART. XVIII.—*Stress-Strain Relations in Crystalline Cylinders;*  
by P. W. BRIDGMAN.

IN a preceding paper I have made experimental examination of the manner of failure under high pressure of cavities in various materials of geological interest. In order to simplify the question as much as possible a number of the specimens were cut from single crystals; these were made in the form of circular cylinders, pierced axially with circular holes concentric with the outer surface. It appeared, however, on assembling the results, that the mathematical problem of the elastic behavior of crystalline material, even under such simple conditions as above, had never been discussed. I have been able to obtain an approximate solution, and the results for several systems of crystals are recorded here.

In the following mathematical analysis there are two main guiding ideas. It appeared very soon that an exact solution was out of the question; the form of the solution could be determined, but in order to compute the numerical coefficients it was necessary to solve a system of infinitely many linear algebraic equations. However, an approximate solution, which would be expected to give the most important terms, was obtained by the device of varying the elastic constants, allowing them to approach infinitely close to those of an isotropic body, and finding the infinitesimal terms which must in consequence be added to the well known solution for an isotropic body. The second guiding idea was to discover the nature of the terms present by considering the symmetry relations of the crystals. This saved an enormous amount of time, for if an ordinary series were assumed for the solution most of the coefficients would be found to be zero.

In the following the solution is obtained to first order terms for cubic and tetragonal crystals, and to second order terms for trigonal crystals. For the latter the solution has been carried through numerically in the case of quartz, which was one of the materials experimented upon, and the closeness of the approximation is discussed.

The mathematical problem consists in finding such a set of displacements that the set of strains determined by them will in turn determine such a set of stresses that the equations of equilibrium and the boundary conditions (which are conditions on the stresses) shall be satisfied. The boundary conditions are that all components of stress on the inner curved surface of the cylinder vanish, and on the external surface the stresses reduce to a uniform normal pressure. With regard to the stresses on the infinitely distant ends the following method of procedure, which is usual for isotropic solids, is applicable. Since the cylinder is infinitely long, the stress and strain must be independent of  $z$ .

We first solve supposing that on the infinitely distant ends normal to the axis there is such a stress as to make the displacement along the  $z$  axis independent of  $z$ , and later add such a normal stress on the ends as to satisfy the actual conditions there. This modification of the first solution is always exceedingly easy to make.

Cylindrical coordinates are, of course, the natural choice for this problem. The equations are copied here for convenience of reference; they may be found in any work on elasticity. The displacements radially, circumferentially, and axially are denoted respectively by  $u_r, u_\theta, u_z$ . The strains are then given by:

$$e_{rr} = \frac{\partial u_r}{\partial r}, \quad e_{\theta\theta} = \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r}, \quad e_{zz} = \frac{\partial u_z}{\partial z},$$

$$e_{\theta z} = \frac{1}{r} \frac{\partial u_z}{\partial \theta} + \frac{\partial u_\theta}{\partial z}, \quad e_{zr} = \frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}, \quad e_{r\theta} = \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta}.$$

and the stress equations of equilibrium are;

$$\frac{\partial r\hat{r}}{\partial r} + \frac{1}{r} \frac{\partial r\hat{\theta}}{\partial \theta} + \frac{\partial rz}{\partial z} + \frac{r\hat{r} - \theta\hat{\theta}}{r} = 0$$

$$\frac{\partial r\hat{\theta}}{\partial r} + \frac{1}{r} \frac{\partial \theta\hat{\theta}}{\partial \theta} + \frac{\partial \theta z}{\partial z} + \frac{2}{r} \frac{r\hat{\theta}}{r} = 0$$

$$\frac{\partial rz}{\partial r} + \frac{1}{r} \frac{\partial \theta z}{\partial \theta} + \frac{\partial z\hat{z}}{\partial z} + \frac{rz}{r} = 0$$

Considerable simplification might be made at once in these equations, which are general, because the solutions in which we are interested are independent of  $z$ .

These equations will now be applied to the simpler groups of crystals.

*Cubic Crystals.*—The first task is to obtain the stress-strain relations in cylindrical coordinates. The equations in rectangular coordinates are given in Love; the transformations, which may be made by familiar methods, give the following results:

$$\left\{ \begin{array}{l} r\hat{r} = (a - c \cos 4\theta)e_{rr} + (b + c \cos 4\theta)e_{\theta\theta} + c_{12}e_{zz} + c \sin 4\theta e_{r\theta} \\ \theta\hat{\theta} = (b + c \cos 4\theta)e_{rr} + (a - c \cos 4\theta)e_{\theta\theta} + c_{12}e_{zz} + c \sin 4\theta e_{r\theta} \\ r\hat{\theta} = c \sin 4\theta(e_{rr} - e_{\theta\theta}) + \left(\frac{a-b}{2} + c \cos 4\theta\right)e_{r\theta} \\ \hat{z}z = c_{12}(e_{rr} + e_{\theta\theta}) + c_{11}e_{zz} \\ \hat{\theta}z = c_{44}e_{\theta z} \\ \hat{z}r = c_{44}e_{zr} \end{array} \right.$$

One of the cubic axes is along the  $z$  axis; the two others are in the  $r$ - $\theta$  plane, one being the origin of  $\theta$  and the other at right angles to it. The constants  $a$ ,  $b$ , and  $c$  which appear above are connected as follows with the elastic constants  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ . (See Love, p. 157.)

$$\begin{aligned} c_{11} &= a - c \\ c_{12} &= b + c \\ c_{44} &= \frac{a - b}{2} + c. \end{aligned}$$

The reason for writing the constants in this form is that for an isotropic solid  $c$  becomes zero. In accordance with the approximate method used here,  $c$  is to be regarded as an infinitesimal of the first order.

If now the stresses above are expressed in terms of the displacements and substituted in the equations of equilibrium, a great simplification takes place. Because of the independence of the solutions of  $z$ ,  $e_{zz}$  vanishes, and  $\widehat{\theta z}$  and  $\widehat{zr}$  enter only the third equation of equilibrium. Also  $u_z$  enters only  $\widehat{\theta z}$  and  $\widehat{zr}$ . Now under such conditions the third equation of equilibrium is satisfied if  $u_z = 0$ . This also satisfies the boundary conditions in  $\widehat{zr}$ , and because the solution is unique, it follows that  $u_z$  must actually vanish.

That is, the deformation under external hydrostatic pressure of an infinitely long hollow cylinder cut from a cubic crystal with its axis along one of the cubic axes is one in which plane cross sections remain plane. This is exactly true, without approximation. We shall see that trigonal crystals behave quite differently.

We have left to consider now only  $u_r$  and  $u_\theta$ . These enter into only  $\widehat{r\theta}$ ,  $\widehat{\theta\theta}$ , and  $\widehat{r\theta}$ , and only the first two equations of equilibrium. We now assume an approximate solution of the form

$$\begin{cases} u_r = A_1 r + A_2 r^{-1} + f_1(r, \theta) \\ u_\theta = f_2(r, \theta) \end{cases}$$

$u_r = A_1 r + A_2 r^{-1}$  is the solution for an isotropic substance, and hence  $f_1$  and  $f_2$  are to be regarded as infinitesimals of the same order as  $c$ . The form of  $f_1$  and  $f_2$  may now be guessed from the symmetry relations. In the first place the elastic properties have tetragonal symmetry about the  $z$  axis. The applied stress system has circular symmetry about the  $z$  axis. The solution must, therefore, repeat itself every  $90^\circ$ , and we expect a trigonometric function of  $4\theta$ . Furthermore, the elastic properties have digonal symmetry about the origin of  $\theta$ . If the cylinder

is rotated through  $180^\circ$  about this diagonal axis, the applied stress system is unaltered. It follows that the displacements must have diagonal symmetry about this axis. A moment's consideration shows that  $u_r$  must be an even function of  $\theta$  and  $u_\theta$  an odd function. The two simplest trigonometric functions satisfying all these conditions are  $k + \cos 4\theta$ , and  $\sin 4\theta$ , where  $k$  is any constant. Symmetry relations impose no conditions on the kind of function of  $r$  that the solution is, and we therefore try a solution of the form

$$\begin{cases} u_r = A_1 r + A_2 r^{-1} + [\phi_1(r) + \phi_2(r) \cos 4\theta] \\ u_\theta = \phi_3(r) \sin 4\theta \end{cases}$$

where  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  are all first order terms. Direct substitution in the equilibrium equations, keeping only first order terms, verifies that this is a possible solution and gives ordinary differential equations of the second order in  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$ , which are simple enough to be readily solved. The solutions are polynomials, giving for the explicit form of the first approximation

$$\begin{cases} u_r = A_1 r + A_2 r^{-1} + \left[ \frac{2A_2 c}{a-b} r^{-1} + B_1 r^3 + B_2 r^{-3} + C_1 r^5 + C_2 r^{-5} \right] \cos 4\theta \\ u_\theta = \left[ \frac{A_2 c}{a} r^{-1} - B_1 r^3 + \frac{2bB_2}{3a+b} r^{-3} - \frac{4a+2b}{a+3b} C_1 r^5 + C_2 r^{-5} \right] \sin 4\theta. \end{cases}$$

There are just enough arbitrary constants in this solution to enable one to make  $\widehat{r}r = 0$  when  $r = r_0$ ,  $\widehat{r}r = -P$  when  $r = r_1$ , and  $\widehat{r}\theta = 0$  when  $r = r_0$  and  $r = r_1$ . The condition  $\widehat{r}z = 0$  when  $r = r_0$  and  $r = r_1$  is already satisfied by putting  $u_z = 0$ . It is not worth while writing out the explicit values of the constants; they may be determined numerically readily enough in any special case.

Better approximations may be obtained by adding terms in  $\cos 8\theta$ ,  $\cos 12\theta$  and  $\sin 8\theta$ ,  $\sin 12\theta$ , etc. Each of these higher terms will involve new arbitrary constants, and the equations for determining these constants will become more complicated.

*Tetragonal Crystals.*—(A) Six Constant Group. The stress-strain relations are given in Love for rectangular coordinates. When transformed to cylindrical coordinates they are as follows:

$$\begin{aligned} \widehat{r}r &= (a - c \cos 4\theta) e_{rr} + (b + c \cos 4\theta) e_{\theta\theta} + c_{13} e_{zz} + c \sin 4\theta e_{r\theta} \\ \widehat{\theta}\theta &= (b + c \cos 4\theta) e_{rr} + (a - c \cos 4\theta) e_{\theta\theta} + c_{13} e_{zz} - c \sin 4\theta e_{r\theta} \\ \widehat{z}z &= c_{13} e_{rr} + c_{13} e_{\theta\theta} + c_{33} e_{zz} \end{aligned}$$

$$\widehat{\theta z} = c_{44} e_{\theta z}$$

$$\widehat{zr} = c_{44} e_{zr}$$

$$\widehat{r\theta} = c \sin 4\theta (e_{rr} - e_{\theta\theta}) + \left[ \frac{a-b}{2} + c \cos 4\theta \right] e_{r\theta},$$

where

$$c_{11} = a - c$$

$$c_{12} = b + c$$

$$c_{66} = \frac{a-b}{2} + c.$$

Although these equations are characterized by six constants instead of three as are the cubic crystals, we notice that under the conditions of this particular problem the two sets of equations are precisely the same in form. If a solution is assumed independent of  $z$  the equations separate into two groups as before, and the value of  $u_z$  which satisfies the boundary conditions is seen to be identically zero as before. Under these conditions the only stresses left to consider are  $\widehat{rr}$ ,  $\widehat{\theta\theta}$ , and  $\widehat{r\theta}$ , and these are precisely the same in form as were the equations for cubic crystals, the only change being the substitution of  $c_{66}$  for  $c_{44}$  in the equations for  $a$ ,  $b$ , and  $c$ . The solution will then be precisely of the same form as that already written down; we need not trouble to write it again. The equations for determining  $\widehat{z\theta}$ , the stress to be applied over the ends, will, however, be somewhat different. This results only in a term which is to be added to the others and is so simple that it need not be written out explicitly.

**Tetragonal Crystals. (B) Seven Constant Case.** This differs from the six constant case only by the appearance of one new elastic constant,  $c_{16}$ , but the symmetry relations are thereby changed, so that the solution is altered in appearance. The stress-strain relations are the same as before for the  $\widehat{z\theta}$ ,  $\widehat{rz}$ , and  $\widehat{z\theta}$  stresses; the other three stresses now become

$$\widehat{rr} = (a - c \cos 4\theta + c_{16} \sin 4\theta) e_{rr} + (b + c \cos 4\theta - c_{16} \sin 4\theta) e_{\theta\theta} + c_{13} e_{zz} + (c \sin 4\theta + c_{16} \cos 4\theta) e_{r\theta}$$

$$\widehat{\theta\theta} = (b + c \cos 4\theta + c_{16} \sin 4\theta) e_{rr} + (a - c \cos 4\theta - c_{16} \sin 4\theta) e_{\theta\theta} + c_{13} e_{zz} - (c \sin 4\theta + c_{16} \cos 4\theta) e_{r\theta}$$

$$\widehat{r\theta} = (c \sin 4\theta + c_{16} \cos 4\theta) (e_{rr} - e_{\theta\theta}) + \left( \frac{a-b}{2} + c \cos 4\theta - c_{16} \sin 4\theta \right) e_{r\theta}.$$

An examination shows that just as before the exact solution is one in which there is no warping, but the symmetry conditions on  $u_r$  and  $u_\theta$  no longer hold, and the only condition to be satisfied

is that they have tetragonal symmetry. Under these conditions a first approximation to the solution may be shown to be of the form ;

$$\begin{aligned} u_r &= f_1'(r) + f_2'(r) \cos 4\theta + f_3'(r) \sin 4\theta \\ u_\theta &= f_4'(r) \cos 4\theta + f_5'(r) \sin 4\theta \end{aligned}$$

where  $f_2'$ ,  $f_3'$ ,  $f_4'$ , and  $f_5'$  are infinitesimals of the first order, as is also  $c$ . Substitution in the stress equations of equilibrium as before gives ordinary differential equations of the second order which may be solved, giving for the explicit form of the first approximation

$$\begin{aligned} u_r &= Ar + Br^{-1} \\ &+ \left[ \frac{2c}{b-a} Br^{-1} + Cr^3 + Dr^{-3} + Er^5 + Fr^{-5} \right] \cos 4\theta \\ &+ \left[ \frac{4c_{10}}{3(a-b)} Br^{-1} + Gr^3 + Hr^{-3} + Ir^5 + Jr^{-5} \right] \sin 4\theta \\ u_\theta &= \\ &\left[ \frac{-c_{10}}{6a} Br^{-1} + Gr^3 - \frac{2b}{3a+b} Hr^{-3} + \frac{4a+2b}{a+3b} Ir^5 - Jr^{-5} \right] \cos 4\theta \\ &+ \left[ \frac{c}{a} Br^{-1} - Cr^3 + \frac{2b}{3a+b} Dr^{-3} - \frac{4a+2b}{a+3b} Er^5 + Fr^{-5} \right] \sin 4\theta. \end{aligned}$$

This solution contains ten constants instead of six as in the previous case; these ten constants may be so determined in any special case as to satisfy the boundary conditions. The boundary conditions which may be satisfied by these constants are somewhat more general in character than those which have been imposed above, for we are in a position by means of them to solve for the case of different arbitrary hydrostatic pressures simultaneously on the external and internal surfaces.

The solution for the two cases previously given may be obtained from the solution for this case by a specialization of constants.

*Trigonal Crystals.*—Six Constant Group. The stress-strain relations in cylindrical coordinates are

$$\left\{ \begin{aligned} \widehat{r}r &= c_{11}e_{rr} + c_{12}e_{\theta\theta} + c_{13}e_{zz} + c_{15} \cos 3\theta e_{\theta z} + c_{15} \sin 3\theta e_{zr} \\ \widehat{\theta}\theta &= c_{12}e_{rr} + c_{11}e_{\theta\theta} + c_{13}e_{zz} - c_{15} \cos 3\theta e_{\theta z} - c_{15} \sin 3\theta e_{zr} \\ \widehat{z}z &= c_{13}e_{rr} + c_{13}e_{\theta\theta} + c_{33}e_{zz} \\ \widehat{\theta}z &= c_{15} \cos 3\theta e_{rr} - c_{15} \cos 3\theta e_{\theta\theta} + c_{14}e_{\theta z} - c_{15} \sin 3\theta e_{zr} \\ \widehat{z}r &= c_{15} \sin 3\theta e_{rr} - c_{15} \sin 3\theta e_{\theta\theta} + c_{14}e_{zr} + c_{15} \cos 3\theta e_{z\theta} \\ \widehat{r}\theta &= -c_{15} \sin 3\theta e_{rr} + c_{15} \cos 3\theta e_{\theta\theta} + \frac{1}{2}(c_{11} - c_{12})e_{r\theta} \end{aligned} \right.$$



The  $z$  axis is the axis of trigonal symmetry; the axis of digonal symmetry is the origin of  $\theta$ , and there is a plane of symmetry through the trigonal axis at right angles to the digonal axis. The digonal axis and the plane of symmetry are here interchanged in position as compared with Love.

The conditions are more complicated than for cubic and tetragonal crystals in that the axial displacement does not separate itself from the others, but enters all the equations. But the complication actually results in a simplification as far as the first approximation to the solution goes, for it will be found that the first approximation is given by the warping function alone, the radial and circumferential displacements requiring no corrective terms. This means that the most important difference between a trigonal crystal and an isotropic solid is in the presence of the warping term.

In virtue of the symmetry relations we see that  $u_z$  must be an odd function of  $\theta$  and an even function of  $\theta - \frac{\pi}{2}$ . Furthermore it must have a period of  $\frac{2\pi}{3}$ . The simplest trigonometric function satisfying these requirements is  $\sin 3\theta$ , and actual trial shows that this does indeed give a solution. The first approximation is

$$\begin{cases} u_r = B'r + A'r^{-1} \\ u_\theta = 0 \\ u_z = \left[ A'_1 r^3 + A'_2 r^{-3} + \frac{2A'_3 c_{15}}{c_{11} - c_{12}} r^{-1} \right] \sin 3\theta \end{cases}$$

The first approximation involves only the constant  $c_{15}$  peculiar to the crystal. This solution contains four arbitrary constants, with which the boundary conditions may be satisfied. This case is simple enough so that the explicit form of these constants may be written out easily, if one cares to stop with the first approximation.

The simple form of the first approximation, only a warping term, makes it feasible to go on and obtain the second approximation. Symmetry considerations including the condition of trigonal symmetry show that  $u_\theta$  is an odd function of  $\theta$  and an odd function of  $\theta - \frac{\pi}{2}$ , and  $u_r$  is even in  $\theta$  and even in  $\theta - \frac{\pi}{2}$ . The simplest trigonometric functions which satisfy these conditions are  $\sin 6\theta$  and  $\cos 6\theta$  respectively. Accordingly we assume as the second approximation

$$\begin{cases} u_r = Br + Ar^{-1} + \phi_1(r) + f_1(r) \cos 6\theta \\ u_\theta = f_2(r) \sin 6\theta \\ u_z = f_3(r) \sin 3\theta, \end{cases}$$

where  $\phi_1$ ,  $f_1$ , and  $f_2$  are second order terms, and  $f_3$  is of the first order. Substitution in the differential equations shows that the assumption is justified, and gives differential equations for  $\phi_1$ ,  $f_1$ ,  $f_2$ , and  $f_3$  involving enough constants to allow the boundary conditions to be satisfied. The solutions are as follows:

$$\begin{cases} \phi_1(r) = -\frac{3}{2} \frac{c_{15}}{c_{11}} A_1 r^3 \\ f_1(r) = D_1 r^5 + D_2 r^{-5} + D_3 r^7 + D_4 r^{-7} + B_1 r^{-3} + B_2 r^{-1} \\ f_2(r) = \alpha_1 D_1 r^5 + \alpha_2 D_2 r^{-5} + \alpha_3 D_3 r^7 + \alpha_4 D_4 r^{-7} + C_1 r^{-3} + C_2 r^{-1} \\ f_3(r) = A_1 r^3 + A_2 r^{-3} + A \frac{c_{15}}{c_{44}} r^{-1}. \end{cases}$$

The constants A, B,  $A_1$ ,  $A_2$ ,  $D_1$ ,  $D_2$ ,  $D_3$ ,  $D_4$ , are arbitrary as far as the equations of equilibrium go, and may be so chosen as to satisfy the boundary conditions. In any special case they will involve the elastic constants and the dimensions of the specimen. The constants  $B_1$ ,  $B_2$ ,  $C_1$ ,  $C_2$ ,  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$  on the other hand are determined in terms of the elastic constants only, being required to cancel the constant terms of certain non-homogeneous equations.  $\alpha_1$  and  $\alpha_4$  have the especially simple values  $-1$  and  $+1$  respectively.

During the process of solution of the equations it was most interesting to watch how the equations for the unknown exponents of  $r$  in  $f_1(r)$  and  $f_2(r)$  divested themselves of the elastic constants, standing forth in the end as equations with numerical coefficients, the solutions of which furthermore were integers. The same thing was true for cubic and tetragonal crystals. There may be a point here of some mathematical interest.

The same general type of solution applies to those trigonal crystals characterized by five instead of six elastic constants. (See Love, p. 157.) It may be obtained from the six constant case above by putting  $c_{15}=0$ . The solution is of the same form, but certain terms vanish;  $\phi_1$  vanishes, the terms in  $r^{-3}$  and  $r^{-1}$  in  $f_1$  and  $f_2$  vanish, and the term in  $r^{-1}$  in  $f_3$  vanishes.

The solution as given above is now in shape for numerical computation. In the following will be given the values for quartz of the dimensions used in the experiments. The inside diameter of the cylinders was 1 and the outside diameter 5.5 on an arbitrary scale. The following numerical solution differs from the literal solution above in that the terms are added to

give the correct longitudinal compression. This compression

was  $\widehat{z\bar{z}} = -\frac{Pr_1^2}{r_1^2 - r_0^2}$ , and corresponds to a cylinder with closed

ends, hydrostatic pressure being exerted entirely over the ends as well as on the curved external surface. The constants  $c_{13}$  and  $c_{33}$  both enter this additional term, so that the second approximation, unlike the first, involves all the elastic constants.

The elastic constants for quartz are taken from Love, p. 160,

$$\left. \begin{aligned} c_{11} &= 868, & c_{12} &= 70, & c_{13} &= 143 \\ c_{33} &= 1074, & c_{44} &= 582, & c_{15} &= -171 \end{aligned} \right\}$$

These constants are so chosen that a stress of 1000 *kg/cm*<sup>2</sup> is regarded as unity. The values of the constants of the solution are now as follows:

$$\begin{aligned} A &= -1.388 \times 10^{-3} P & D_1 &= +5.603 \times 10^{-9} P \\ B &= -1.107 \times 10^{-3} P & D_2 &= +3.623 \times 10^{-4} P \\ A_1 &= +4.307 \times 10^{-7} P & D_3 &= -9.811 \times 10^{-11} P \\ A_2 &= -4.037 \times 10^{-4} P & D_4 &= -1.174 \times 10^{-4} P \\ \alpha_1 &= -1, & \alpha_2 &= +0.2985, & \alpha_3 &= -2.258, & \alpha_4 &= 1, \end{aligned}$$

$$B_1 = .8160A_2, B_2 = -.06287A, C_1 = -0.1217A_2, C_2 = +0.0289A.$$

With these values of the constants the displacements may be found, then by differentiation of the strains, and then by substituting in the stress-strain equations the stresses. In this way the stresses corresponding exactly to the given system of displacements may be found. The goodness of the approximation is now to be estimated from the closeness with which the exact stresses satisfy the given boundary conditions and the equations of equilibrium.

The  $\widehat{r\bar{r}}$  and  $\widehat{r\bar{\theta}}$  components of stress exactly satisfy the boundary conditions on both exterior and interior curved surfaces, but the component  $\widehat{r\bar{z}}$  fails to satisfy the boundary conditions exactly. At the external surface the effect is only 0.1% of the applied stress, but at the inner surface  $\widehat{r\bar{z}}$  fails to vanish by a term fluctuating in value, the trigonometric part of which is  $\cos 3\theta \sin 6\theta$ , rising at the maximum to 7% of the applied stress. The approximation to the equilibrium conditions was tested by direct differentiation and substitution of the stresses, expressed as products of trigonometric terms and polynomials in *r*. The first two equations of equilibrium are exactly satisfied; the third fails by an amount which at the maximum is 10% of the largest terms entering the equations of equilibrium. Hence one may say that

at the worst the boundary conditions are satisfied within 7% and the equilibrium conditions within 10%. The approximation is perhaps better than might be expected when one considers the magnitude of the departure of the constants of quartz from the condition of isotropy; the terms in the equations which have been treated as infinitesimals are not actually small at all.

The numerical values of displacements, strains, and stresses were next computed at various points in the crystal, and are given in the following tables. The strains are those which correspond exactly to the displacements, but the stresses satisfy exactly the boundary conditions and the equations of equilibrium, and correspond only approximately to the displacements and strains.

If the substance were isotropic, there would be only two displacements,  $u_r$ , and  $u_z$  proportional to  $z$ , only three strains  $e_{rr}$ ,  $e_{\theta\theta}$ , and  $e_{zz}$ , and only three stresses  $\widehat{rr}$ ,  $\widehat{\theta\theta}$ , and  $\widehat{zz}$ . The additional terms shown in the tables above are introduced by the crystalline structure. It is curious that the extra displacements occasioned by crystalline structure vanish at the inner surface; there is here no warping, and all radii are shortened by the same amount with no angular change. In general we should expect the greatest extra displacement to be that given by the warping function, because this is the only term in the first approximation. As a matter of fact the warping is the greatest extra effect, rising at its maximum to 6.5% of the radial displacement at the same point. If one assumed the substance isotropic with the actual values of  $c_{11}$  and  $c_{12}$  the radial displacement at the inner surface would be found to be  $-2.32 \times 10^{-3}$ , which is close to the actual value. Or if the displacement is computed for an isotropic substance of the same cubic compressibility as quartz with a Poisson ratio equal 0.25, the inner radial displacement will be found to be  $-2.43 \times 10^{-3}$ . It appears, then, that the crystalline

## DISPLACEMENTS.

$r$	$\frac{1}{P} u_r$	$\frac{1}{P} u_\theta$	$\frac{1}{P} u_z$
1	$-2.39 \times 10^{-3} + 0 \cos 6\theta$	$0 \sin 6\theta$	$-6.97 \times 10^{-4} z + 0 \sin 3\theta$
2	$-2.70 \quad " \quad + 1.27 \times 10^{-5} \quad "$	$-1.16 \times 10^{-5} \quad "$	$" \quad + 1.56 \times 10^{-4} \quad "$
3	$-3.46 \quad " \quad + 1.94 \quad " \quad "$	$-1.20 \quad " \quad "$	$" \quad + 1.32 \quad " \quad "$
4	$-4.34 \quad " \quad + 2.11 \quad " \quad "$	$-1.13 \quad " \quad "$	$" \quad + 1.23 \quad " \quad "$
5	$-5.27 \quad " \quad + 2.48 \quad " \quad "$	$-0.78 \quad " \quad "$	$" \quad + 1.32 \quad " \quad "$
5.5	$-5.74 \quad + 2.72 \quad " \quad "$	$-0.10 \quad " \quad "$	$" \quad + 1.39 \quad " \quad "$



structure of this particular substance does not have an important effect on the large scale phenomena.

The largest extra term introduced into the strains by crystalline structure is in  $e_{rz}$ , which at the inner surface reaches 3±% of the maximum strain at any point of the cylinder. This is comparatively large; one might expect that it would be instrumental in leading to rupture, but the discussion of the previous paper shows that this is not the case. For all the substances examined rupture seemed to have no connection with any strains or stresses introduced by crystalline structure. The greatest extra stress introduced by crystalline structure is in  $\hat{\theta}_z$ , which at the inner surface reaches 47% of the applied stress and 23% of the maximum stress at any point of the cylinder. Here again the effect is large, but it seemed to have no determining effect in rupture.

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Harvard University.

ART. XIX.—*Influence of a Series Spark on the Direct Current Corona;* by SYLVAN J. CROOKER.

In the paper entitled "Some Brush Discharge Phenomena Produced by Continuous Potentials," S. P. Farwell<sup>1</sup> published some experiments in which he noted changes in the appearance of the direct current corona between coaxial cylindrical electrodes when a short spark was placed in series with the corona tube. The typical negative corona discharge with constant voltage consists in more or less evenly spaced bright beads; the positive glow (the wire being positive) is uniform in most cases. If now a short spark is introduced in series with the corona tube, this difference in the discharge is largely wiped out, and the discharge appears almost the same whether the wire is positive or negative. This effect of the spark is well illustrated by the last four photographs of fig. 2 of the mentioned article. Farwell was inclined to attribute this effect to oscillations or surges set up in the system by the spark. He found indeed that an induction coil gave rise to the same kind of discharge in the corona tube as the spark in series, but at the same time he remarked that the resistance in the corona tube was so high as to exclude oscillations. A condenser in parallel with the tube also gave rise to the beaded discharge characteristic of the direct current. The question was then open whether there were oscillations or not and it was the purpose of this investigation to decide this question, if possible, to measure the frequency and the amplitude of the oscillations and to perform further experiments which might throw light on the nature of the phenomenon.

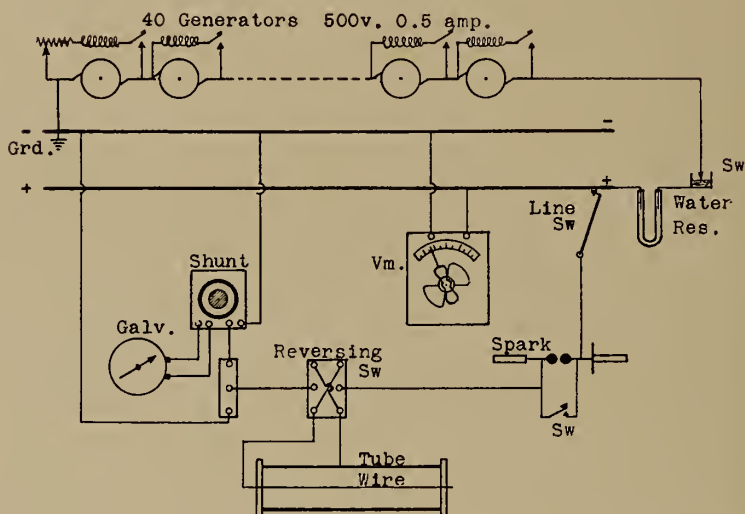
A part of Farwell's experiments were repeated by means of the same tube and the same dynamos. The electrodes of the spark gap were polished brass spheres one centimeter in diameter fastened to brass rods which were supported by hard rubber blocks on a solid hard rubber base. One of the electrodes was supplied with a micrometer screw and an insulated handle which permitted an easy adjustment of the spark distance. The connection of the corona tube with the auxiliary apparatus is shown in fig. 1.

<sup>1</sup> Physical Review, vol. 4, p. 31, 1914.

The observations of Farwell were essentially confirmed. There was one phenomenon, however, very pronounced and fairly regular, which Farwell mentions only occasionally. If a short spark is placed in series with the corona tube, at atmospheric pressure, a few bright radial pencils or streamers of light will shoot out regularly from the wire toward the tube (see fig. 2c); these streamers increase in number and in brightness as the

FIG. 1.

## ELECTRICAL CONNECTIONS



spark gap is opened and may at times completely fill the tube with purple light. The phenomenon is very beautiful indeed, especially in hydrogen or illuminating gas, where the streamers fill the tube with an almost uniform white or blue-green light. Occasionally the beginning positive streamers remind us of the negative beads, so that we have as it were a reversal of the phenomena through the spark. The originally uniform positive glow breaks up into streamers, the negative beads go over into a more or less uniform glow. A closer observation, however, of the positive and negative corona with a spark in series shows always differences so conspicuous that one would hardly conclude that the effect is due to oscillations. If there were oscillations, they could not be



symmetrical with respect to the time axis. The same phenomenon can also be seen in a spherical glass bulb of about 8 cm. diameter, one half of whose inner surface is silvered, and connected with an electrode. The other electrode is a copper ball of 3 mm. diameter in the center of the glass bulb. If the tube is filled with nitrogen at about one half of an atmosphere and subjected to a potential difference of 4500 volts, then the central ball when positive is covered with a very thin uniform layer of light. If, however, a small spark gap is introduced in the circuit, more than half of the bulb is filled with most beautiful streamers of purple light. It is indeed one of the most beautiful phenomena of electric discharge. If we use hydrogen instead of nitrogen, at somewhat lower pressure, the streamers appear in the same way as in nitrogen, but in addition, the negative silver mirror shows a most beautiful display of bright scintillations. Fig. 2a represents a photographic picture of the streamers in nitrogen. According to the length of the spark gap the streamers may be well separated from each other, or flow together, filling the tube with a more or less uniform light.

In order to find the wave form of the current through the tube, different methods suggest themselves. The oscillograph and the vibration galvanometer can not be used, because the current is too weak and the inertia element too large. Three methods, however, have been used which gave accordant results; the telephone, revolving lenses and a photographic plate, and a cathode ray tube with a hot lime cathode. The last method can be made very sensitive and gives satisfactory results.

In the first experiments a telephone receiver connected in parallel with a resistance was used in place of a galvanometer. The passage of the faintest spark can be detected. When the voltage is high enough to produce corona, as each consecutive spark passes a sharp click will be heard in the telephone and a flash of glow will appear on the wire in the tube. If the sparks pass in very rapid succession the glow will appear to be practically continuous. The discharge between the spheres has the character of a spark rather than of an arc. It is intermittent, forming a white line in the gas between the electrodes.

FIG. 2.

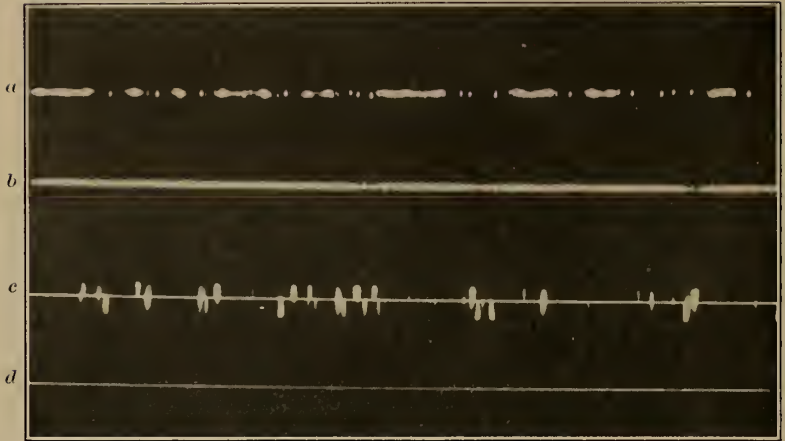


FIG. 2. Corona discharges with and without a series spark ; *a*, negative ; *b*, negative with spark ; *c*, positive with spark ; *d*, positive.

FIG. 2a.



The corona tube acts like a condenser charging up and discharging at intervals depending on the length of the spark gap. It can be arranged so that, for long sparks, only one spark passes per second, or for short sparks, several thousand pass per second, and as each spark passes it will register a sharp click in the telephone receiver. On decreasing the spark length from the

FIG. 3.

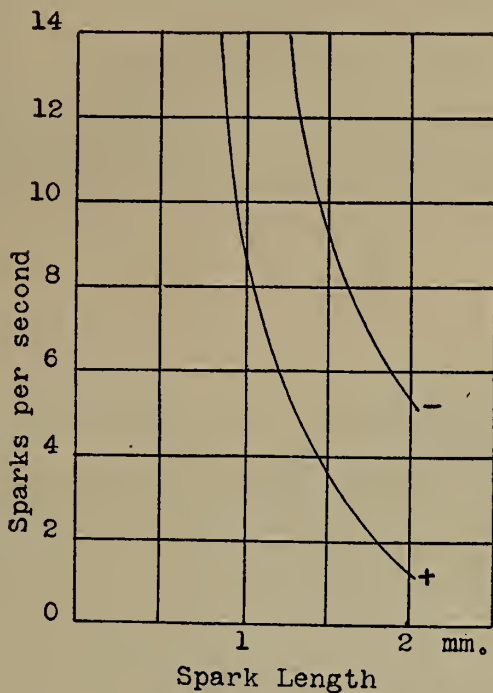


FIG. 3. Spark-length frequency curves.

longest sparking distance the sparks will jump faster and faster until for very short spark lengths the sound in the telephone passes practically out of the audible range.

For a given spark length more sparks pass per second if the axial wire is charged negatively than when it is charged positively. This is to be expected since the current passes through the tube easier when the wire is negative. For a given constant line voltage and air at atmospheric pressure, plotting the spark length against the frequency of the passing sparks for both positive and negative wires, curves as shown in fig. 3 are obtained.

When a condenser is placed in parallel with the corona tube, the positive streamers do not appear and the negative beads are not broken up. The results obtained with the telephone are compatible with the assumption that the corona current with a spark in series is only intermittent and not oscillatory.

More evidence in favor of this view is arrived at by means of Boys' method. It consists in photographing

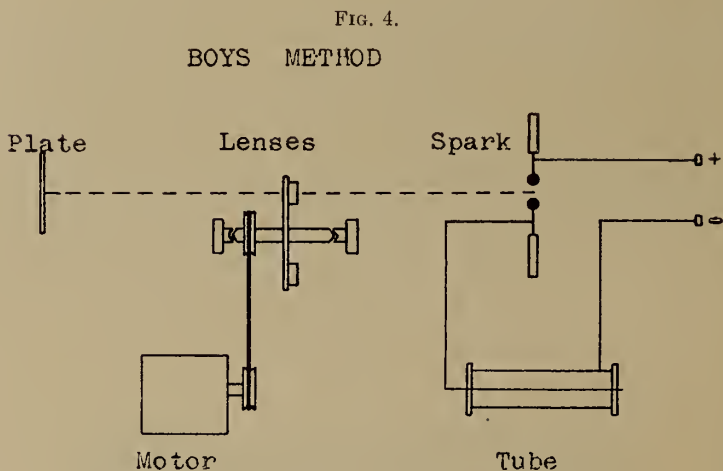


FIG. 4. Arrangement for photographing the spark.

the spark directly as the image from it sweeps across a photographic plate. C. V. Boys<sup>2</sup> used a system of six revolving lenses set in one solid disc. Each lens was mounted a little offset from the center of the disc as compared to the adjacent ones so that the image from it would not overlap the others. The arrangement of the apparatus is shown in fig. 4. All of the lenses have the same focal length so the spark gap can be focused on the plate through any one of them. The spark gap and the photographic plate are stationary but since the lenses move the focus of the spark shifts from one point to another across the plate leaving its record of instantaneous images.

A small motor drives the lenses at a speed of about

<sup>2</sup> Phil. Mag., vol. 30, p. 253; Proc. Phys. Soc., London, vol. 9, p. 1, 1890.

FIG. 5a.



FIG. 5b.



FIGS. 5a, 5b. Photographs of oscillatory and unidirectional sparks.

6,000 RPM. The lenses are set about four inches from the center of the disc so that it is possible to get a linear speed of approximately 100 feet per second across the face of the photographic plate.

By this method it is possible to analyze the spark and to determine whether it is of an oscillatory or unidirectional character. An oscillatory spark will give an irregular band of light across the plate (see fig. 5a), while a unidirectional spark leaves only a sharp line (see lines in fig 5b).

For rough determinations it is easy to observe the image of the spark on the ground glass plate of the camera and quickly find if the spark is oscillatory or not. If it is oscillatory one can observe the approximate frequency and duration of the spark. For more accurate determinations photographs must be made on sensitive plates and observations and measurements made from them.

Several observations were made with this method for various spark lengths and speed of lenses using both air and hydrogen in the corona tube. In the first experiment corona was produced in air at a pressure of 500 mm. by a potential of 14,000 volts. The spark gap was about 1.5 mm. in length and the lenses were driven at a speed of 2,000 RPM. A photograph was taken but the individual sparks showed no trace of being oscillatory.

To spread the individual spark images out the lenses were driven at a higher speed of 6,000 RPM. and the spark gap set at 1.19 mm. This arrangement allowed a passage of about 2,500 sparks per second and a speed of about 100 feet per second across the plate. The photograph, fig. 5b, clearly showed that the sparks were not of an oscillatory character but unidirectional, only a sharp line was recorded as each spark passed and their duration was less than  $1/100,000$  second. Moreover, each spark was a little brighter at the negative electrode, showing that they all passed in the same direction and were of the same character.

With hydrogen in the tube at a pressure of 744 mm. and a potential of 9,400 volts photographs were taken when the spark gap was 0.75 mm. and 0.3 mm. in length. For the 0.75 mm. gap the frequency of the sparks was about ten per second producing a large number of silvery streamers in the corona tube. When the gap was reduced

FIG. 6.

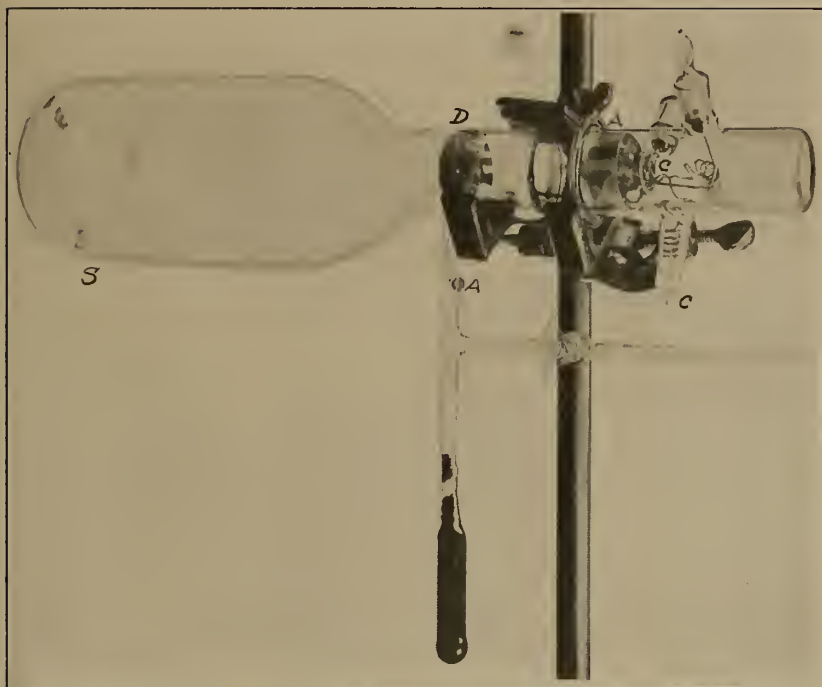


FIG. 6. Photograph of Braun tube.

FIG. 7.

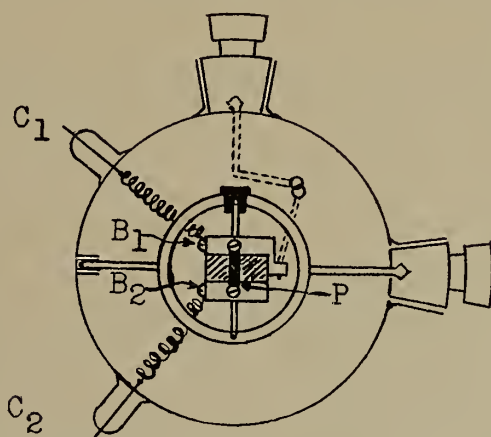


FIG. 7. Detailed drawing of the adjustable hot-lime cathode.

to 0.3 mm. several hundred sparks passed per second and the corona tube was completely filled with streamers. In every case the sparks were unidirectional, sharp and clean-cut showing no oscillatory character whatever.

In order to confirm the results obtained by the Boys method and to determine the form of the current curves when a spark is in series a hot-lime-cathode Braun tube was designed and constructed as shown in figs. 6 and 7.

A narrow platinum strip P fastened to the insulated brass blocks  $B_1$   $B_2$  is heated by an auxiliary current passing through the leading-in conductors  $C_1$   $C_2$ . A small spot of CaO placed upon this heated strip has a peculiar property of giving off a stream of slow moving electrons when used as cathode in a discharge tube at a very low pressure. It is necessary to use only a low potential of about 400 volts between anode A and cathode C. The block holding the platinum strip was mounted upon a gimbal support, as shown, in order that the soft cathode beam could be easily adjusted through a hole in the diaphragm D, fall upon the fluorescent screen S and there produce a spot of maximum brightness. This double adjustment is necessary for it is impossible to assure by construction the exact direction of the beam.

If a very weak magnetic field is placed at right angles to this beam of slow moving electrons the beam will be deflected, shifting the bright spot on the fluorescent screen. When the magnetic field is alternating or pulsating the rapidly moving spot will cause a line to be seen on the screen. Now if this line is observed in a mirror which rotates at right angles to it, the line is spread out into a curve which represents the variations in the current of the coil which excites the magnetic field.

The coil used had about 3,000 turns of No. 26 enameled copper wire wound in two sections and mounted so that it could be fitted closely to the neck of the tube.

It might be advantageous to note briefly some of the details necessary in constructing and operating the hot-lime-cathode Braun tube.

1. The cathode should be adjustable in order to get a spot of maximum brightness.

2. A diaphragm D is necessary to cut out extraneous light from the hot platinum strip and to stop down the divergent cathode beam.

3. The cathode should be as near the fluorescent screen as the sensitiveness of the apparatus permits.



4. CaO mixed with a small quantity of BaNO<sub>3</sub> insures a longer life to the lime and may be easily applied as a paste.

5. The anode should be near the cathode, say 1 cm. distant.

6. The potential may be as low as 300 volts and preferably from a constant source as storage cells.

7. The pressure must be very low and may even be assisted with charcoal and liquid air. Gases are given off from the lime cathode quite freely necessitating con-

FIG. 8.

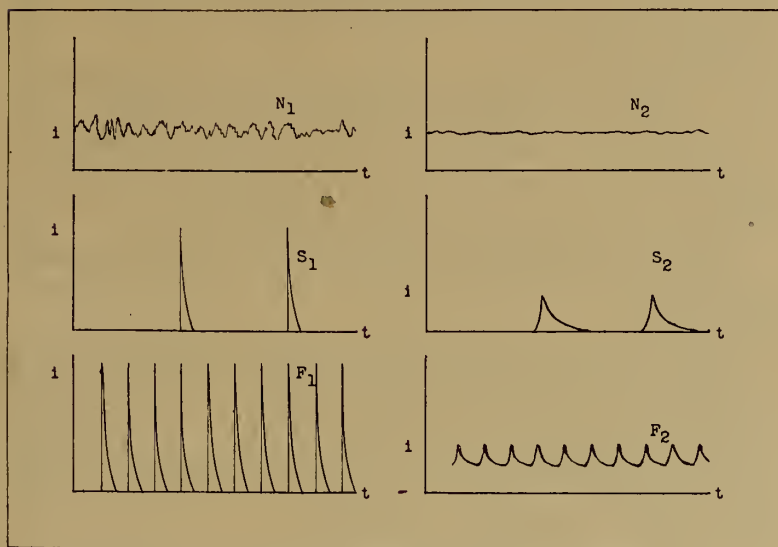


FIG. 8. Currents in the spark and corona tube.

stant pumping if the tube is to be used for any length of time.

With this hot-lime-cathode apparatus it was easy to observe in the rotating mirror the forms of the current curves when a spark passed and the current flowed through the corona tube. The field coil was connected in series with the circuit, (1) between the spark gap and the corona tube, and (2) between the corona tube and ground or negative terminal of the generators (see fig. 1). The current forms are sketched in fig. 8 as they were observed in both of these positions and for the condi-

tions, (N) when there was no spark, (S) when sparks were passing slowly and (F) when sparks were passing rapidly.

With the coil in the position (1) and with no spark, the current  $N_1$  was observed to be a small pulsating one having an irregular and ragged edge. These irregularities are quite noticeable and are probably due to poor commutation at the machines as well as fluctuations in their speed of rotation.

With a few sparks passing, say three per second, the current  $S_1$  suddenly jumps to a maximum each time a spark passes and then more gradually falls to zero. The current is always in one direction and its maximum value is larger than  $N_1$ .

When the spark gap is adjusted so that sparks pass more rapidly, the current  $F_1$  has the same shape as  $S_1$  except that the impulses are crowded closer together.

Connecting the field coil in the position (2), without spark, the current  $N_2$  is quite constant giving a straight line.

With only a few sparks per second we have a peaked current form  $S_2$  rising rapidly and decaying more slowly than in  $S_1$ .

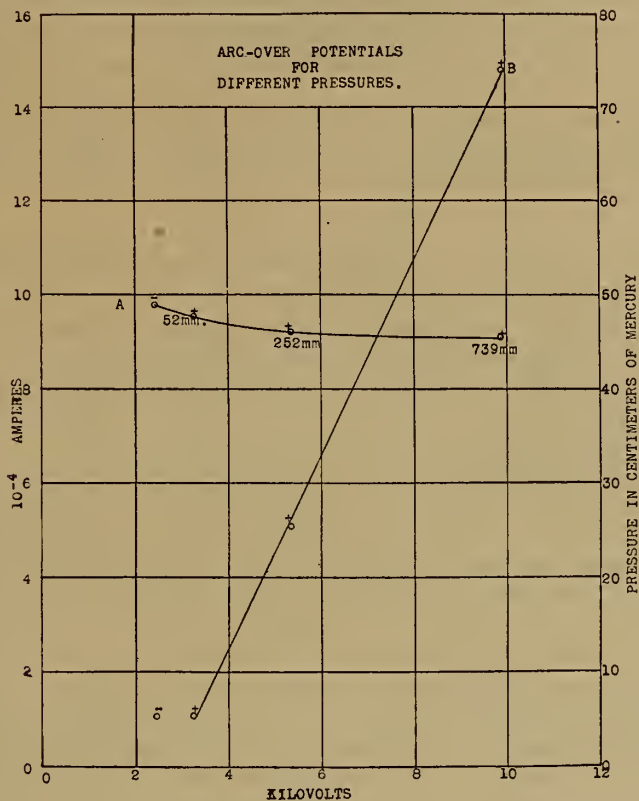
For a greater frequency of sparks the ionization comes into play in a more pronounced fashion. The ionization current does not have time to reduce to zero between consecutive impulses from the spark and so the resultant effect is a direct current  $F_2$  with peaks, which correspond to the sparks passing on the other side of the tube, ordinarily called a pulsating current.

These current forms are essentially the same when the wire is positive and when it is negative. They show directly that there are no oscillations in either the series spark or the corona tube. If there were still surges or oscillations left, they would have to be exceedingly weak and of very high frequency. Oscillations can no doubt be produced easily by means of transformers, the intermittent current passing through the primary coil. It may also be possible to use the corona tube with a third electrode of wire net like an audion.

While the three methods applied to the corona discharge show that the current is only intermittent and not oscillatory, the effect of the spark, destroying the negative beads and giving rise to the positive streamers, is not

yet explained. But during the previous experiments some observations have been made which suggest a close relation between the corona discharge and the arc, and which throw some light on the complicated nature of the corona itself. In the following paragraphs a brief account of some of these experiments will be given.

FIG. 9.



It has often been observed that an arc easily forms in the tube when the line switch connecting the tube is opened, especially when the wire in the corona tube is positive and a fairly large current is passing in the discharge.

The Curve A, fig. 9, shows the current and arc-over potential relation at different pressures for a corroded steel wire 0.041 cm. diameter strung in a cylinder 3.63 cm.

inside diameter. The current recorded is that passing in the corona discharge just before arcing takes place. It is seen that it is nearly constant for all pressures.

Curve B, fig. 9, shows the relation between pressure and arc-over voltage for this constant current. The conclusions which have been drawn from the available data are as follows:

1. For a given configuration of electrodes the arc-over takes place as soon as the current has reached a certain value which is nearly constant for all pressures.

2. Arc-over occurs at lower voltages for smaller wires.

3. For a constant current the arc-over voltage for the positive wire is nearly a linear function of the pressure, and may be written

$$V = (aP + b) cR$$

where,  $V$  = arc-over voltage,  $P$  = pressure,  $R$  = Radius of wire, and  $a$ ,  $b$ ,  $c$ , are constants.

4. At low pressures arc-over for the negative wire occurs at a less voltage than for the positive wire.

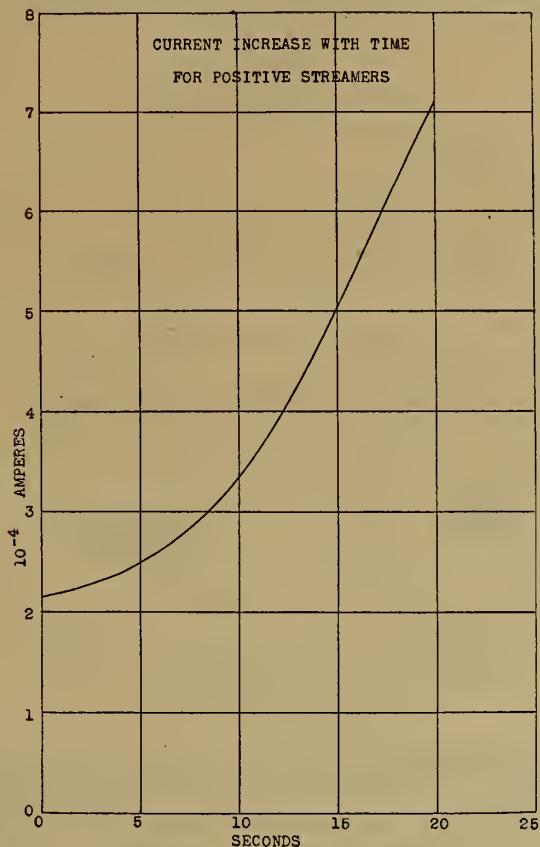
5. At high pressures (near atmospheric) arc-over for the positive wire takes place at a less voltage than for the negative wire.

The water resistance connected between the generators and the main bus bar was replaced by a 0.5 ampere fuse in order to see if it had any effect on the corona discharge with and without a spark. The visual forms were studied with the coaxial cylinders (the inner one No. 20 copper wire) as well as with parallel (No. 20 copper) wires as electrodes.

With the cylindrical electrodes the general results obtained showed that the usual characteristic visual forms of the corona discharge were not materially altered either for positive wire or negative wire, with and without a series spark. The only noticeable change was an increased brightness in the positive uniform glow, streamers and negative beads. With the water resistance cut out the available energy was increased about 100 times or in other words to 10 kilowatts. The negative beads and the positive streamers while much brighter were also in a more agitated state moving rapidly back and forth on the wire and would go over into the arcing stage much easier than they would with water resist-

ance connected. The axial wire was No. 20 copper tightly stretched but it was easily set into violent vibrations, at 739 mm. pressure and 12,700 volts, within a few seconds after closing the line switch. The applied potential fluctuated at times as much as 100 volts resulting in

FIG. 10.



the more unsteady discharge. The water resistance has the effect of damping out the smaller variations.

The ease with which the arc formed was also noticed in experiments with No. 20 wires strung parallel to each other, spaced 1½ inches apart and sealed into a glass tube.

While working with hydrogen it was noticed that when the wire was at a given potential above the critical glow

voltage, the current in the beads would increase with the time, the beads would increase in size and in a short time would combine to form an arc. Detailed observations were made on this point.

On closing the switch several beads were formed which soon combined into one, much larger and brighter as shown in fig. 10a. This bead seemed to take hold on the wire at a surface irregularity and remain fixed. A bright reddish spot on the wire formed the base of the bead,

FIG. 10a.

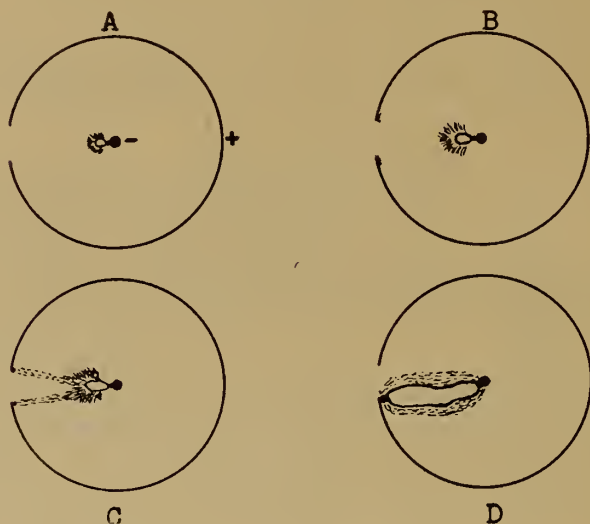


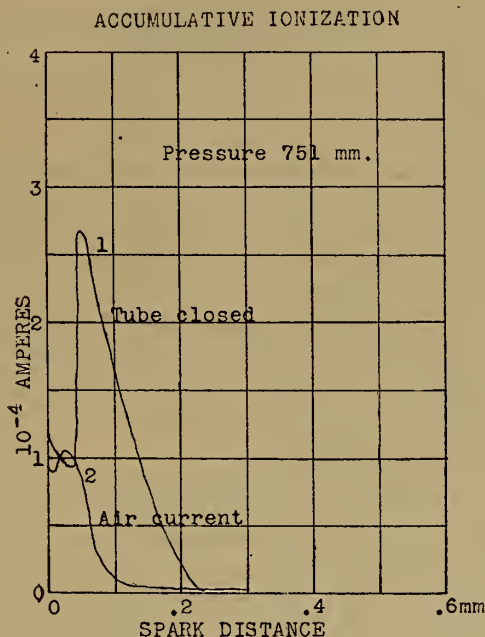
FIG. 10a. Evolution of beads into the arc.

while a bright blue-white core extended out from that toward the bright spots on the edge of the observation slot and shaded off into a milky glow or brush. As time proceeded the core grew larger and brighter and the milky glow of the brush reached farther toward the tube, as in B. Soon a faint reddish glow, C, appeared in the gas proceeding from the bright spots on the tube and extending toward the bead. This glow continued to increase in brightness for a short time until the arc D flashed into existence. The arc had a very bright tubular blue-white core surrounded by a hazy reddish glow and extended

from a bright reddish spot on the wire to a bright white one on the tube. We may now speak of the negative beads and perhaps the positive streamers as miniature or beginning arcs which unite to form a single arc when the current density reaches a certain value.

The curve in fig. 10 will serve to show how the current in the streamers increases with the time. At a potential of 11,850 volts, somewhat above that for starting corona

FIG. 11.



glow in air at 751 mm. pressure, a spark gap of 0.18 mm. length was placed in series with the tube. Readings of the current were taken at intervals of five seconds and when plotted resulted in the given curve. An arc passed shortly after 20 seconds but the maximum current before it occurred was not obtained.

The increase of the current depends largely on the sparking distance and on the applied voltage (see curve 1 fig. 11). When the spark distance from zero is increased the current for the positive streamers decreases at first accompanied by a decreased brightness of the uniform glow, reaches a minimum value, and as the streamers

appear rises to a maximum rapidly and falls off to zero for a large spark distance. The streamers are brightest at the maximum current value and are always connected with a large current. The corresponding negative curves show no such a maximum. With increasing voltage the positive current increases very rapidly. When a current of air was sweeping through the tube the maximum in the positive current was much decreased as shown by fig. 11.

The ordinary characteristic current-voltage curves as obtained in the process of experiments without a series spark give the negative characteristic as lying above the positive. This relative position is maintained in all cases, with one or two minor exceptions.

When a short spark is placed in series with the corona these positions are reversed and the positive curve lies above the negative, except at the starting point where the curves cross giving a lower starting potential for the negative wire (see fig. 12). However, the starting potential with the spark in series is higher than for the other case. It might be pointed out also that the characteristics taken with a series spark are more widely separated than those taken without, showing a wider variation in the current from the positive and negative wires for a given voltage.

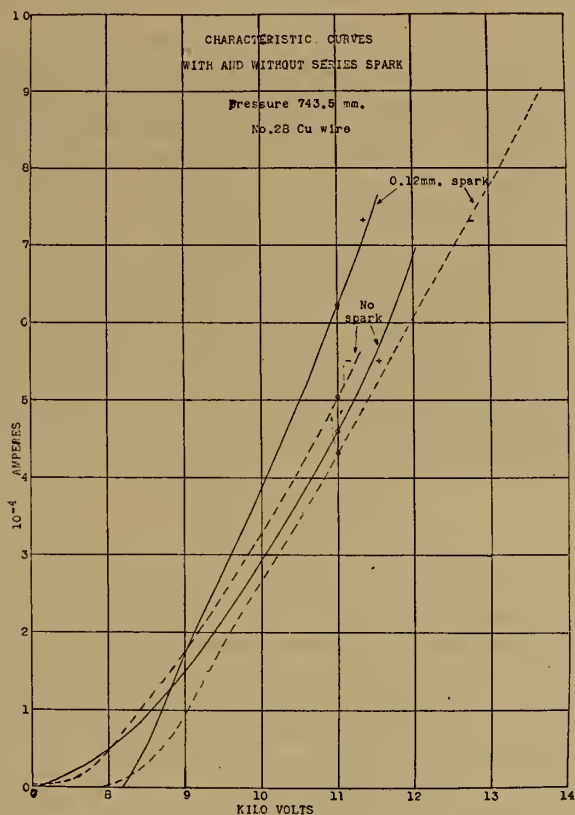
It was found when the spark gap was closed while current was flowing that the current would drop in a short time to a position on the ordinary characteristic curve. For instance, if the wire is positive at 11,000 volts and a 0.12 mm. spark is in series, a current of  $6.2 \cdot 10^{-4}$  amperes will flow. Short-circuiting the spark gap will cause the current to drop to the value  $4.6 \cdot 10^{-4}$  amperes which is a point on the ordinary positive characteristic curve. Similarly by short-circuiting the spark gap when the wire is negative the current will increase to a value which lies on the ordinary negative characteristic. These observations again show that the positive streamers carry a large current.

Without a spark gap in series with the tube the ordinary uniform positive glow is formed by ionization in the gas near the wire where the field strength is greater than thirty kilovolts per centimeter, the current being carried by both positive and negative ions. The usual negative corona discharge begins critically as a uniform



glow similar to that of the positive discharge but has a greater thickness. The brushes or negative beads soon formed by a slight potential increase bear a similarity to the arc, and in addition from the position of the negative characteristic curves and the influence which the surface condition and the material of the wires have on them<sup>3</sup>

FIG. 12.



lead us to the belief that an electron emission is present in addition to ionization by collision in the gas.

The case is somewhat different when a series spark gap is used. We may consider the corona tube as a leaky condenser connected in series with a spark gap and a constant source of high potential. A charge will build

<sup>3</sup> "Direct Current Corona from Different Surfaces and Metals," Phys. Rev., October 1916.

up on the condenser until the potential difference of the spark gap is sufficient to break down the air between the electrodes. An instantaneous unidirectional current will flow across the spark gap and at the same time the potential across the tube will increase to a point where the corona is formed. The current now through the tube will immediately reduce the potential of the spark gap below its critical point and the circuit will be broken. The process is then repeated.

The more nearly uniform appearance of the negative corona can now be explained as a superimposed building up and decay of the negative glow discharge through its different stages as the potential on the tube fluctuates. The positive streamers have at times been observed at critical voltages on rough wires when no spark was in series. These streamers are similar to the positive brush discharges observed from pointed electrodes maintained at high positive potentials. Their characteristic presence in the corona tube when a spark is in series is due probably to the sudden impression of a strong field and may be accompanied by a discharge of positive metallic ions, since it has been observed that the surface of the wire becomes disintegrated at points where these streamers are maintained.

#### SUMMARY.

1. A spark gap in series with the discharge tube affects the positive and negative corona in very characteristic and striking ways.
2. The changes are due to intermittent currents.
3. A hot-lime-cathode Braun tube has been developed and used in observing the weak pulsating currents which pass through the spark and the corona tube.
4. Evidence has been given to show the relation of the corona to the arc discharge.
5. An attempt at an explanation of the pulsating current has been made.

In conclusion I wish to thank Dr. Jakob Kunz for suggesting this work and for his kind interest and help during its progress. I am also indebted to Professor A. P. Carman who has provided the necessary facilities for the investigation.

ART. XX.—*The Ternary System MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>*; by  
G. A. RANKIN and H. E. MERWIN.

Introduction.

The Crystalline Phases.

General Procedure.

Limits of the Fields.

Stable Compounds.

Slow crystallization of certain glasses high in Al<sub>2</sub>O<sub>3</sub>.

Unstable Compounds.

Melting Temperatures within the Fields.

The Boundary Curves.

The Quintuple Points.

Composition and Properties of the Ternary Compound (Cordierite), especially with regard to solid solution.

The Concentration-temperature Solid Model.

Natural Cordierite.

FeO in Magnesian minerals and rocks.

Summary.

## INTRODUCTION.

The investigation of the ternary system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> was undertaken in order to determine all the crystalline substances formed from pure melts of these oxides, and to establish the equilibrium relations of such of the crystals as are stable in contact with the liquid. Stated briefly, this involved a microscopical study to identify the different crystalline substances, and a thermal study to determine the melting temperatures of these substances when alone or in mixtures.

## THE CRYSTALLINE PHASES.

The crystalline substances found to be stable in contact with liquid are here enumerated: the three components, MgO (periclase), Al<sub>2</sub>O<sub>3</sub> (corundum), SiO<sub>2</sub> (tridymite, cristobalite); the four binary compounds, 2MgO.SiO<sub>2</sub> (forsterite), MgO.SiO<sub>2</sub> (clinoenstatite), MgO.Al<sub>2</sub>O<sub>3</sub> (spinel), Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (sillimanite); and a ternary compound, 2MgO.2Al<sub>2</sub>O<sub>3</sub>.5SiO<sub>2</sub> (which may be considered an end member in the series of cordierites). Since the properties of the components and binary compounds have been described in previous papers,<sup>1</sup> they will be treated

<sup>1</sup> The following papers summarize and amplify what had been done previously: The Binary System MgO-SiO<sub>2</sub>, N. L. Bowen and Olaf Andersen, this Journal, 37, 478, 1914; The Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, G. A. Rankin and F. E. Wright, *ibid.*, 39, 1-79, 1915; The Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-MgO, G. A. Rankin and H. E. Merwin, J. Am. Chem. Soc., 38, 568, 1916; and The Ternary System Diopside-forsterite-silica, N. L. Bowen, this Journal, 38, 207, 1914.

only incidentally here,<sup>2</sup> but the equilibrium relations of these forms in ternary mixtures of  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  will be considered in detail. On the other hand, cordierite of such composition, and an unstable form having similar composition which appears at lower temperatures, have not been described before,<sup>3</sup> therefore their properties and mode of formation will be taken up.

#### GENERAL PROCEDURE.

In this account only such additional apparatus, experimental methods and applications of the phase rule will be described as seem to be necessary for understanding this particular problem.

The first step in this investigation consisted in the preparation from especially pure  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  of a few furnace charges whose composition represented random intervals over the entire range of ternary mixtures. It may be said concerning these: (1) that compositions high in  $\text{SiO}_2$ , being viscous, require repeated fusions with subsequent fine grinding in order to insure chemical homogeneity throughout the charge. This condition is established in melts which do not crystallize readily on cooling by the determination of the uniformity in the refractive index of the glass obtained from such melts; (2) that those melts containing so high a percentage of either  $\text{MgO}$ , or  $\text{Al}_2\text{O}_3$  that they melt but little if any below the melting point of platinum,<sup>4</sup> about 1750, further heated in the iridium furnace; this insures the formation of sufficient liquid to permit complete combination to take place; (3) that in many of the compositions, particularly those high in alumina, the compounds are readily formed from their components at temperatures at which there is but little if any liquid present.

Having prepared a number of chemically homogenous charges of different compositions, the next step was the

<sup>2</sup>In these melts clinoenstatite is seldom twinned. Needles, prisms and tables have been found in the same quench.

<sup>3</sup>J. Morozewicz, "Experimentelle Untersuchungen über die Bildung der Minerale im Magma," p. 68, briefly described crystals obtained from silicate melts, which are similar to this high temperature form, and which he called cordierite. The relation of various anhydrous crystals to cordierite will be discussed under another heading.

<sup>4</sup>All charges are fused in platinum crucibles placed in a Fletcher gas-blast furnace.

determinations of their primary crystalline phases; that is, the determinations of the crystalline substance which is the first to crystallize from a completely melted cooling charge, or the last to melt in a crystalline charge when heated. The determination of the primary crystalline phase in a given composition is carried out by heating a small charge of the material to various constant temperatures for a period of time sufficient to establish equilibrium, and suddenly cooling (quenching) so as to prevent the crystallization of any liquid which may have formed. By proceeding systematically in this way one eventually obtains a quench which contains a single crystalline substance embedded in glass.

In this manner the primary phases which could be obtained below 1600°<sup>5</sup> were determined in the first composition prepared. These data give one an idea not only as to the different crystalline compounds which will be found in the system MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> but also an idea as to the melting temperatures throughout this system. With the preliminary data, thus obtained, as a working basis, other compositions were made up and the primary phases determined. Proceeding systematically in this way to prepare charges, whose compositions are such as to give further information as to the crystalline substances found in this system, the range of compositions in which each such substance occurs as a primary phase was determined. In other words, using phase rule terms, the equilibrium field of each such crystalline substance was established.

For the study of the composition of the ternary compound, glasses were required which contained no crystals. Many of these glasses required preparation at temperatures considerably above 1600°. Small charges were melted in the gas blast furnace and subsequently rapidly chilled by immersing in water.

#### LIMITS OF THE FIELDS.

Data which determine the limits of each field are given in tables 1-7 inclusive. These data are presented graphically in the triangular diagram, figure 1.

<sup>5</sup> 1600° C is about the upper limit of the platinum-resistance furnace from which the charges are quenched by dropping into a dish of mercury.

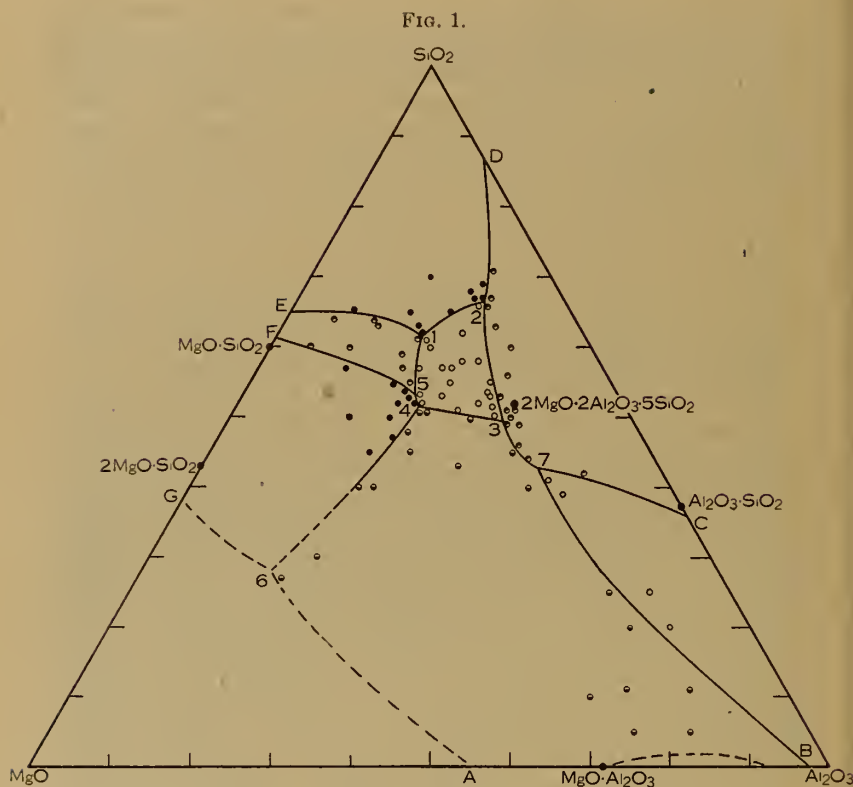


TABLE 1.

Quenchedings which determine the limits of the field of spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ )<sup>1</sup>; see also Table 8.

Composition MgO	Phases present, glass + spinel.			Temp.	Time in hours
	Weight Al <sub>2</sub> O <sub>3</sub>	Per cent SiO <sub>2</sub>			
22.0	73.0	5.0		1900 <sup>2</sup>	
15.0	80.0	5.0		1900 <sup>2</sup>	
15.0	60.0	25.0		1750 <sup>2</sup>	
55.0	18.0	27.0		1750 <sup>2</sup>	
49.0	21.0	30.0		1700 <sup>2</sup>	
37.0	23.0	40.0		1600	.25
39.0	21.0	40.0		1600	.25
17.0	38.0	45.0		1475	.5
30.0	25.0	45.0		1450	.5
25.0	24.0	51.0		1375	.5

<sup>1</sup> Formulas written thus are ideal. The actual crystals formed in parts of the field may have quite a different composition. In the case of spinel solid solution is extensive.

<sup>2</sup> Iridium furnace melt.

TABLE 2.

Quenchings which determine the limits of the field of forsterite ( $2MgO.SiO_2$ ); see also Table 9.

<i>Phases present, glass + 2MgO.SiO<sub>2</sub>.</i>				
Composition	Weight	Per cent	Temp.	Time
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		in hours
31.0	22.0	47.0	1450	.5
30.0	20.0	50.0	1450	.5
26.0	22.0	52.0	1370	.5
28.0	20.0	52.0	1400	.5
26.0	20.0	54.0	1377	.5
32.0	11.0	57.0	1465	.5

TABLE 3.

Quenchings which determine the limits of the field of clinoenstatite ( $MgO.SiO_2$ ); see also Table 10.

<i>Phases present, glass + MgO.SiO<sub>2</sub>.</i>				
Composition	Weight	Per cent	Temp.	Time
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		in hours
25.0	18.0	57.0	1360	.5
30.0	10.0	60.0	1465	1.0

TABLE 4.

Quenchings which determine the limits of the field of SiO<sub>2</sub>; see also Table 11.

<i>Phases present, SiO<sub>2</sub> + glass.</i>				
Composition	Weight	Per cent	Temp.	Time
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		in hours
20.0	17.0	63.0	1370	.5
15.0	20.0	65.0	1390	.5
27.0	8.0	65.0	1475	.5
10.0	23.0	67.0	1445	.5
9.0	22.0	69.0	1450	.5

TABLE 5.

Quenchings which determine the limits of the field of sillimanite ( $Al_2O_3.SiO_2$ ); see also Table 12.

<i>Phases present, glass + Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>.</i>				
Composition	Weight	Per cent	Temp.	Time
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		in hours
12.0	46.0	42.0	1575	.5
16.0	38.0	46.0	1490	.5
16.0	35.0	49.0	1465	2.0
15.0	35.0	50.0	1500	.5
15.0	34.0	51.0	1465	1.0
12.4	31.6	56.0	1490	.5
10.4	26.6	63.0	1425	.5
9.0	24.0	67.0	1450	.5
7.0	22.0	71.0	1475	.5

TABLE 6.

Quenchings which determine limits of field of cordierite  
( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ); see also Table 13.

*Phases present, cordierite + glass.*

Composition MgO	Weight $\text{Al}_2\text{O}_3$	Per cent $\text{SiO}_2$	Temp.	Time in hours
16.0	34.0	50.0	1450	1.0
17.0	33.0	50.0	1460	.5
16.0	33.0	51.0	1450	1.0
21.0	28.0	51.0	1430	1.0
16.5	32.0	51.5	1450	1.0
18.0	30.0	52.0	1400	1.5
16.0	31.0	53.0	1450	1.0
25.0	22.0	53.0	1370	.5
16.0	30.3	53.7	1450	1.0
15.0	30.0	55.0	1440	.5
20.0	19.0	61.0	1350	.5

TABLE 7.

Quenchings which determine the limits of the field of  $\text{Al}_2\text{O}_3$ .

*Phases present, glass +  $\alpha$   $\text{Al}_2\text{O}_3$  (corundum).*

Composition MgO	Weight $\text{Al}_2\text{O}_3$	Per cent $\text{SiO}_2$	Temp.	Time in hours
10.0	70.0	20.0	1750 <sup>1</sup>	
10.0	65.0	25.0	1750 <sup>1</sup>	
14.0	47.0	39.0	1585	.5
15.0	44.0	41.0	1575	.5

<sup>1</sup> Iridium furnace melt.

While it is not our present purpose to discuss each of these fields at length, it may be well to state here certain special facts concerning the fields and their respective crystalline phases.

#### *Fields of Stable Compounds.*

The components  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and the compounds  $2\text{MgO}\cdot\text{SiO}_2$ ,  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  and probably  $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  do not dissociate when melting, therefore the composition of each necessarily lies within its respective field. The accurate determinations of the limits of these fields were in most cases made without difficulty. The limits of the field of  $\text{MgO}$  and certain portions of the fields of  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ ,  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  and  $2\text{MgO}\cdot\text{SiO}_2$ , however, could not be determined with extreme accuracy for the reason that the temperatures required are beyond the range of the platinum quenching furnace,  $1600^\circ$ . Due to the pecu-



liar circumstance, however, that the excess glass from compositions containing between 65%  $Al_2O_3$  and 85%  $Al_2O_3$  did not crystallize readily even when slowly cooled from the high temperature ( $2100^\circ$ ) obtained in the iridium furnace, it was possible to obtain  $Al_2O_3$  (corundum) and spinel<sup>6</sup> each alone imbedded in glass in certain compositions. This enabled us to determine more accurately than would otherwise have been possible the limits of certain portions of the fields of  $Al_2O_3$  and spinel. Aside from these data the limits of the portions of the fields mentioned which are at temperatures too high for direct study were determined indirectly from certain theoretical reasonings based on experimental evidence. This evidence and theory will be taken up later when we come to consider the boundary curves and quintuple points.

#### *Fields of Unstable Compounds.*

Clinoenstatite,  $MgO.SiO_2$ , and cordierite have no definite melting points, each being a crystalline substance of such a nature that when pure it dissociates when melting begins, therefore their compositions lie outside of their respective fields. The determinations of the limits of these two fields involved no especial difficulty since each lies wholly within the range of temperatures possible in the platinum quenching furnace. The determination of the composition of such unstable crystalline substances may be, however, a matter of extreme difficulty. Of the two such substances which we have to consider in this ternary system one,  $MgO.SiO_2$ , is a definite compound of constant composition; the other, cordierite, is affected by solid solution, and is so fine-grained when crystallized from a glass at temperature below that at which it begins to melt, that its homogeneity cannot be accurately tested. (See p. 316.)

#### MELTING TEMPERATURES WITHIN THE FIELDS.

Of the eight fields of the diagram two have melting temperatures all of which may be determined in the platinum quenching furnace. These are the fields of  $MgO.SiO_2$  and the ternary compound (cordierite).

<sup>6</sup> Microscopical examination of various iridium furnace melts containing only spinel and a small percentage of glass would seem to indicate that spinel in ternary mixtures takes up a small amount of  $SiO_2$  in solid solution. This together with the extent of the solid solution between  $Al_2O_3$  and  $MgO.Al_2O_3$  in the binary system is indicated in fig. 1.

Part of the melting temperatures of all the other fields, except the field of MgO, may be thus determined. Tables 8-13 show these ascertained melting temperatures for various compositions within each field. From these temperatures and others referred to later the isotherms of fig. 6 were drawn.

TABLE 8.

Quenchings which determine melting temperatures of various compositions within field A-6-4-3-7-B; Primary phase is (MgO.Al<sub>2</sub>O<sub>3</sub>) spinel.

Composition MgO	Weight Al <sub>2</sub> O <sub>3</sub>	Per cent SiO <sub>2</sub>	Temp.	Time in hours	Phases present
17.5	42.5	40.0	1600	.25	Glass + tr. spinel
25.0	32.0	43.0	1583	.5	Glass
			1570	.5	Glass + spinel
29.0	23.0	48.0	1450	.5	Glass
			1430	.5	Glass + spinel
20.0	30.0	50.0	1450	.5	Glass
			1435	.5	Glass + spinel
25.0	25.0	50.0	1410	.5	Glass
			1390	.5	Glass + spinel
26.0	23.0	51.0	1380	1.0	Glass
			1376	1.0	Glass + spinel

TABLE 9.

Quenchings which determine melting temperatures of various compositions within the field G-6-4-5-F; Primary phase is 2MgO.SiO<sub>2</sub>.

Composition MgO	Weight Al <sub>2</sub> O <sub>3</sub>	Per cent SiO <sub>2</sub>	Temp.	Time in hours	Phases present
35.0	20.0	45.0	1555	.5	Glass
			1550	.5	Glass + tr. 2MgO.SiO <sub>2</sub>
35.0	15.0	50.0	1560	.5	Glass
			1530		Glass + tr. 2MgO.SiO <sub>2</sub>
26.0	21.0	53.0	1375	.5	Glass
			1365	.5	Glass + 2MgO.SiO <sub>2</sub>
27.0	18.0	55.0	1415	.5	Glass
			1390	.5	Glass + 2MgO.SiO <sub>2</sub>

TABLE 10.

Quenchings which determine melting temperatures of various compositions within field is F-5-1-E; Primary phase is MgO.SiO<sub>2</sub>.

Composition MgO	Weight Al <sub>2</sub> O <sub>3</sub>	Per cent SiO <sub>2</sub>	Temp.	Time in hours	Phases present
25.0	20.0	55.0	1375	.5	Glass
			1365	.5	Glass + MgO.SiO <sub>2</sub>
24.0	17.0	59.0	1383	1.5	Glass
			1370	1.0	Glass + MgO.SiO <sub>2</sub>
35.0	5.0	60.0	1515	.5	Glass
			1510	.5	Glass + MgO.SiO <sub>2</sub>
21.0	18.0	61.0	1370	.5	Glass
			1360	.5	Glass + MgO.SiO <sub>2</sub>
25.0	12.0	63.0	1440	.5	Glass
			1420	1.0	Glass + MgO.SiO <sub>2</sub>
30.0	6.0	64.0	1500	.5	Glass
			1498	.5	Glass + MgO.SiO <sub>2</sub>
25.0	11.0	64.0	1450	1.0	Glass
			1425	.5	Glass + MgO.SiO <sub>2</sub>

TABLE 11.

Quenchings which determine melting temperatures of various compositions within field E-1-2-D; Primary phase is  $SiO_2$ .

Composition MgO	Weight $Al_2O_3$	Per cent $SiO_2$	Temp.	Time in hours	Phases present
20.0	15.0	65.0	1455	.5	Glass
			1450	.5	Glass + $SiO_2$
11.0	22.0	67.0	1445	.5	Glass
			1435	.5	Glass + $SiO_2$
20.0	18.0	62.0	1355	.5	Glass
			1352	.5	Glass + $SiO_2$
15.0	15.0	70.0	1530	.5	Glass
			1500	.5	Glass + $SiO_2$

TABLE 12.

Quenchings which determine melting temperatures of various compositions within field D-2-3-7-C; Primary phase is  $Al_2O_3.SiO_2$ .

Composition MgO	Weight $Al_2O_3$	Per cent $SiO_2$	Temp.	Time in hours	Phases present
15.0	32.0	53.0	1460	1.0	Glass
			1457	1.0	Glass + $Al_2O_3.SiO_2$
10.0	24.0	66.0	1438	1.0	Glass
			1435	1.0	Glass + $Al_2O_3.SiO_2$
16.0	40.0	44.0	1550	.25	Glass
			1525	.25	Glass + $Al_2O_3.SiO_2$
14.5	36.5	49.0	1550	.25	Glass
			1525	.25	Glass + $Al_2O_3.SiO_2$
10.0	30.0	60.0	1550	.25	Glass
			1525	.25	Glass + $Al_2O_3.SiO_2$

TABLE 13.

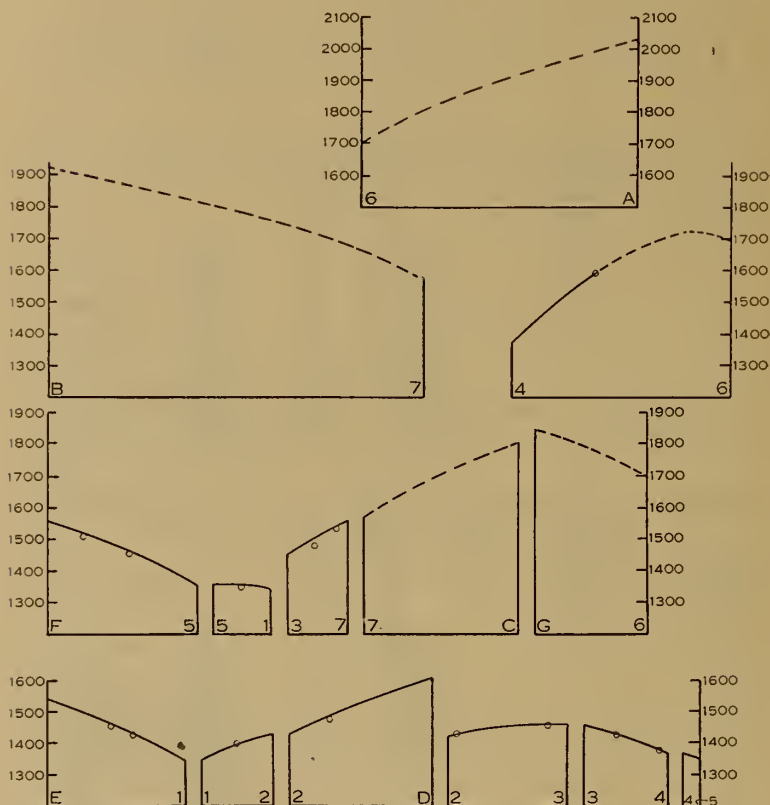
Quenchings which determine melting temperatures of various compositions within field 1-2-3-4-5; Primary phase is the ternary compound (cordierite).

Composition MgO	Weight $Al_2O_3$	Per cent $SiO_2$	Temp.	Time in hours	Phases present
16.0	34.0	50.0	1460	1.0	Glass
			1457	1.0	Glass + cordierite
20.0	23.0	57.0	1400	.5	Glass
			1375	.5	Glass + cordierite
18.0	30.0	52.0	1450	.5	Glass
			1425	.5	Glass + cordierite
25.0	23.0	52.0	1370	.5	Glass
			1365	.5	Glass + cordierite
20.0	25.0	55.0	1415	.5	Glass
			1400	.5	Glass + cordierite
15.0	30.0	55.0	1460	.5	Glass
			1450	.5	Glass + cordierite
23.0	20.0	57.0	1375	.5	Glass
			1350	1.0	Glass + cordierite
15.0	27.0	58.0	1450	.5	Glass
			1425	.5	Glass + cordierite
20.0	20.0	60.0	1365	1.0	Glass
			1340	.5	Glass + cordierite
15.0	23.0	62.0	1425	.5	Glass
			1400	.5	Glass + cordierite
11.0	23.0	66.0	1450	1.0	Glass
			1440	.5	Glass + cordierite

## THE BOUNDARY CURVES.

The boundary lines in fig. 1 represent the projection upon the horizontal plane of the lines on the solid concentration-temperature diagram. In order to make clear the way in which the temperature varies along these

FIG. 2.



lines, we have made projections upon a vertical plane, obtaining in this way the series of boundary curves reproduced in fig. 2, in which the numbers and letters used correspond to those given in fig. 1. The ordinates represent temperatures which were determined experimentally.

These temperatures which are ascertained by the quenching method are contained in Table 14. The temperatures at the ends of the boundary curves are given later as quintuple and quadruple point temperatures.

Of the 14 boundary curves in this system, all of which are given in fig. 2, there are three which are represented by dotted lines to indicate that the compositions and temperatures along these lines could not be accurately determined, because direct methods could not be used. The indirect methods employed will be described when quintuple point 6 is considered. Two other boundary curves, 2-3 and 1-5, are so flat at their summits that from temperatures of complete melting alone it has not been feasible to determine whether or not either contains a maximum. However, from crystallization curves a maximum is evident in 2-3 (see Table 14a), and must lie between 53% and 60%  $SiO_2$ . Several crystallization curves for compositions near point 5 were run, but they did not definitely indicate a maximum on line 1-5.

TABLE 14.

Quenchings which determine temperatures for points on the boundary curves.

Comp. Weight MgO	Per cent $Al_2O_3$	Per cent $SiO_2$	Temp.	Time in hours	Phases present	Bound- ary
30.0	6.0	64.0	1482	.5	Glass + MgO.SiO <sub>2</sub>	E-1
			1460	2.0	Glass + MgO.SiO <sub>2</sub> + SiO <sub>2</sub>	
27.0	8.0	65.0	1475	.5	Glass + SiO <sub>2</sub>	1-2
			1450	1.0	Glass + SiO <sub>2</sub> + MgO.SiO <sub>2</sub>	
20.0	19.0	61.0	1365	1.0	Glass + cordierite	1-2
			1350	.5	Glass + cordierite + SiO <sub>2</sub>	
15.0	20.0	65.0	1400	.5	Glass	D-2
			1390	.5	Glass + SiO <sub>2</sub> + cordierite	
7.0	22.0	71.0	1485	.5	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	D-2
			1475	.5	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + SiO <sub>2</sub>	
10.0	24.0	66.0	1435	1.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	2-3
			1430	1.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + cordierite	
15.0	32.0	53.0	1460	.5	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	3-7
			1455	.5	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + cordierite	
16.0	35.0	49.0	1465	2.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	3-7
			1460	1.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + cordierite	
16.0	38.0	46.0	1490	.5	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	3-7
16.0	40.0	44.0	1550	.5	Glass	3-7
			1525	.5	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + spinel (tr.)	
17.0	33.0	50.0	1458	.5	Glass + cordierite	3-4
			1456	1.0	Glass + cordierite + spinel	
20.0	30.0	50.0	1435	.5	Glass + spinel	3-4
			1425	.5	Glass + spinel + cordierite	
25.0	25.0	50.0	1390	.5	Glass + spinel	3-4
			1375	1.0	Glass + spinel + cordierite	
21.0	28.0	51.0	1430	1.0	Glass + cordierite	3-4
			1425	1.0	Glass + cordierite + spinel	
26.0	23.0	51.0	1376	1.0	Glass + spinel	4-6
			1375	.5	Glass + spinel + 2MgO.SiO <sub>2</sub>	
31.0	22.0	47.0	1450	.5	Glass + 2MgO.SiO <sub>2</sub>	4-6
			1435	.5	Glass + 2MgO.SiO <sub>2</sub> + spinel	
37.0	21.0	42.0	1600	.25	Glass	4-6

TABLE 14 (continued).

Quenchings which determine temperatures for points on the boundary curves.

Comp.	Weight	Per cent	Temp.	Time	Phases present	Boundary
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		in hours		
			1585	.25	Glass + tr. 2MgO.SiO <sub>2</sub> + tr. spinel	
37.0	23.0	40.0	1600	.25	Glass + spinel	
			1550	.5	Glass + spinel + 2MgO.SiO <sub>2</sub>	
26.0	23.0	51.0	1376	1.0	Glass + spinel	4-5
			1370	1.0	Glass + spinel + 2MgO.SiO <sub>2</sub> + [cordierite	
			1365	.5	Glass + 2MgO.SiO <sub>2</sub> + cordierite	
18.0	30.0	52.0	1390	.5	Glass + cordierite	
			1360	1.0	Glass + cordierite + 2MgO.SiO <sub>2</sub>	
22.0	25.0	53.0	1362	.5	Glass + cordierite	
			1359	1.0	Glass + cordierite + 2MgO.SiO <sub>2</sub>	
32.0	11.0	57.0	1465	.5	Glass + 2MgO.SiO <sub>2</sub>	F-5
			1450	.5	Glass + 2MgO.SiO <sub>2</sub> + MgO.SiO <sub>2</sub>	
27.0	18.0	55.0	1390	.5	Glass + 2MgO.SiO <sub>2</sub>	
			1370	.5	Glass + MgO.SiO <sub>2</sub>	
26.0	20.0	54.0	1377	.5	Glass + 2MgO.SiO <sub>2</sub>	
			1370	.5	Glass + 2MgO.SiO <sub>2</sub> + MgO.SiO <sub>2</sub>	
25.5	21.0	53.5	1361	.5	Glass	
			1360	.5	Glass + 2MgO.SiO <sub>2</sub> + MgO.SiO <sub>2</sub>	
26.0	21.0	53.0	1365	.5	Glass + 2MgO.SiO <sub>2</sub>	
			1360	.5	Glass + 2MgO.SiO <sub>2</sub> + MgO.SiO <sub>2</sub>	
25.0	20.0	55.0	1355	.5	Glass + MgO.SiO <sub>2</sub>	5-1
			1350	.5	Glass + MgO.SiO <sub>2</sub> + cordierite	
23.0	20.0	57.0	1352	1.0	Glass + cordierite	
			1350	.5	Glass + cordierite + MgO.SiO <sub>2</sub>	
21.0	18.0	61.0	1360	.5	Glass + MgO.SiO <sub>2</sub>	
			1350	.5	Glass + MgO.SiO <sub>2</sub> + cordierite	
12.0	46.0	42.0	1575		Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + <i>a</i> Al <sub>2</sub> O <sub>3</sub> (tr.)	C-7
15.0	44.0	41.0	1575		Glass + spinel (tr.) + <i>a</i> Al <sub>2</sub> O <sub>3</sub>	B-7
14.0	47.0	39.0	1600		Glass + spinel (tr.) + <i>a</i> Al <sub>2</sub> O <sub>3</sub>	

TABLE 14a.

Quenchings which indicate a maximum on the boundary curve between sillimanite and the ternary compound (cordierite).

Comp.	Weight	Per cent	Temp.	Phases present
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		
16.0	33.0	51.0	1460	Glass + <i>a</i> ternary compound
			1400	Glass + <i>a</i> ternary compound + spinel
15.0	34.0	51.0	1465	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>
			1460	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> (not yet resorbed) + ternary compound + spinel
18.0	30.0	52.0	1400	Glass + ternary compound
			1360	Glass (?) + ternary compound + 2MgO.SiO <sub>2</sub> [+ ?
14.4	35.6	50.0	1525	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>
			1400	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> (not yet resorbed) + spinel

## THE QUINTUPLE POINTS.

Of the seven quintuple points in this system, one (point 1, fig. 1) is a well-established eutectic; another

(point 6, fig. 1), at a temperature beyond the reach of the platinum resistance furnace, is probably a eutectic; and a third (point 5, fig. 1) at the end of a flat boundary curve where it has been found impossible to be certain of equilibrium within a reasonable time, may be a eutectic.

Point 6 has been located and characterized as a eutectic according to theoretical reasoning based on such experimental evidence as could be obtained. If this point is a eutectic its composition must necessarily lie within the triangle MgO, MgO.Al<sub>2</sub>O<sub>3</sub>, 2MgO.SiO<sub>2</sub>, but if it is not a eutectic its composition must lie outside of this triangle. In either case, however, it is necessary that the three boundary curves which meet at this point be of such a nature that each one will intersect the angle formed by the other two. From these considerations and a glance at points 4, A, and G (fig. 1), the starting points of these three boundaries, 4-6, A-6 and G-6 respectively, it is evident that if point 6 is a eutectic it will probably be of a composition near the line joining MgO.Al<sub>2</sub>O<sub>3</sub> and 2MgO.SiO<sub>2</sub> and inside the triangle MgO.Al<sub>2</sub>O<sub>3</sub> - MgO - 2MgO.SiO<sub>2</sub>, since the general direction of boundary 4-6 is fixed by actual data, and theoretically boundary G-6 will only intersect the angle formed by A-6 and 4-6 if such is the case. Granting for the moment that point 6 is a eutectic, let us consider the nature of indirect experimental evidence which would prove this to be so. If point 6 is thus a eutectic the composition line MgO.Al<sub>2</sub>O<sub>3</sub>-2MgO.SiO<sub>2</sub> will be the projection of the concentration-temperature diagram for the binary eutectic system of these two compounds, and the binary eutectic composition will be at the intersection of this line and the boundary 4-6. This point of intersection represents a composition which is the maximum melting temperature on the boundary 4-6. That MgO.Al<sub>2</sub>O<sub>3</sub> - 2MgO.SiO<sub>2</sub> is a binary eutectic system was shown experimentally by microscopic examination of mixtures of these two compounds which had previously been fused in the iridium furnace. These examinations showed such material to contain only these two compounds, while if MgO.Al<sub>2</sub>O<sub>3</sub> - 2MgO.SiO<sub>2</sub> did not form a true eutectic series, well-developed crystals of MgO undoubtedly would have been present. Also such melting temperatures as could be determined for these mixtures in the iridium furnace would tend to show

that the intersection point P represents a maximum temperature on the boundary 4-6.

It is upon such indirect evidence that point 6 is designated as a eutectic.

TABLE 15.

Quenchings which show the course of the crystallization curves which pass through quintuple points (not eutectics) 2 and 4, and that cross the field of the ternary compound (cordierite) near point 3.

Comp.	Weight	Per cent	Temp.	Time	Phases	Point
	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	in hours		
10.0	24.0	66.0	1438	1.0	Glass	(2)
			1435	1.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	
			1428	1.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + cordierite	
			1425	1.0	Glass + SiO <sub>2</sub> (tridymite) + cordierite	
16.0	35.0	49.0	1465	2.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	(3)
			1457	1.0	Glass + Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> + cordierite	
			1450	4.0	Glass + spinel + cordierite	
26.0	23.0	51.0	1378	1.0	Glass	(4)
			1376	1.0	Glass + spinel	
			1375	.5	Glass + 2MgO.SiO <sub>2</sub> + cordierite	

Following is a list of the 7 quintuple points giving composition in weight percentages of MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and the corresponding temperatures as determined by quenches. The numbers assigned to each quintuple point correspond to the numbers in fig. 1.

Point 1 is the eutectic for MgO.SiO<sub>2</sub>, SiO<sub>2</sub> and the ternary compound (MgO 20.3, Al<sub>2</sub>O<sub>3</sub> 18.3, SiO<sub>2</sub> 61.4). Its melting point (1345° ± 5°) is based on the values obtained from various compositions as given in Table 16.

TABLE 16.

Melting temperature: Quintuple point 1 for MgO.SiO<sub>2</sub>, SiO<sub>2</sub> and ternary compound as determined from various compositions.

Composition, weight, per cent	MgO	20.0	18.9	25.0	20.0	25.0
	Al <sub>2</sub> O <sub>3</sub>	19.0	24.1	18.0	18.0	20.0
	SiO <sub>2</sub>	61.0	57.0	57.0	62.0	55.0
Temperature	.....	1348	1340	1340	1345	1345

Point 2 is the quintuple point for SiO<sub>2</sub>, ternary compound and Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (MgO 10.0, Al<sub>2</sub>O<sub>3</sub> 23.5, SiO<sub>2</sub> 66.5). Its melting temperature (1425° ± 5°) is based on the values obtained from compositions given in Table 17.

TABLE 17.

Melting temperature: Quintuple point 2 for SiO<sub>2</sub>, ternary compound and Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> as determined from various compositions.

Composition, weight, per cent	MgO	12.4	10.0	10.0	9.0
	Al <sub>2</sub> O <sub>3</sub>	31.6	30.0	24.0	24.0
	SiO <sub>2</sub>	56.0	60.0	66.0	67.0
Temperature	.....	1425	1425	1425	1425



Point 3 is the quintuple point for ternary compound,  $Al_2O_3 \cdot SiO_2$  and spinel ( $MgO$  16.1,  $Al_2O_3$  34.8,  $SiO_2$  49.1). Its melting temperature ( $1460^\circ \pm 5^\circ$ ) is based on the values obtained from various compositions as given in Table 18.

TABLE 18.

Melting temperature: Quintuple point 3 for ternary compound,  $Al_2O_3 \cdot SiO_2$  and spinel as determined from various compositions.

Composition, weight, per cent	$\left\{ \begin{array}{l} MgO \\ Al_2O_3 \\ SiO_2 \end{array} \right.$	15.3 38.8 45.9	16.0 38.0 46.0	16.0 35.0 49.0	16.5 34.5 49.0
Temperature . . . . .		1460	1455	1465	1460

Point 4 is the quintuple point for spinel, ternary compound, and  $2MgO \cdot SiO$  ( $MgO$  25.7,  $Al_2O_3$  22.8,  $SiO_2$  51.5). Its melting temperature ( $1370^\circ \pm 5^\circ$ ) is based on the values obtained from compositions as given in Table 19.

TABLE 19.

Melting temperature: Quintuple point 4 for ternary compound, spinel and  $2MgO \cdot SiO_2$  as determined from various compositions.

Composition, weight, per cent	$\left\{ \begin{array}{l} MgO \\ Al_2O_3 \\ SiO_2 \end{array} \right.$	26.0 23.0 51.0	29.0 23.0 48.0	25.0 24.0 51.0
Temperature . . . . .		1370	1370	1363

Point 5 is the quintuple point (eutectic?) for  $2MgO \cdot SiO_2$ ,  $MgO \cdot SiO_2$ , and ternary compound ( $MgO$  25.0,  $Al_2O_3$  21.0,  $SiO_2$  54.0). Its melting temperature ( $1360^\circ \pm 5^\circ$ ) is based on the values obtained from various compositions as given in Table 20.

TABLE 20.

Melting temperature: Quintuple point 5 for ternary compound,  $MgO \cdot SiO_2$ , and  $2MgO \cdot SiO_2$  as determined from various compositions.

Composition, weight, per cent	$\left\{ \begin{array}{l} MgO \\ Al_2O_3 \\ SiO_2 \end{array} \right.$	22.0 25.0 53.0	25.0 22.0 53.0	26.0 21.0 53.0	25.5 21.0 53.5	25.0 21.0 54.0
Temperature . . . . .		1357	1360	1355	1353	1363

Point 6 is the eutectic point for  $2MgO \cdot SiO_2$ ,  $MgO$ , and spinel ( $MgO$  56.0,  $Al_2O_3$  16.0,  $SiO_2$  28.0). Its melting temperature ( $1700^\circ \pm 25^\circ$ ) is based on values obtained from several compositions melted in the iridium furnace, temperature measurements being made with an optical pyrometer.

Point 7 is the quintuple point for  $Al_2O_3$ , spinel and  $Al_2O_3 \cdot SiO_2$  ( $MgO$  15.2,  $Al_2O_3$  42.0,  $SiO_2$  42.8). Its melt-

ing temperature ( $1575^{\circ} \pm 5^{\circ}$ ) is based on values obtained from various compositions as given in Table 21.

TABLE 21.

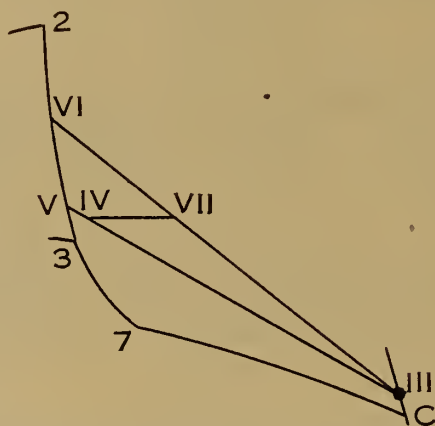
Melting temperature: Quintuple point 7 for spinel,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , and  $\alpha\text{Al}_2\text{O}_3$  as determined from various compositions.

Composition, weight, per cent	{ MgO	10.0	15.0	15.0	14.0	15.0
	{ $\text{Al}_2\text{O}_3$	70.0	60.0	44.0	47.0	48.0
	{ $\text{SiO}_2$	20.0	25.0	41.0	49.0	37.0
Temperature .....		1575	1585	1570	1568	1568

### THE COMPOSITION AND PROPERTIES OF THE TERNARY COMPOUND (CORDIERITE).

The temperatures in the field of the ternary compound are highest along the boundary toward sillimanite, but

FIG. 3.



there is no maximum within the field, therefore the composition of the crystals of the compound which begin separating near the point 3 must be between sillimanite and the maximum in the boundary curve 2-3, that is within the triangle III, IV, V of fig. 3. But the courses of the crystallization curves of Table 14a show that the composition must lie within about the limits IV, V, VI, VII. The simplest formulas that can be written for compositions within this quadrilateral are  $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$  and  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ .

If the crystals separating in the other parts of the field of the ternary compound have compositions thus represented then there should be a maximum on boundary curve 1-5. If the composition of the crystals of the ter-

nary compound at this maximum is near 1:1:3 the maximum should be easily located; on the other hand if near 2:2:5 it would be so near point 5 that it might not be definitely established. As already stated, melting temperatures gave no decisive information concerning such a maximum, therefore a supposedly favorable sample ( $MgO$  25,  $Al_2O_3$  20,  $SiO_2$  55) was heated 18 hours at  $1345^\circ$  to  $1355^\circ$  to determine if forsterite would appear in recognizable form, as a means of settling the question of a maximum. No forsterite was detected. Thus 2:2:5 must be approximately the composition of the ternary compound separating near point 5. But before a more definite conclusion is arrived at the properties of the crystals of this compound separating in various parts of the field must be considered, and such properties compared with optical properties of crystalline aggregates obtained by crystallizing at lower temperatures glasses having the supposed composition of the compound.

Faceted crystals of cordierite are best obtained from melts in which it (or sillimanite) is the primary phase. Such crystals can be studied to best advantage when they occur in glass of considerable higher refractive index, *i. e.*, in melts containing less than 55 percent  $SiO_2$ . All the crystals observed, with the exception of those in one quench, were stout six-sided prisms with basal termination and negative elongation. The prism angle, within the limits of error of measurement, was  $120^\circ$ , and basal sections gave a nearly or quite uniaxial negative interference figure. In the one exceptional case several crystals were observed which gave unmistakable evidence of orthorhombic symmetry, although their general habit was just described. These crystals had the  $120^\circ$  prism and the side and basal pinacoids corresponding to the faces on all the other crystals; they had also the front pinacoid, and a second prism which bevels the edge between the side pinacoid and the unit prism.

The double refraction on the base is too small to give the orientation of  $\beta$  and  $\gamma$  but  $a \parallel \hat{c}$ . The refractive indices of crystals from melts highest in  $SiO_2$  (66%) are  $a = 1.519$ ,  $\beta$  and  $\gamma = 1.522$ . From melts containing about 50%  $SiO_2$   $a = 1.524$ ,  $\beta$  and  $\gamma = 1.528$ . The differences are not much greater than the error of determination,  $\pm 0.002$ , but yet they may represent considerable

solid solution.<sup>7</sup> The birefringence,  $\gamma - \alpha$  as measured independently on several prisms is .003-.004.

The optical method of determining the composition of an unstable compound consists in obtaining from a glass of proper composition at a temperature below that of dissociation, an optically homogeneous crystalline aggregate having optical properties corresponding to the optical properties of crystals which are stable in the field of the compound. The desired aggregate should be obtainable, provided minute porosity does not develop during crystallization. In the case in hand we assume that there is no porosity, for there appears to be expansion instead of contraction during crystallization (the crystals have lower refraction than the glass). Glasses having the compositions MgO 11-13, Al<sub>2</sub>O<sub>3</sub> 31-29, SiO<sub>2</sub> 57 crystallize to aggregates with a mean refractive index of  $1.521 \pm .003$ , that is, like crystals formed in the most siliceous melts within the field of the ternary compound. Likewise glasses of compositions MgO 13-15, Al<sub>2</sub>O<sub>3</sub> 35-33, SiO<sub>2</sub> 52 give  $n = 1.527 \pm .003$ , like crystals from the least siliceous melts. The only simple ternary compounds approximating these compositions are MgO.Al<sub>2</sub>O<sub>3</sub>.3SiO<sub>2</sub> (MgO 12.4, Al<sub>2</sub>O<sub>3</sub> 31.6, SiO<sub>2</sub> 56) and 2MgO.2Al<sub>2</sub>O<sub>3</sub>.5SiO<sub>2</sub> (MgO 13.7, Al<sub>2</sub>O<sub>3</sub> 34.6, SiO<sub>2</sub> 51.7).

What were apparently very nearly homogeneous crystalline aggregates were prepared from glasses of a considerable range of composition extending on the composition diagram as a thin lens-shaped area, with its long axis the silica-spinel line, and one curved boundary nearly coinciding with the boundary curves 7-3-2. This area covers a range of silica content from about 45 to 70 per cent. In fact, if homogeneity of such aggregates had been the sole method of determining the composition of this unstable crystalline phase, the conclusion that it was a solid solution over a long range of compositions would have been reached.

There are three chief points to be considered in the interpretation of such aggregates: (1) the absolute sizes of grain of the crystals. (2) the shapes of the crystals, (3) the relative refractions of the crystals and possible glass. Obviously, whatever the other conditions, if the constituents have nearly the same refractive index, or if

<sup>7</sup> Compare the case of spinel, *J. Am. Chem. Soc.*, **38**, 568, 1916.

the crystals have one dimension or more below microscopic size, the aggregate will appear homogeneous. The substance present in largest amount may crystallize in a meshwork which limits the size of the particles of the other substances. In such a texture diffusion would be so hindered that a very long heating might be required to allow the excess constituent to grow to appreciable size.

Aggregates in which the ternary compound was the chief constituent were prepared by heating for periods of 15 minutes to 5 hours at 900° to 1400°. While the glass was heating the  $\mu$ , or unstable, form of the ternary compound began crystallizing at 900° or less as fine fibers which radiated from points on the surface of the grains. At temperatures of 925° to 1150° this form inverted to the  $\alpha$ -form. The inversion in different portions of the same charge, and in different aggregates from glasses of the same composition, had an extreme temperature range of about 200°. This range is mostly accounted for in a lag in the starting of the inversion. When once started in a grain the inversion proceeded so rapidly that only in a few instances was a grain found, after quenching, to contain both forms. It is significant that the apparent homogeneity of aggregates containing the low temperature, or  $\mu$ -form, covered a greater range of composition than that of the high temperature form. Finer grained and therefore more homogeneous-appearing aggregates would presumably be formed at the lower temperatures. The refractive indices of the aggregates decrease practically linearly with increase of silica. The average refractive index of clear aggregates containing the  $\mu$ -form ranges from 1.535 at 68% SiO<sub>2</sub> to 1.560 at 40% SiO<sub>2</sub>; and of aggregates of the  $\alpha$ -form, 1.515 at 64% SiO<sub>2</sub> to 1.540 at 44% SiO<sub>2</sub>.

The form appearing at the lower temperatures is called unstable because repeated attempts to produce it by heating the stable form at temperatures below those at which the stable form could be produced from the unstable met with no success. Thus there appears to be no true inversion point in this case, but the temperatures at which the rate of inversion becomes notable may be different for aggregates differing in silica content. An apparent rise of this temperature amounting to about 100° for an increase of 30 per cent of silica was observed.

Table 22 contains other details of the observations on these forms.

Thus the optical comparison of crystals from various parts of the cordierite field with crystal aggregates formed from glasses having compositions in which MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> range from 1:1:3 to 2:2:5, indicate that the possibility of solid solution of nearly this extent should be considered. Already it has been shown that the crystallization curves, the temperatures, and the optical properties of the crystals over about one-third of the cordierite field are satisfactorily explained by assuming the existence of a 2:2:5 compound. Solid solution over the range just indicated would account for the optical properties of the rest of the crystals. A diagrammatic representation of change of composition of crystals and course of crystallization curves in this case is shown in fig. 4. A case of more extensive changes is shown in fig. 5.

TABLE 22.

Quenchings showing the characteristics of aggregates of the $\alpha$ - and $\mu$ -ternary compound. <sup>1</sup>				
Composition	Weight	Per cent	Temp.	Phases
MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		
17.5	42.5	40.0	915	$\mu$
			925	$\mu + \text{MgO} \cdot \text{Al}_2\text{O}_3 + ?$
			1000	$\alpha + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + ?$
16.0	40.0	44.0	925	$\mu + \alpha + ?$ (tr.)
			950	$\mu + \alpha + ?$ (tr.)
			975	$\alpha + \mu + \text{MgO} \cdot \text{Al}_2\text{O}_3$ (tr.)
14.5	40.0	45.5	950	$\mu$
			1000	$\alpha + ?$
			1010	$\alpha + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + ?$
			1025	Indefinable aggregate
15.3	38.8	45.9	1000	$\mu + \alpha$
			1050	$\mu + \alpha + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
			1100	$\alpha + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + ?$
14.5	36.5	49.0	950	$\mu$
			1050	$\alpha$
			1300	$\alpha + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + ?$
14.4	35.6	50.0	950	$\mu$
			1050	$\alpha$
			1300	$\alpha + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{MgO} \cdot \text{Al}_2\text{O}_3 ?$
14.0	35.0	51.0	1450	$\alpha$
			1460	Glass + Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>
16.0	33.0	51.0	1360	$\alpha + \text{MgO} \cdot \text{Al}_2\text{O}_3$
			1450	$\alpha + 10\%$ (?) glass
16.5	32.0	51.5	1430	$\alpha + 5\%$ (?) glass
15.0	32.0	53.0	1450	$\alpha + 5\%$ (?) glass
15.0	30.0	55.0	900	$\mu + \text{glass}$
			1000	$\mu + \alpha + ?$ (tr.)

<sup>1</sup> The MgO·Al<sub>2</sub>O<sub>3</sub> and other binary compounds reported here were usually in small amounts and in very small crystals, so that their identification was not always certain.

TABLE 22 (continued).

Quenchings showing the characteristics of aggregates of the  $\alpha$ - and  $\mu$ -ternary compound.

Composition MgO	Weight Al <sub>2</sub> O <sub>3</sub>	Per cent SiO <sub>2</sub>	Temp.	Phases
12.4	31.6	56.0	1100	$a + ?$
			1350	$a + MgO \cdot Al_2O_3 (?)$
			1000	$\mu$
			1100	$a$
			1425	$a$
15.0	27.0	58.0	1435	$a + tr. Al_2O_3 \cdot SiO_2$
			950	Not homogeneous
			1100	Not homogeneous
10.0	30.0	60.0	1100	$\mu$ (a little cloudy)
			1170	$\mu + ?$
			1400	$a + ?$
			1100	$\mu$
10.4	26.6	63.0	1250	$\mu + a + Al_2O_3 \cdot SiO_2$
			1350	$a + Al_2O_3 \cdot SiO_2 + ?$
			1400	$a + Al_2O_3 \cdot SiO_2 + SiO_2 (?)$
			1400	$a + ?$
			1425	$a + ?$
9.	24.0	67.0	1400	$a + ?$

FIG. 4.

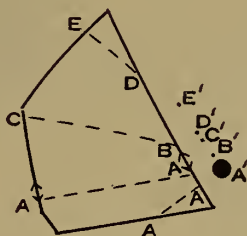


FIG. 4. General relations as in fig. 6. In the area A-A-A-A crystals have composition A' and the crystallization curves are straight lines. In the other parts of the field, because of solid solution, the crystallization curves are not straight lines, and crystals at C, E, etc., have compositions C', E', etc. The maxima are between the arrows.

FIG. 5.

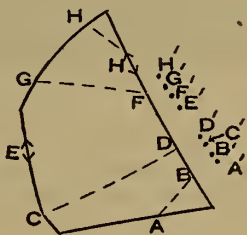


FIG. 5. General relations as in fig. 4 except that solid solution is more extensive.





boundary curves. A solid model corresponding to fig. 6 is shown in fig. 7, and the structure<sup>9</sup> of the model before filling with plaster can be seen in fig. 8.

#### NATURAL CORDIERITE.

So little is known concerning natural cordierite that very definite comparisons between it and the ternary

FIG. 7.



compound just described can not be made. The ternary compound has been called cordierite for various reasons which appear in the text, but which need not be enumerated here. Possibly as much as 2 or 3 per cent of

<sup>9</sup> For description see *The Ternary System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>*, this Journal, 39, 16, 1915.

water may be present in certain unaltered cordierites,<sup>10</sup> others may be nearly or quite anhydrous.<sup>11</sup> After the expulsion of water the residues of all the cordierites analyzed approach very closely the formula  $2(\text{MgO} \cdot \text{FeO}) \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ . A hydrous iron-bearing cordierite after heating 30 minutes at  $1440^\circ$  consisted of glass and

FIG. 8.



sillimanite. Dehydration for 5 minutes at  $600^\circ$  caused a decrease of .010 in the average refractive index of the same material. Probably the escape of water was not accompanied by corresponding shrinkage, and the liquid used to immerse the grains for the refractive index

<sup>10</sup> See "Untersuchungen an Cordierite." Leopold Oppenheimer, *Vehr. Heidelb. Nat. Med. Ver.*, N. F. 13, 257-302, 1914.

<sup>11</sup> H. Bücking, *Neues Jahrb. Min. Geol.*, 1901, I, 72 (ref.).

determination did not at once penetrate the pores.<sup>12</sup> Such behavior has prevented the determination of a possible inversion in cordierite corresponding to that of the  $\mu$ -form of the ternary compound into the  $\alpha$ -form.

#### FeO IN MAGNESIAN MINERALS AND ROCKS.

The magnesia compounds of this ternary system are represented among rock-forming minerals by compounds in which ferrous oxide plays the role of magnesia to a considerable extent. Although it is probable that FeO can thus replace MgO without causing the formation of new phases, yet the temperature relations must be so different that fig. 1 cannot represent the shapes of the fields of these phases. It is conceivable—but not probable unless FeO largely predominates—that the field of cordierite might disappear, and that the field of corundum might approach or even border the field of olivine, but even then corundum would not be expected as an early phase in the crystallization of a dry magma near olivine in composition.

#### SUMMARY.

The temperature-concentration relations of the various crystalline phases in equilibrium with liquid in the ternary system  $MgO-Al_2O_3-SiO_2$  have been investigated, and are represented by diagrams and a model. A ternary compound,  $2MgO.2Al_2O_3.5SiO_2$ , unstable at its melting point and considerably affected by solid solution has been observed in two forms. The  $\mu$ -form (unstable) crystallizes from glass at temperatures below about  $950^\circ$ , and transforms at somewhat higher temperatures into the  $\alpha$ -form (stable). The properties of both forms, but especially the  $\alpha$ -form, are close to those of the mineral cordierite. The effects of solid solution in flattening two of the boundary curves of the field of this compound are discussed.

The preparation and properties of crystalline aggregates of substances which disassociate when melting are considered.

Crystals of natural cordierite disassociate when melting. Brief consideration is given to the effects of FeO in magnesian rocks and minerals.

Geophysical Laboratory, Carnegie Institution of Washington,  
Washington, D. C.

<sup>12</sup> The progressive refilling of pores of crystals from which volatile matter has been expelled can often be observed thus in a viscous liquid under the microscope.

## ABBÉ RÉNÉ JUST HAÜY

1743-1822.

The 175th anniversary of the birth of the Abbé René Just Haüy was celebrated on February 28 at the American Museum of Natural History in New York City. Papers were presented, written for the occasion, by Edgar T. Wherry, Herbert P. Whitlock, George F. Kunz, Edward H. Kraus and Henry S. Washington; and also one prepared for the meeting by the late L. P. Gratacap. Other gentlemen made informal remarks and messages were read from a number of mineralogists unable to be present. There was also an interesting exhibit of portraits of Haüy; of early editions of his books in mineralogy, crystallography and physics; of mineral species described by him and other valuable memorabilia.

Professor Alfred Lacroix, who now occupies Haüy's chair in mineralogy in Paris, was the honorary chairman of a committee which included many gentlemen connected with the prominent universities in the United States and Canada. The active chairman was Dr. George F. Kunz,\* president of the New York Mineralogical Club.

Haüy's treatise on mineralogy, published in four volumes and atlas in 1809 (revised in 1822), is one of the most important works in the literature of the subject and will always remain a classic in the science. In crystallography his contributions were even more original and he has justly been called the father of the science. As early as 1784 he published a work entitled "Essai d'une Théorie sur la Structure des cristaux." In this he showed that a few types of symmetry were the basis of all the varieties of crystal forms; further, the fundamental law of rational indices was established by him, and the identity of cleavage in crystals of the same species but of different type, as in calcite, led him to the conception of what he called "molécules intégrantes." His deductions from this original idea are not far removed from the present theory of the molecular structure of crystals.

\* The editor is indebted to Dr. Kunz for the block from which the frontispiece of this number has been printed. The drawing was designed by F. Massard and engraved on wood by Remi Henri Joseph Delvaux.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *The Solubility of Pure Radium Sulphate*—S. C. LIND, J. E. UNDERWOOD and C. F. WHITEMORE, of the U. S. Bureau of Mines have found that the solubility of radium sulphate at 25° C. is  $2.1 \times 10^{-8}$  g. in 1 c.c. of water, thus placing it among the least soluble of known salts. The solubility was found by the measurement of the emanation, a method giving accurate results with very small quantities of solution. Concordant results were obtained by directly saturating solutions with the solid sulphate and by precipitating it in solutions, and in each case examining the carefully filtered liquid, so that it is evident that there was no supersaturation.

The solubility of radium sulphate, thus found, is about 1/100 of that of barium sulphate, and it corresponds to the expected solubility derived from the solubility curve of the sulphates of the family of metals, where the solubility of  $\text{CaSO}_4$  is  $2.09 \times 10^{-2}$ , of  $\text{SrSO}_4$  is  $1.5 \times 10^{-4}$  and  $\text{BaSO}_4$  is  $2.3 \times 10^{-6}$ . Now it is known that when a solution containing a mixture of barium and radium salts is partially precipitated by means of a sulphate, the ratio of radium to barium is the same in the precipitate as in the original solution, a result that is entirely contrary to the usual behavior of precipitates of such different solubility. Moreover when both barium and radium are completely precipitated as sulphates from solutions containing radium and barium in the proportion 1 to 1,000,000, the filtrate contains only about  $10^{-12}$  g. of radium per cubic centimeter, an amount much smaller than that to be expected from its solubility. There appears to be no perfectly satisfactory explanation of these unexpected relations.

Another rather peculiar circumstance has been brought out in this investigation in the fact that an excess of sulphuric acid has little or no effect upon the solubility of radium sulphate until the acid is of more than 50 per cent strength, when the solubility begins to increase rapidly. The usual effect of the mass-action of a common ion in diminishing the solubility is therefore apparently absent in this case. The solubility of radium sulphate in sulphuric acid solutions up to 25 per cent acid increases by about one-half from 25° to 35° and again to the same extent from 35° to 45° C.—*Jour. Amer. Chem. Soc.*, 40, 465.

H. L. W.

2. *The Specific Heats at Low Temperatures of Several Metals*.—E. D. EASTMAN and W. D. RODEBUSH have studied the specific heats of sodium, potassium, magnesium and calcium in reference to the law of Dulong and Petit. This law states that

the heat capacity per gram-atom of all the solid elements, excluding those of very low atomic weight, is the same and equal to 6.4 calories per degree. The value varies considerably with different elements and also at different temperatures. A few years ago attention was called by G. N. Lewis to the fact that if the specific heat at constant volume is considered, the deviations from the average are considerably smaller and also that the new value, 5.9 calories per degree, is identical with that calculated on the basis of equipartition. The specific heats at constant volume are derived from the usual ones at constant pressure by taking into consideration the expansion by heat and the compressibility of the elements.

The specific heats under consideration were determined at temperatures between 65 and 300° absolute, and the results show, in accordance with other recent work, that the atomic heats even at constant volume are by no means uniform. In the case of each metal a series of determinations of the atomic heats was made at different temperatures, but only those at the extreme temperatures need be given here:

Metal	Absolute temperature	Constant pressure	Constant volume
Sodium	{ 64.6°	4.52	4.47
	{ 293.5°	6.79	6.29
Potassium	{ 68.6°	5.76	5.69
	{ 286.7°	7.10	6.52
Magnesium	{ 74.9°	2.90	2.87
	{ 288.5°	6.11	5.91
Calcium	{ 67.6°	3.93	3.91
	{ 293.5°	6.75	6.48

At the higher temperatures, which are at about ordinary room-temperature, the atomic heats of all the metals except magnesium are very high, while that of the latter is very near the ideal value, although it is very low at the lower temperature. It appears that no modification of the atomic heat law has as yet been found which makes it other than an approximation even at ordinary temperatures.—*Jour. Amer. Chem. Soc.*, 40, 489.

H. L. W.

3. *Reagents and Reactions*; by EDGARDO TOGNOLI. Translated from the Italian by C. Ainsworth Mitchell. 12mo, pp. 228. Philadelphia, 1918 (P. Blakiston's Son & Co.).—This is a useful little book from the standpoint of the analytical chemist. Its principal part is devoted to clear descriptions of such chemical tests as are frequently referred to, especially in foreign literature, only by the authors' names. These names are arranged alphabetically in the book, but a collective index is

supplied which gives reference to the substances detected by the tests. The number of tests given is in some cases remarkable; for instance, no less than 49 methods are given for detecting dextrose. Another section of the book is devoted to the tests of purity of the more important reagents. Another chapter gives descriptions and methods of preparation of a large number of test-papers, and several tables, mostly of specific gravities of liquids, are given.

4. *Treatise on Applied Analytical Chemistry*; by VITTORIO VILLAVECCHIA (with collaborators), translated by Thomas H. Pope. Vol. I. Large 8vo, pp. 475. Philadelphia, 1918 (P. Blakiston's Son & Co.).—This is the first installment of a proposed two-volume work dealing with methods and standards for the chemical analysis of the principal industrial and food products. The present volume takes up the analysis of potable and industrial waters, commercial chemicals, fertilizers, cement materials, metals and alloys, fuels, tar and its derivatives, mineral oils and fatty substances and the industrial products derived therefrom. The second volume will deal with flesh-foods, milk products, flour and starches, sugars and saccharine products, beer, wine, spirits and liqueurs, essential oils, turpentine, varnishes, rubber, tanning materials, leather, coloring matters, and textile fibers and fabrics.

The author is the director of the chemical laboratories of the Italian Customs. He states that most of the methods described have been tested in the laboratories under his direction, and many of them carried out and studied almost daily by specialists who have coöperated in preparing the book.

In examining the portions of the book covering the fields with which he is most familiar the reviewer has been most favorably impressed with the general excellence of the methods recommended as well as with the clear and concise manner in which they are described. It is believed that the work will be particularly useful to all who are interested in industrial analysis.

H. L. W.

5. *Motion of a Spinning Projectile*.—In a long (48 pages) mathematical paper by J. PRESCOTT some very interesting properties of the motion of solid projectiles of standard form in air at small angles of elevation are brought to light. To simplify the analytical processes Bashforth assumed that the resistance of the air varies as the cube of the velocity of the projectile. It is shown in the present paper that this relation is unsatisfactory because, in general, it holds true only for very small ranges of velocity. Let  $R$  and  $V$  denote resistance and velocity respectively. By plotting  $RV^{-2}$  as ordinate against  $V$  as abscissa the curve is approximately a horizontal straight line for values of  $V$  lying between 0 and about 800 feet per sec. Between 800 and 1300 ft. per sec. the curve rises abruptly and almost vertically to

a new higher ordinate. For all observed values of the velocity greater than 1300 ft. per sec. the graph is again a horizontal (roughly) straight line. In explanation of the apparently strange course of the graph Prescott says: "It is reasonable that there should be a change in the law of resistance at the velocity of sound, for when the velocity of the projectile is less than that of sound, the particles of air encountered by it at any instant had already been set in motion, before the projectile arrived, by the pressure which was transmitted ahead of it, this pressure being transmitted with the velocity of sound. But when the projectile is travelling with a velocity greater than that of sound no pressure waves are transmitted ahead, so that the projectile meets, and has to set in motion, stationary air particles. This change in the behaviour of the air is shown in photographs of flying bullets."

Instead of attempting to find a single empirical equation for  $RV^{-2}$  as a function of  $V$ , the author uses the relations  $R = KV^2$  and  $R = K_1V^2$ , where  $K$  and  $K_1$  are constants pertaining to the horizontal portions of the graph below and above 1060 ft. per sec., respectively. The formulæ for the range, trajectory, etc., obtained on this hypothesis together with the observed (Bashforth) fact that the resistance of the air is proportional to the area which the shot presents to the air in its motion, are then derived and are found to give good agreement between the observed and calculated data. Another fact which is taken account of in the derivation of the equations is involved in the following statement: "It is known that a rifle jumps up or down on being fired, so that the angle of elevation of the rifle barrel just before firing, which is the angle observed in experiments, is not the same thing as the angle of departure of the bullet; that is, the axis of the rifle before firing is not a true tangent to the trajectory."

In the next part of the paper it is shown that the axis of the projectile follows the line of flight while lagging a little behind it, the angle of lag increasing with the range. Also, the action of the air on the side of the shot exposed by the deflection of the axis causes a shot with right-handed spin to veer bodily to the right, giving the deviation known as "drift." It is thus seen that the analogy often drawn between the motion of a projectile and that of a spinning top is not admissible. The fallacy lies in the fact that the external force (gravity) on the top acts in a fixed direction whereas the resistance to a projectile rotates with the line of flight. The precise behaviour of the axis of the shot cannot, therefore, be foreseen from that of the top." "Although the numerical results will have to be modified to suit shells, it is clear from the results worked out that the spin of a shot carries out very faithfully the task of keeping the nose foremost during the flight, and that the deflexion of



the axis is less at effective ranges for the larger shot than for the smaller ones."—*Phil. Mag.*, **34**, 332, 1917.

H. S. U.

6. *A New Secondary Radiation of Positive Rays.*—The question as to whether positive rays are capable of exciting the characteristic X-radiation has been recently investigated by M. WOLFFE. The experimental method may be briefly outlined as follows. A pencil of positive rays was allowed to pass through a channel of circular cross-section (one cm. in diameter) and to impinge upon the covering of a circular opening in a brass box. Each half of this opening was covered by a double layer of metal foil composed of a heavy metal (tin or lead) and a light metal (aluminium). In one half of the window the heavy metal of the double foil was turned toward the incident rays and in the other half the light metal faced the exit end of the long channel. Behind the foils the photographic plate was placed. The foils used were 0.016 mm., 0.028 mm., and 0.007 mm., in the cases of tin, lead, and aluminium, respectively. Such secondary cathode rays as might have been produced by the positive rays and the X-rays in the channel were deflected behind the channel and prevented from striking the window of the box by means of a magnetic field of sufficient strength established between the channel and the box. In order to eliminate the effect that might have been produced by any irregularity of thickness of the two foils, every test was checked by a second exposure with the faces of the double foils reversed.

The characteristic radiation of the heavy metal being more intense and harder than that of aluminium, it reaches the photographic plate with an intensity not appreciably diminished. On the other hand, the characteristic radiation of aluminium is weak and soft and is absorbed to a large extent by the layer of heavy metal through which it has to pass before striking the sensitized surface. Therefore, if it be true that the characteristic radiation of the heavy metal is stimulated by positive rays, then the impression produced on the photographic plate must be stronger behind that half of the window where the positive rays impinge upon the heavy metal, and less strong behind the other half where they first encounter the aluminium foil. The higher the intensity of excitation of the characteristic rays the more pronounced will be this difference in the strength of the impression produced. These theoretical considerations were verified by all of the experimental data. The author summarizes his results in the following words: "1. For the first time the excitation of a *penetrating* radiation by positive rays was observed. This effect was retained on photographic plates in the case of tin and lead, and it is surmised that it is the characteristic X-radiation of these elements. 2. A lower *limit* was found to exist for the voltage necessary for excitation. 3. Einstein's quantum condition leads to the supposition that the new effect that has been

observed is excitation of the L-characteristic rays of either element."—*Phil. Mag.*, 35, 59, 1918. H. S. U.

7. *A Textbook in the Principles of Science Teaching*; by GEORGE RANSOM TWISS. Pp. xxvi, 486. New York, 1917 (The Macmillan Co.).—"This book is intended primarily to be used in the instruction of young men and women who are preparing themselves in colleges and normal schools for careers as teachers of one or more of the natural sciences; but it is hoped that it will be scarcely less useful to science teachers now in service and to superintendents of school systems and principals of public and private secondary schools whose duties involve the direction and supervision of science instruction." The nature of the subject-matter and the exhaustive treatment of the field make it impossible to do justice to the volume in the space at our disposal. Nothing of real value seems to have been overlooked by the author. The first eleven chapters deal with general pedagogical principles which are applicable to all phases of science teaching. Chapters twelve to twenty-three are somewhat more specialized and they pertain primarily to biology, geography, physics, chemistry, and "general science." The last chapter (XXIV) relates to tests and examinations. Appendix A gives a selected list of books for the high school library, while appendices B and C comprise respectively bibliographies for science teachers and the titles of scientific periodicals. The text has been very carefully prepared and it merits the attention of all instructors in science who are really interested in attaining as high a condition of efficiency as possible. H. S. U.

## II. GEOLOGY.

1. *The Fauna of a Medial Tertiary Formation and the Associated Horizons of Northeastern Mexico*; by ROY E. DICKERSON and WILLIAM S. W. KEW. *Proc. California Acad. Sci.*, 4th ser., vol. 7, No. 5, 1917, pp. 125-156, pls. 17-26a. *Climate and its Influence upon the Oligocene Faunas of the Pacific Coast. with Descriptions of some New Species from the Molopophorus lincolnensis Zone; Climatic Zones of Martinecz Eocene Time; Ancient Panama Canals*; by ROY E. DICKERSON. *Ibid.*, Nos. 6, 7, 8, 1917, pp. 157-205, pls. 27-31. In No. 5 of this volume of the Proceedings of the California Academy of Sciences, the listed fauna has 60 forms, and of these 5 are new species of echinids. The horizon is that of the Bowden or Chattahoochee. *Clypeaster cubensis*, *Agassizia clevi*, *Lovenia dumblei*, *Pecten condylomatus*, *P. oxygonum optimum*, and *P. gatunensis* are the best guide fossils of the medial Tertiary.

No. 6. Even though the Oligocene of the Pacific coast is between 10,000 and 15,000 feet thick, the faunas are as yet

poorly known. Now from one locality 48 forms are at hand, and of these 36 are here described for the first time. While there is a time break of considerable duration between the Eocene and Oligocene, "the climatic conditions of the Tejon and Lower Oligocene were much the same," and of a subtropical nature (165).

In No. 7, the climatic zones of the Martinez or early Eocene are described, showing that "the Martinez of the Los Angeles basin was deposited in subtropical seas, while that of the San Francisco basin was deposited in waters which more nearly correspond to temperate conditions of to-day" (196).

In No. 8, the author dissents from previous correlations in regard to the Bowden, Alum Bluff, and the Orthaulax pugnax beds, and concludes that they "are not upper Oligocene but middle or lower Miocene" in age. The paper is essentially devoted to indicating when the Atlantic was in open connection with the Pacific through the Panama and Tehuantepec portals.

"The Panama Portal was closed during Cretaceous time and this gateway was not opened until upper Eocene time. During a period of widespread uplift—Oligocene time—the Antilles were probably connected with southern Florida and possibly Central America. Following this emergent stage, a wide submergence occurred during Miocene time, marked by the Bowden horizon. At this period North and South America were disconnected and wide straits in Central America were formed. Since the Miocene, the Panama portal has remained closed." (205.)

"Spencer and Vaughan's conclusions concerning Pliocene connections between the Atlantic and Pacific appear very doubtful. This problem will be discussed at length in another paper." (201.)

"The evidence concerning the lower Oligocene or Vicksburg stage is quite deficient and it is impossible to determine any connections at this time." (202.)

*Orbitoid Foraminifera of the Genus Orthophragmina from Georgia and Florida*; by C. W. COOKE and J. A. CUSHMAN. U. S. Geol. Survey, Prof. Paper 108-G, 1917, pp. 109-118, pls. 40-44, text figs. 19, 20.—The first named author discusses the geologic occurrence and faunal associates of the gigantic composite foraminifer *Orthophragmina*, found in the Ocala limestone of upper Eocene age; while the second author describes seven new species of this interesting genus. The half-tones are much enlarged illustrations of these stellate foraminifers. c. s.

2. *Summary of Geological Results*; by OLAF HOLTEDAHL. Rept. Second Norwegian Arctic Expedition in the "Fram" 1898-1902, No. 36, 27 pp., 6 pls., 4 text figs., geological map, 1917.—In this interesting paper on the historical geology of Ellesmere and Grinnell lands, the author brings together and modernizes all that is known about the geologic sequence and

the paleontology of these arctic countries. The Paleozoic marine section is a long one, followed by marine Triassic, undated intrusives, Tertiary lignitic beds with a few plants, and Pleistocene sands. The good photographs are interesting for their glaciers, elevated peneplains and sea-cut terraces. c. s.

3. *Paleontology of the Oligocene of the Chehalis Valley, Washington*; by KATHERINE E. H. VAN WINKLE. University of Washington Publications in Geology, vol. 1, No. 2, 1918, pp. 69-97, pls. 6, 7.—The author here describes the stratigraphy and fossils (about 150 species, of which 24 are new) of the subtropical Oligocene faunas of the Chehalis valley, Washington. The strata are at least 1200 feet in thickness. c. s.

4. *Papers from the Geological Department, Glasgow University*, vol. 3, 1916.—This volume of sixteen reprints shows some of the activities of the Geological Department of Glasgow University during 1916. The first paper, by Professor J. W. Gregory, gives an interesting account of the life and work of the Pennsylvania state geologist, H. D. Rogers, who was professor of geology at Glasgow from 1857 until his death in 1866. The other papers relate to the geology of Scotland, Australia, New Guinea, and South Georgia. A timely article by Gregory is on The Geological Factors affecting the Strategy of the War and the Geology of the Potash Salts. c. s.

5. *New generic names for Upper Cretaceous Gastropoda*.—In a recent paper entitled New and Little Known Gastropoda from the Upper Cretaceous of Tennessee, published in the Proceedings of the Academy of Natural Sciences of Philadelphia for September, 1917, pp. 280-304, there were several errors which crept in because of the necessity of preparing the paper for publication after the writer left Baltimore and had entered the U. S. Artillery service.

It is the purpose of this brief note to rectify these mistakes and omissions. The family name Fusidæ should have been inserted over the genus *Falsifusus* on page 284, and similarly the family name Busyconidæ should have been inserted over the genus *Boltenella* on page 285.

The generic term *Hyllus* (page 281) has been found to be much preoccupied, and the new name *Parafusus* is here proposed to take its place, the type thus becoming *Parafusus callilateris* and the second species, *Parafusus coloratus*. Similarly the term *Scobina* (page 286) is preoccupied and for the latter the name *Haplovoluta* is proposed, the type species becoming *Haplovoluta bicarinata*. The new Buccinoid genus *Seminolæ* is not regarded as being preoccupied by the coleopteroid genus *Seminolus* of Mulsant (1869) although the two are dangerously alike and a different term would have been proposed in the first instance if the writer had been aware of Mulsant's genus. BRUCE WADE.

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## III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Principles of Economic Zoology*; by L. S. DAUGHERTY and M. C. DAUGHERTY. Second edition, revised. Pp. ix, 428, with 301 illustrations. Philadelphia, 1917 (W. B. Saunders Co.).—Emphasis is here placed on the natural history of animals, particularly in respect to their influence on human welfare, and with only such of the structural details of the different groups of animals as are necessary for the proper understanding of their activities. The book contains a vast amount of interesting and useful information about the common animals.

In this new edition suggestions, problems and questions have been incorporated for each chapter to guide the inexperienced teacher or student toward the most important aspects of the subject.

W. R. C.

2. *The Conduction of the Nervous Impulse*; by KEITH LUCAS, revised by E. D. ADRAIN. Pp. xi, 102. London and New York, 1917 (Longmans, Green and Co.).—This new volume in the "Monographs on Physiology," edited by Ernest H. Starling, consists of an excellent general summary of the most recent discoveries relating to the nature of the nervous impulse and its method of transmission. It is mainly the work of one of the most eminent investigators in this difficult branch of physiology, whose life was sacrificed to his country before the completion of the book, the concluding chapter being written by the reviser.

W. R. C.

3. *A Text-book of Mycology and Plant Pathology*; by JOHN W. HARSHBERGER. Pp. xiii, 779, with 271 text figures. Philadelphia, 1917 (P. Blakiston's Son & Co.).—Professor Harshberger has brought together in his book a vast amount of information which will prove of service not only to the mycologist and pathologist but also to the general botanist. The subject-matter is divided into four parts and eleven appendices. The first part is devoted to Mycology; the second, to General Plant Pathology; the third, to Special Plant Pathology; and the fourth, to Laboratory Exercises in Cultural Study of Fungi. The appendices include a variety of subjects, such as fungicides, a spray-calendar, a synopsis of the slime-moulds, and keys for the determination of species in critical genera and larger groups. The references to mycological and pathological publications are unusually full and add much to the value of the work, while the detailed directions given in the fourth part will be especially helpful to teachers of the subject.

A. W. E.

4. *Italian investigations in Oceanography*.—At a time when Italy, with the other nations of Europe, is feeling the severe pressure of the world war, it is highly interesting to have the publications of the Royal Italian Oceanographic Committee

(R. Comitato talassografico Italiano) actively continued. The latest sendings include the semi-monthly bulletins for 1916 and a series of memoirs chiefly on biological subjects bearing the dates of 1916 and 1917.

A special volume (Memoir XXI) by GIOVANNI MAGRINI is included; this appears both in Italian and in English, and describes the Scope and Activities of the Committee, the work of which was begun in 1910. The fields of research open to it are given as: (1) the physiology and chemistry of the sea; (2) the biology of salt water; (3) the exploring of the upper air. This general volume describes in detail, with numerous illustrations, the Institute of Marine Biology in Messina; the various cruises in the Adriatic; the researches carried on, both oceanographic and atmospheric. Of the publications issued by the Committee, or now in preparation, 3 monographs are mentioned and 56 memoirs, besides the bulletins. It is not without interest, in view of the occurrences in the latter part of 1917, that all the volumes received are dated from Venice.

5. *Publications of the Allegheny Observatory of the University of Pittsburgh.*—The following has been recently received:

Vol. 4, No. 1. Photographic Determinations of the Parallaxes of Fifty Stars with the Thaw Refractor; by FRANK SCHLESINGER. Pp. 67. Also title page and contents of Volume 3.

6. *Publications of the Cincinnati Observatory.*—No. 18. Pp. 113, 4to. Cincinnati, 1917 (published by authority of the Board of Directors of the University).—This publication is Part III of the Catalogue of Proper Motion Stars; by JERMAIN G. PORTER, Director, E. I. YOWELL, first astronomer, ELLIOTT SMITH, second astronomer.

7. *Third Melbourne General Catalogue of 3068 Stars for the Equinox 1890.* Pp. 77, 4to. Melbourne, 1917.—The Second Melbourne General Catalogue of 1,211 stars for the Equinox of 1880 was published in 1889. The MS. of the present catalogue was prepared fifteen years ago. The observations were made at Melbourne Observatory from 1884-7 to 1894-0 under the direction of R. L. J. ELLERY, Government Astronomer to 1895. The present volume has been revised and prepared for the press under the direction of PIETRO BARACCHI, Government Astronomer, 1895-1915.

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# AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XXI.—*Fossil Footprints from the Grand Canyon of the Colorado*; by RICHARD SWANN LULL. With Plates I, II, III.

[Contributions from the Paleontological Laboratory, Peabody Museum, Yale University, New Haven, Connecticut, U. S. A.]

Material containing the imprints of Paleozoic quadrupeds from the Grand Canyon has come to me from three different sources: from the Wesleyan University Museum through the courtesy of Professor William North Rice, from the United States National Museum, and from Professor Schuchert of Yale. The first consists of two small fragments of gray sandstone, each impressed with a single obscure track. They were collected by Mr. W. H. Weber, and bear catalogue number 3572 of the Wesleyan University collection. The second is a fine slab collected in 1916 by Doctor L. F. Noble at Hermit basin, at the same place discovered the year before by Professor Schuchert, and bears no fewer than ten impressions of manus and pes pertaining to the larger species of *Laoporus*, n. gen. I am indebted to the United States National Museum for the privilege of studying this specimen. Part of Professor Schuchert's find consists of two slabs of sandstone collected in 1915 at Hermit basin, on the trail down to Hermit Camp and about 150 feet above the base of the Coconino sandstone. These have been tinted red by weathering, although the fractured rock is grayer in color. The assumption is that all of the material is contemporaneous. Of Schuchert's material the larger slab contains about thirteen pairs (manus and pes) of impressions, varying in their

distinctness, while the smaller bears but three such pairs, the latter from the right side of the body. These two slabs appear to bear the impressions of two different species of animals and will be described accordingly.

The creatures which made the footprints were quadrupeds of moderate size, with broad, stumpy feet, apparently clawed, and having at least four toes in front and five behind. The hind foot, which is somewhat the larger, bore a proportionately greater share of the creature's weight, especially in the smaller species. The limbs were apparently short, with a wide trackway, implying a bulky body. No trace of a dragging tail is discernible on any of the specimens, and the body was evidently carried clear of the ground. Several known genera of Paleozoic footprints may be compared with the present species, but none agrees with sufficient closeness to warrant the inclusion of these forms. They therefore seem to pertain to a new genus which will be called *Laoporus*, and the affinities of which, from the criteria which they present, seem to lie with the genus *Limnopus* Marsh from the Kansas Coal Measures.<sup>1</sup>

*Laoporus*, n. gen.

(*λᾶς*, stone + *πόρος*, track)

*Generic characters*.—Quadrupedal, without tail trace, with four digits in the manus and five in the pes, semi-plantigrade, broad-soled, with short digits which in the impressions lack phalangeal pads. Traces of claws appear to be present but they could have had no grasping or predatory function. Feet turned inward toward the line of march.

*Laoporus schucherti*, n. sp.

(Plate I; text fig. 1.)

This species I take as the type of the genus, the type specimen being the larger slab collected by Professor Schuchert, catalogue number 2143, Yale Museum.

*Specific characters*.—Small, the greater portion of the weight being borne upon the pes. Digits pointed, those of the pes showing in at least one impression distinct

<sup>1</sup> O. C. Marsh, Footprints of vertebrates in the Coal Measures of Kansas, this Journal, (3), 48, pp. 81-84, 1894.

traces of rather slender claws, the apparent length of which may be exaggerated by slipping (see fig. 1, *b*, ii and iii). Palm of the manus apparently not impressing; generally but three, sometimes four, subequal digits imprinted in the track. Digits of both manus and pes approximately parallel.

## DIMENSIONS.

## Manus.

	mm.
Width of impression .....	16·8
Length of digit iii .....	5·8

## Pes.

Width .....	21·0
Length to tip of digit iii, without claw .....	18·2
Length of digit i .....	4·8
“ “ “ ii, without claw .....	7·3
“ “ “ iii, “ “ .....	8·5
“ “ “ iv .....	12·2
“ “ “ v .....	6·0
From tip to tip of outer digits .....	16·0
Length of stride, same foot, 84·5, 60, 75, average .....	73·8
Width of trackway .....	60·0

The trail is nearly straight, the forward part of the hand and foot rather deeply impressed, with a wave of sand under the sole of the foot, so that approximately the entire plantar aspect is recorded as shown in the figure (fig. 1, *b*). This might be interpreted as evidence of rapid movement were it not for the foresetting of the beds. As it is, the inference is clear that the animal was advancing *up* the slope, which would not only account for the greater relative weight borne by the pes, but also for the banking of the sand beneath the sole. Were the fore-set slope about  $16^\circ$ , the plantar impression would be approximately level. As all the slabs in question were detached from their original position, the actual dip could not be ascertained (see article by Schuchert, following this).

*Laoporus noblei*, n sp.

(Plate II; text fig. 2.)

Type specimen the second of the two Schuchert slabs, catalogue number 2144, Yale Museum, supplemented by

that collected by Doctor Noble (U. S. National Museum catalogue number 8422), for whom the species is named.

*Specific characters.*—Somewhat larger than *Laoporus schucherti*, the manus making in each instance a clearer impression, including the palm; the claws, however, are less distinctly marked, although in the Noble specimen, in which the creature dragged the feet of the left side,

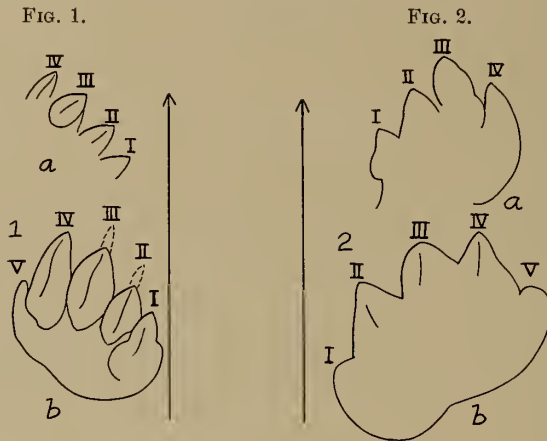


FIG. 1. *Laoporus schucherti*, n. sp. a, left manus; b, pes. Natural size.  
FIG. 2. *Laoporus noblei*, n. sp. a, right manus; b, pes. Natural size.

the footprints being in relief, the long narrow scratches made by the claws are distinctly visible (see Plate II, fig. 2). Manus and pes imprints further apart in the Noble specimen, due probably to difference in gait, or because the creature was partly water borne. Digits of the pes seeming relatively shorter and blunter than in *Laoporus schucherti*.

#### DIMENSIONS.

##### Manus.

	Schuchert slab mm.	Noble slab mm.
Length .....	20	21.2
Width .....	21	24
Length of digit i .....		7.4
“ “ “ ii .....		12.5
“ “ “ iii .....		8.0
“ “ “ iv .....		6.5 <sup>2</sup>

<sup>2</sup> Apparently longer from claw scratch.

	Schuchert slab mm.	Noble slab mm.
Pes.		
Length .....	22	c. 24.0
Width .....	31	c. 28.5
Digital lengths unobtainable.		
Length of stride .....	112	av. 130.0
Width of trackway .....		100.0

Doctor G. F. Matthew in his paper *An attempt to classify Paleozoic batrachian footprints*<sup>3</sup> arranges the known Paleozoic ichnites under eleven groups, the criteria being the number of toe marks impressed, also the general form, whether broad or slender, heeled or heelless, and so forth. According to his scheme, our genus would fall into group seven, *Limnopus*, to which, as we have seen, it bears the greatest resemblance. The present genus differs from *Limnopus*, however, in the fact that the impressions of fore and hind feet do not interfere, whereas in *Limnopus* that of the pes always overlaps the manus. The latter genus shows no trace of claws and the digits terminate roundly instead of being acuminate as in *Laoporus*. Furthermore the digits in *Limnopus* are more distinctly separated at their base.

*Megapezia* (?) *coloradensis*, n. sp.

(Plate III, fig. 2; text fig. 3.)

In addition to the above described forms from the Coconino sandstone, there are several other specimens in the Schuchert collection from an older horizon, the Upper Supai of Hermit trail in the Grand Canyon. In this lot there are several specimens representing at least two species which vary exceedingly in size as well as in other details of structure. They pertain to unknown species and probably to undescribed genera of Paleozoic ichnites.

The larger species is impressed upon three small slabs of red impure sandstone, one apparently of the manus obscured by crushing and mud-cracking, another of the pes, and a third with two impressions each of hand and foot which determine the width of trackway but not the length of stride.

*Specific characters.*—The creature seems to have been five-toed in front and behind; there is, however, some

<sup>3</sup> Trans. Roy. Soc. Canada, 9, pp. 109-121, 1903.

question as to the presence of the fifth digit of the pes which is very questionably indicated on the second slab but is apparently present on the third, hence it is included in the drawing. The digits of the pes are rounded at their extremity, while those of the manus are acuminate. The difference in character of manus and pes is so great,

FIG. 3.

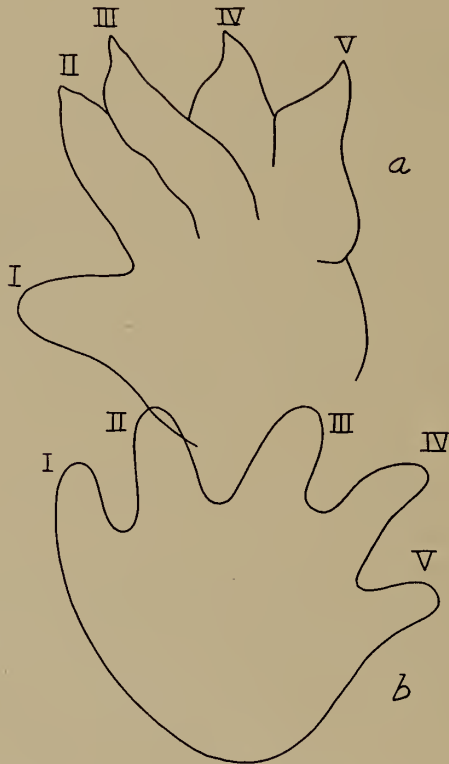


FIG. 3. *Megapezia?* *coloradensis*, n. sp. Right manus (a) and pes (b). Natural size.

except for an agreement in size, that one would not, perhaps, be justified in associating them together were it not for the third slab. As it is, their relative position in the drawing, although based upon this specimen, may not be quite correct.

Manus: The manus has five digits of which the first is widely offset. It is, however, obscured by an overlying



mud-crack, the slab being in relief, so that the true outline, especially of the distal end, is conjectural. The other digits are each of them clawed, but have been subject to a crushing over toward the outer aspect of the hand so that their outline in the drawing is not natural, as no attempt has been made to "restore" them to their original condition. The outermost digit diverges somewhat more, the third and fourth a little less, and the second and third least of the four. The palm is well impressed and, were it not for the mud-cracks, doubtless its entire outline would be seen.

Pes: The foot is broad-soled, with four or five diverging digits terminating roundly, without indications of claws, and the well-rounded sole is impressed; both hand and foot are therefore plantigrade and approximately equal in extent.

The trackway is broad, indicating a wide-bodied animal.

## DIMENSIONS.

## Manus.

	mm.
Length .....	55.8
Breadth from tip of digit i across palm .....	?44.0
Length of digit i .....	?17.0
"    "    "    ii .....	27.5
"    "    "    iii .....	30.0
"    "    "    iv .....	25.0
"    "    "    v .....	27.0
Between tips of digits ii and v .....	37.5

## Pes.

Length .....	48.5
Breadth .....	50.0
Length of digit i .....	12.6
"    "    "    ii .....	15.0
"    "    "    iii .....	17.0
"    "    "    iv .....	?15.5
Width of trackway .....	c. 140.0

Except for the acuminate claws of the hand and the apparent presence of a fifth digit in the pes, this form comes nearest to the genus *Megapezia* from the Lower Carboniferous shales of Parrsboro, Nova Scotia, described and figured by Matthew.<sup>4</sup> The long stride is

<sup>4</sup> Op. cit., p. 102, pl. II, fig. 4 a, b.

mentioned by Matthew as being indicative of activity. The present specimens, as has been said, give no indication of this, but the hand particularly is suggestive of aggressive use. Another Paleozoic genus which the present form resembles is *Hylopus*, but in that genus there are only four digits in the manus and five in the pes, the reverse of *Megapezia*.

The form now under consideration is provisionally referred to the genus *Megapezia*, the species being called *coloradensis* from the locality where it was found, the Grand Canyon of the Colorado River. It is about the size of the type species *M. pineoi* Matthew, differing therefrom, however, in several particulars, mainly in proportions and the apparent impression of five digits in the pes. The figure of *M. pineoi* given by Matthew shows no claws in the manus track, but Matthew says the first toe had a strong claw and the others probably had also. The prolongation of the palm into a rounded lobe on the outer side is not in evidence in the present species, although another impression of the hand might have shown an agreement here as well.

Type specimen, catalogue number 2145, Yale Museum.

*Exocampe* (?) *delicatula*, n. sp.

(Plate III, fig. 1; text fig. 4.)

The smallest of the forms collected by Professor Schuchert consists of a very delicately impressed fore and hind foot in relief on mud-cracked red shale. The hind foot is the larger and shows four slightly radiating digits, but no trace of sole. The manus is also apparently four-toed, with distinct impressions of terminal claws. The digits radiate more widely, but here again there is no palmar impression. The form may therefore be described as digitigrade. Faint indications which may represent phalangeal limitations may be seen on the second digit of the manus. This form resembles most closely the genus *Exocampe* of the Connecticut Trias, but is a generalized track which almost any small amphibian, such as a modern salamander, for instance, might make, and while it may for convenience be placed within the mentioned genus, genetic relationship with the creatures that made the tracks so designated is not of necessity implied.

*Specific characters.*—Manus: Somewhat smaller than the pes, with three well-defined, radiating digits, the middle one of which is directed forward. An obscure impression of an additional digit lying on the inner side of and more nearly parallel to the second is indicated.

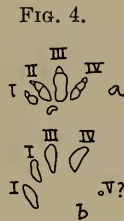


FIG. 4. *Exocampe (f) delicatula*, n. sp. Right manus (a) and pes (b). Natural size.

There is also at the base of the second digit what may represent a palmar pad. It may, however, be accidental, as there are other such on the slab.

Pes: The four phalangeal impressions are more or less ovoid, without indications of claws or phalanges, and, except for the first, curve slightly outward. There is a faint mark which may indicate a fifth digit. The pes impression lies immediately behind that of the manus and a little apart from it as the figure indicates.

DIMENSIONS.

Manus.

	mm.
Length .....	5.5
Width .....	7.0
Length of digit ii .....	4.3
“ “ “ iii .....	4.0
“ “ “ iv .....	2.7

Pes.

Length .....	7.0
Width .....	8.8
Length of digit i .....	2.8
“ “ “ ii .....	3.0
“ “ “ iii .....	3.3
“ “ “ iv .....	3.3

There lies in advance and to the left of the impressions we have discussed a series of five minute rounded marks

whose relative position is precisely the same as the termini of the pedal toes in the track described. These marks seem therefore to indicate the impression of the right pes. If so, they give a trackway width of 33 mm. and an estimated stride of the same foot of 42 mm., thus indicating a rather wide-bodied, short-legged form. This form is provisionally included in the genus *Exocampe* Hitchcock, the species being designated as *delicatula* in allusion to its delicate proportions.

Type specimen, catalogue number 2146, Yale Museum.

These impressions are surely not reptilian, nor should we call them batrachian as Matthew has done. Until their amphibian character is clearly demonstrated, perhaps it were well to place them under Williston's newly proposed ancestral group Protopoda, which, as he says, are thus far known only by their footprints.<sup>5</sup>

I am indebted to my colleague, Professor Schuchert, for the privilege of discussing these interesting forms.

#### EXPLANATION OF PLATES I-III.

##### Plate I.

*Laoporus schucherti*, n. sp. Genoholotype, Cat. No. 2143, Yale Museum. One third natural size.

##### Plate II.

Fig. 1. *Laoporus noblei*, n. sp. Holotype, Schuchert slab, Cat. No. 2144, Yale Museum. One third natural size.

Fig. 2. *Laoporus noblei*, n. sp. Paratype, Noble slab, Cat. No. 8422, U. S. National Museum. Photograph by L. F. Noble. One third natural size.

##### Plate III.

Fig. 1. *Exocampe* (?) *delicatula*, n. sp. Holotype, Cat. No. 2146, Yale Museum. Two thirds natural size.

Fig. 2. *Megapezia* (?) *coloradensis*, n. sp. *a*, manus; *b*, pes. Holotype, Cat. No. 2145, Yale Museum. Two thirds natural size.

Yale University, 24 September, 1917.

<sup>5</sup>S. W. Williston, The phylogeny and classification of reptiles, Jour. Geology, 25, p. 42, 1917.

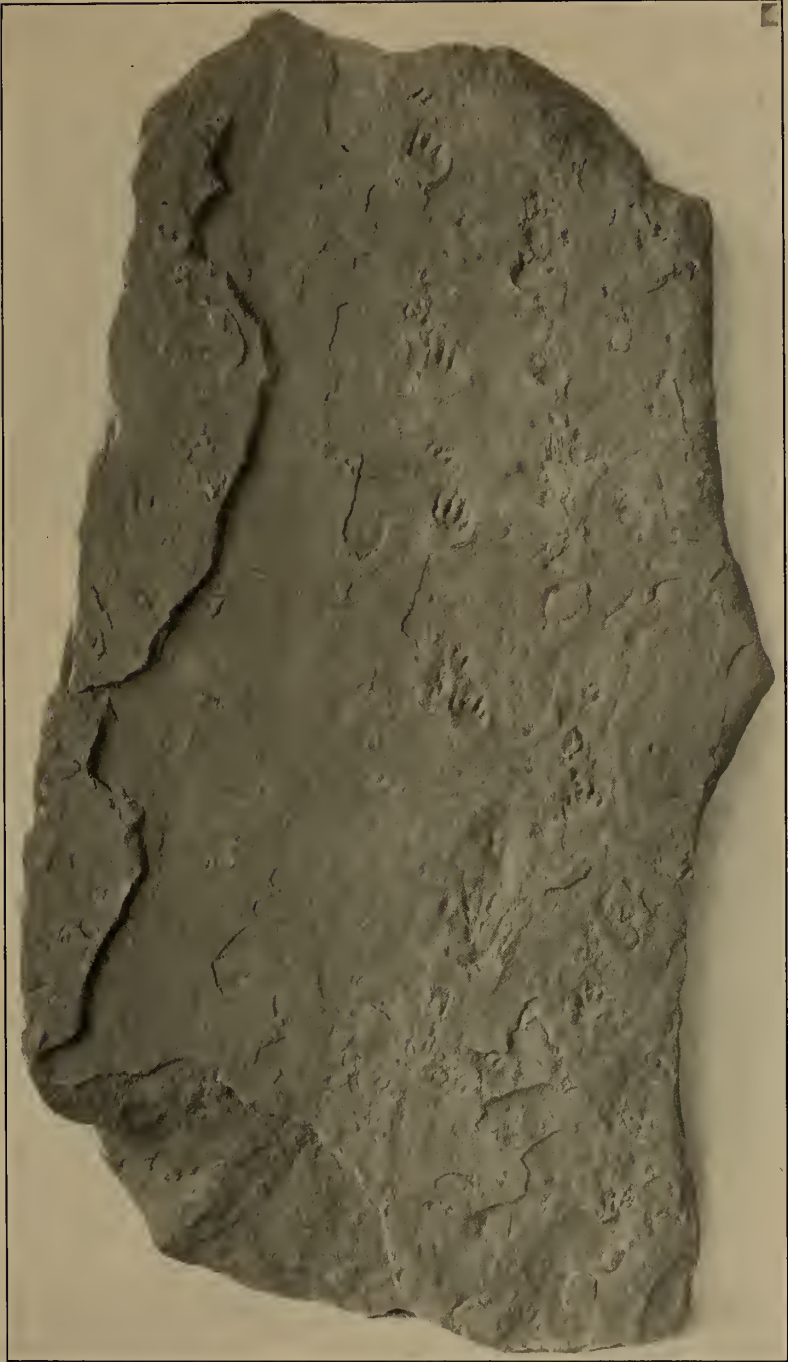




FIG. 1.

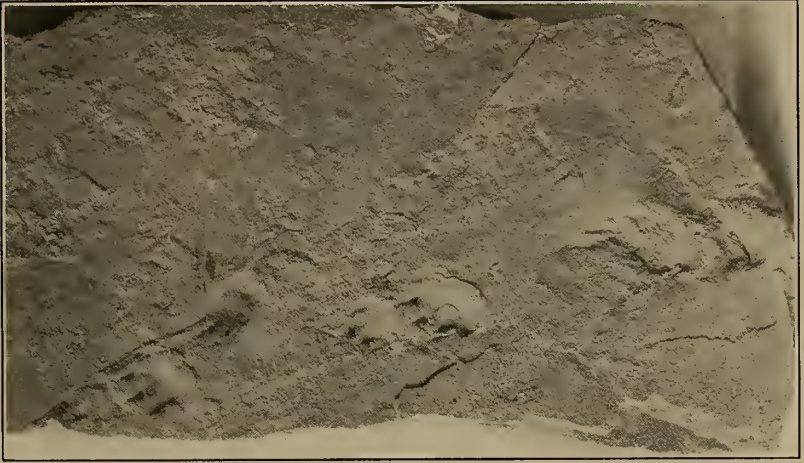
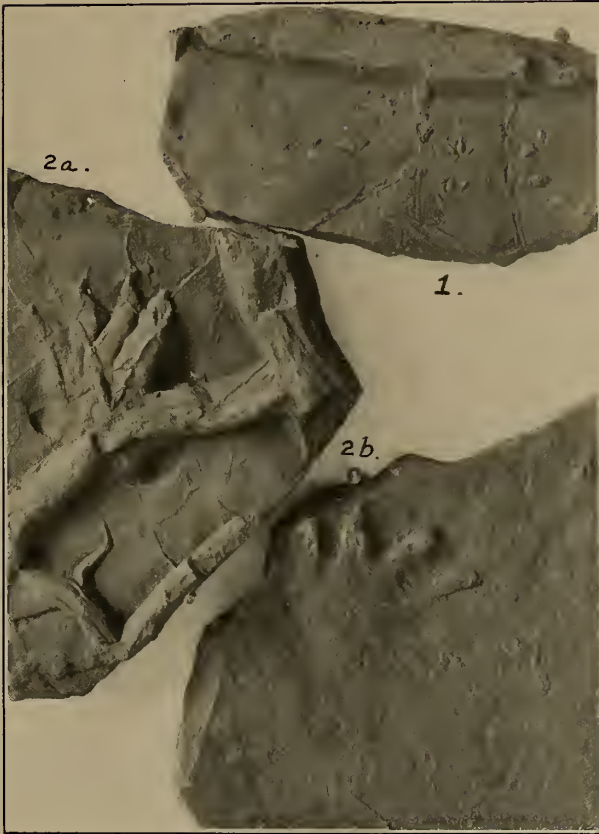


FIG. 2.











ART. XXII.—*On the Carboniferous of the Grand Canyon of Arizona*; by CHARLES SCHUCHERT.

[Contributions from the Paleontological Laboratory, Peabody Museum, Yale University, New Haven, Connecticut, U. S. A.]

For eight days in the month of September, 1915, the writer had the greatest scientific pleasure of his life in that geological wonderland, the Grand Canyon of the Colorado River in Arizona. Here may be studied in greater detail than anywhere else strata of marine, brackish-, or fresh-water origin, and even of eolian making; of the deeper seas and of the littoral; of wet and of semi-arid climates; sandstones, shales, limestones, and dolomites in great masses, and all in their natural and acquired color glories. Of disconformities there are many, and for miles in either direction one may trace two grand unconformities in such continuous detail as can be seen nowhere else. Finally, there are many vertical faults to be seen here, and they are as plain as in any geologic text-book. Think of a vast basin of sedimentary accumulation transected by a series of wide canyons a mile deep and hundreds of miles long. Truly such a geological insight into the structure of the earth's outer shell is nowhere else to be had. Here should be sent all stratigraphers to get their first lessons in sedimentation, for here one follows the formations mile after mile and notes in detail how the sediments are changing and what has been the work of the waters of the sea and land, and of the atmosphere. It is paradise for the stratigrapher studying the strata in mass or in detail, but he will soon learn that it is an earthly paradise, for it is fatiguing to climb its enchanting walls. His thirst for knowledge is constantly being quenched by the results attained, but his throat continually longs for water in the hot and dry atmosphere. Again it is an earthly paradise, for here, even though the strata are in the main of marine origin and visible for every foot of their extent, one looks almost in vain for the "medals of creation." Each day a few are gotten, but at all places beneath the brink they are few in number and usually poor in preservation. It is the land of paleontologic hopes and the scenery is so sublime that one is everlastingly pushed on and on, struggling onward and upward to the crag where the fossils

surely are if one but could attain the place. One looks and longs, struggles and hopes, and most of the time is distracted by the grandeur of the rocks. Among them one sits and ponders his environment and becomes painfully aware of his insignificance.

#### KAIBAB LIMESTONE.

The brink of the Grand Canyon between the Bright Angel and Hermit trails is made by the Kaibab limestone, here about 560 feet thick and of a light buff color (see fig. 1). In this region the formation is not very rich in fossils, but a few are always to be seen and about ten species can be easily gotten. The common ones are sponges, *Composita subtilita*, and *Productus occidentalis*, and rarely one finds *Meekella pyramidalis*. As the Kaibab fauna is fairly well known, and as there are better places for it than about the El Tovar Hotel, not much of the writer's time was devoted to collecting it. On the Bright Angel trail, the brink begins at bench mark 6866 feet above sea level; at bench mark 6575 fossils are not rare, and here may be had, among others, *Productus ivesi* and *Meekella pyramidalis*, both characteristic species of the Kaibab formation. This lower part of the Kaibab is full of bands and nodules of diagenetic flint, some of which include sponges. The formation passes without break through a narrow transition zone of interbedded limestone and sandstones into the Coconino sandstone. In the Shinumo quadrangle<sup>1</sup> to the west the transition into the Kaibab is even more gentle, showing clearly that these two formations belong to one unbroken cycle of deposition. To the southeast the Kaibab appears to thin somewhat and becomes thinner bedded and impure through the introduction of sand.<sup>2</sup>

That the Kaibab limestone is of early Permian age is now admitted by most American stratigraphers. This view, however, has been attained rather from its field relations than through a study of its marine fossils, for these in several forms are very much like those of the Pennsylvanian. The fauna as collected by Noble in the Shinumo quadrangle is listed by Girty<sup>3</sup> and he here correlates the Kaibab limestone with the Manzano group

<sup>1</sup> L. F. Noble, U. S. Geol. Survey, Bull. 549, pp. 70-71, 1914.

<sup>2</sup> H. H. Robinson, U. S. Geol. Survey, Prof. Paper 76, 1913.

<sup>3</sup> Noble, op. cit., p. 71.

of New Mexico. He also suggests that the Kaibab may be equivalent to a part of the Guadalupian of southwestern Texas, a formation of undoubted Permian age.

#### COCONINO SANDSTONE.

The Coconino sandstone in the Bright Angel quadrangle is 385 feet in thickness and is a most persistent formation for one of wholly sand accumulation and, further, one which is nearly devoid of horizontal stratification (see fig. 1). Its yellowish gray to creamy white color is everywhere to be seen, even in the far distance as a white band near the top of the canyon walls. In closer view one notes that it is almost unbedded and composed of foreset beds that have dips averaging between  $20^{\circ}$  and  $25^{\circ}$  to the south. Noble tells me the dips vary between  $5^{\circ}$  and  $30^{\circ}$  (see fig. 2). These very long foresetting planes so clearly shown on all the old weathered surfaces have been noted by all geologists and are also shown in one of Holmes's wonderful drawings, plate 30 published in 1882 in Dutton's *Tertiary History of the Grand Canyon District*. Even though the Coconino formation steadily thins to the north and northwest, the foresetting shows that the sand was derived from that direction. To the southward in the Aubrey Cliffs the thickness is given by Gilbert as 700 feet.<sup>4</sup> In general the quartz sand is sharp and of fine grain, but in limited bands the grains are considerably larger, well rounded and with dull surfaces. The latter kind is clearly wind-blown sand, and it should be expected in near-shore deposits of Permian time because of the then prevalent arid climates. The eolian sand, it appears, has been blown into rivers that have brought it from a long distance to the northward and out of it in the course of transportation has been washed or blown almost all other disintegrated rock material than the quartz. As the Coconino formation stands up in vertical cliffs, it probably has a cement of silica besides the iron that gives it its slightly yellowish color, but the quantity of cement appears to be very slight. Ripple-marking is rare but was noted on both the Hermit and Bright Angel trails. The troughs are very shallow, probably less than 5 mm. deep, with the wave crests about 5 inches apart. From time to time, after 50 to 100 feet

<sup>4</sup>G. K. Gilbert, U. S. Geol. Survey W. 100th Merid., vol. 3, pt. 1, p. 82, 1875.

of sands had been deposited, the area subsided, then another zone of sand was laid over it, and finally the entire area and a great deal more went beneath the sea, for over all of the Coconino lies a typical shallow-water marine deposit, the Kaibab dolomite.

At about 150 feet above the base of the Coconino sandstone, in a bend on the Hermit trail, in the quarried mate-

FIG. 1.



FIG. 1. Upper part of Grand Canyon, Arizona, as seen from Mohave Point. I, Kaibab limestone; II, Coconino sandstone; III, upper part of Supai formation, red shales; IV, lower part or Supai formation proper.

rial of the trail cutting, were collected amphibian tracks of small animals that travelled up and down the foresetting slopes. They were not seen on the very limited surfaces of the horizontal planes. These Professor Lull is describing in this number of the *Journal* as *Laoporus schucherti* and *L. noblei*. He regards them as ancestral amphibia of the group Protopoda. No other organic remains are known from the Coconino formation, and the cause is probably to be sought in the originally loose and repeatedly reworked sands, a most unfavorable habitat for animals. The conclusion as to the origin of this

sandstone reached by the writer while in the field is that it represents the material of a large delta of continental deposits laid down under constant but probably local sheets of water that were evidently entirely fresh. The Coconino may be the deposits of dune sands swept from the north into a series of basins or fresh-water lakes like the present fresh- and brackish-water lakes on the outer

FIG. 2.



FIG. 2. Contact of Coconino sandstone and red shales of Upper Supai, as seen on Bright Angel trail. Note the sharp contact, foresetting lines of Coconino, and sand-filled fissure in Upper Supai.

borders of the Nile delta. (For further discussion of this formation, see Noble, *op. cit.*, p. 85.)

That the Coconino sandstone invaded to the southward a land composed of the Supai formation is shown not only in the very different nature of these underlying strata and the sharp contact between them, but especially in the fact that the surface of the Supai has many vertical solution joints now filled with the Coconino sands. These filled fissures, up to 4 inches wide and 10 feet high, are especially well seen on the Bright Angel trail, and a photograph here reproduced (fig. 2) shows what they

look like at a distance of some hundreds of feet. They are also to be seen in several places on the Hermit trail and here they are filled with undoubted Coconino sands. The contact between the Supai and Coconino formations is everywhere a sharp one, and the plane appears to be as level as such a surface can be. It is also an easily recognizable disconformity. Above this plane is the great cliff of yellowish white sands and beneath them are the slopes of deep red or even maroon fine sandy shales of the Supai. To the eye, no greater contrast in sedimentation is possible than that on either side of this disconformity, and the significance of this plane in Historical Geology will be discussed after a description of the Supai formation and its fossils. However, as Doctor Noble has seen so much more of this contact, it will be best to restate what he has written in a letter of May 10, 1916:

“The fissures in the terminal Supai beds that are filled with Coconino sand are certainly significant, but they may be a local feature of the Coconino-Supai contact. I have examined this contact on all the other trails and never found fissures. I believe the contact between the Supai and Coconino, sharp though it appears, is not so significant as the rough, ragged surface of erosion within the Supai on the Hermit trail. I am therefore not sure that it is significant of a great time break.”

The question as to which one is the more significant break will be discussed later.

In this connection, it may not be out of place to direct attention to evidence of arid climates in Permian time throughout the Colorado Plateau country. To the east of El Tovar, in the Navajo country, is the De Chelly fine-grained sandstone, which in thickness varies from less than 200 up to 800 feet. It is well described by Gregory,<sup>5</sup> from whom these data are taken. It is one of the most cross-bedded formations known to geologists, and the heterogeneity of the sweeping concave lines of sedimentation indicates that the De Chelly is a dune deposit of an arid climate and of “a region of low relief bordering the sea.” It may well be that the marine Kaibab limestone and the Coconino sandstone toward the east change finally into desert dune deposits and that the De Chelly is

<sup>5</sup> H. E. Gregory, U. S. Geol. Survey, Prof. Paper 93, pp. 31-34, 1917.



the time equivalent of more or less of the Moenkopi, Kaibab, and Coconino formations.

### SUPAI FORMATION.

Beneath the Coconino formation lies the terraced and slope-making Supai formation that is 1190 feet in thickness. To the southward the formation has thinned to 600 feet in the Aubrey Cliffs. It is the most accessible formation of all along the Hermit trail, and for nearly 4 miles in September, 1915, the newly made way had thrown out the strata from the walls of the canyon. It was therefore a most excellent time to study the deposits, and, furthermore, Doctor Noble told me that there is no equally accessible exposure of the Supai beds in all of the Grand Canyon country.

The Supai formation consists of alternating beds of hard sandstones and soft shales, all of which are slightly micaceous. The top 200 feet are sandy soft red shales. The cross-bedded sandstones make cliffs and the shales make slopes and ledges. The general color of the formation is a dull brick-red, but as a rule the sandy shales on fresh fracture are bright red or maroon in color, while the sandstones may be red or whitish, but as a rule are of a dirty light greenish color.

*Upper Supai.*—The rock character of the Supai formation is so variable from top to bottom that it is thought best to describe the sequence in more detail as seen on the Hermit trail. It will be described as the Upper and Lower Supai; the former is 290 and the latter 900 feet thick. Beginning at the top the contact with the Coconino sandstone has been described. Beneath this plane the Upper Supai consists of soft sandy red shales through a thickness of about 200 feet (see fig. 2). In the lower half are introduced thin beds of sandstone, and in the next 90 feet the sandstones increase in thickness and in number more and more. The base of this upper zone occurs at the sign post "Red Top."

Just below the sign "Red Top" in the lower turn of the trail and immediately above the thick upper sandstone of the Lower Supai are seen thin-bedded red shaly sandstones alternating with deep red zones of shale (see fig. 3). The surfaces of the glistening and smooth platy sandstones are replete with the fillings of the small

prisms of interbedded sun-cracked shales, are often rain-pitted, and further marked by the feet impressions of fresh-water amphibians described elsewhere in this number of the Journal by Professor Lull as *Megapezia* (?) *coloradensis* and *Exocampe* (?) *delicatula*. Some of the tracks are distinct impressions of the feet and others are mere strokes of the toes. In these same beds also occur plant remains in very fragmentary condition which were badly macerated and coated with a slime of red mud during their entombment. They are therefore difficult to determine, but after much effort Doctor David White tentatively identified them as *Callipteris* sp., cf. *C. conferta*, *Walchia* cf. *W. gracilis*, *Gigantopteris*, and cf. *Sphenophyllum*.

*Age of Upper Supai.*—The amphibian tracks of *Megapezia* (?) *coloradensis* Lull compares with forms of this genus found in the "Lower Carboniferous" (presumably Pennsylvanian) of Parrsboro, Nova Scotia. The other track, which he names *Exocampe* (?) *delicatula*, resembles closely the genus of the Connecticut Triassic but as it "is a generalized track which almost any small amphibian . . . might make" the fossil has little stratigraphic significance. In fact, these tracks can not be depended on more than that they seem to indicate Pennsylvanian age.

The plants listed above and found associated with the tracks in the Upper Supai led White in his letter to the writer dated June 27, 1916, to the following conclusions:

"The condition of preservation of the fragments is so bad that caution is necessary in basing conclusions of any kind on the material submitted. However, the presence of *Gigantopteris*, *Walchia*, and probably of *Callipteris*, if my tentative generic identification of the latter is correct, points to Lower Permian age of the flora . . . In any event, it appears probable that the flora, when it is better known, will be found to indicate a level not below the highest stage of the Pennsylvanian."

It is of interest to note here that *Walchia* has also been found in much higher beds farther to the east in Arizona. Above the thinned Kaibab is the Moenkopi formation of red shales and sandstones in which Gregory<sup>6</sup> reports the presence "on the rim of the Little Colorado Canyon" of marine molluscs of Permian age, and, farther east near

<sup>6</sup> Op. cit., p. 31.

Fort Defiance, of *Walchia pinniformis*, *W. gracilis*, and *W. hypnoides*(?). These plants White states are characteristic of the Permian, and are present in Oklahoma and in the Wichita formation of Texas.

It should be noted that these fossils are found immediately above a marked erosional unconformity. If therefore we give full significance to this unconformity and with it bolster up White's provisional conclusion as to the age of the plants, the upper 290 feet of the Supai are to be referred to the Permian system. The question then is raised, What is the age of the rest of the Supai that is 900 feet in thickness? That it is younger than early Mississippian is clear, and that it is at least as young as Pennsylvanian is also probable, as will be shown later on. On the other hand, the sedimentary character of the entire Supai is strikingly similar. Doctor Noble has determined what the writer did not see at the time of collecting the fossils above mentioned—that beneath the fossiliferous zone is "locally one of the clearest unconformities in the canyon, a counterpart of that at the base of the Devonian. The red shales that have the plant remains lie in little hollows or troughs eroded in the upper cliff-making Supai sandstone. In places the knolls of sandstone rise 50 feet above the base of a hollow. I traced the unconformity for half a mile or more around the head of Hermit Creek to make sure, and then accepted it as a fact. The fossils occur only at the base of a hollow. I have crossed the Supai many times in widely separated parts of the canyon and have never seen a sign of a fossil plant in it before. Perhaps it is only in the places where this unconformity is so well developed that they can be found. The plants appear to have been washed into these hollows and concentrated there." The following diagram (fig. 3) shows the unconformity as determined by Noble.<sup>7</sup> Noble thinks that if further study reveals the presence of the unconformity in other parts of the Grand Canyon, it may be possible to separate the Supai into two distinct formations. "Above the break the rocks are all red shale and shaly sandstones to the base of the Coconino. Not only this, but the red shaly member increases decidedly in thickness to the westward. On the Hermit trail it is 290 feet thick, and in the west end of the adjoining quadrangle, the Shinumo,

<sup>7</sup> Unpublished manuscript in preparation for the U. S. Geological Survey.

it is 550 feet," whereas the underlying sandstone phase of the Lower Supai *thins* slightly in the same direction, for on the Hermit trail the thickness is 900 feet and in the northwestern part of the Shinumo quadrangle it is 850 feet.

These facts show that there is probably an important break in sedimentation in the upper portion of the Supai formation, and that the Upper Supai has fossil plants that seem to indicate a Permian age for these strata. The Lower Supai along the Hermit trail has not yet furnished any fossils, but to the northwest some 30 miles or more the equivalent beds are more calcareous, and here

FIG. 3.

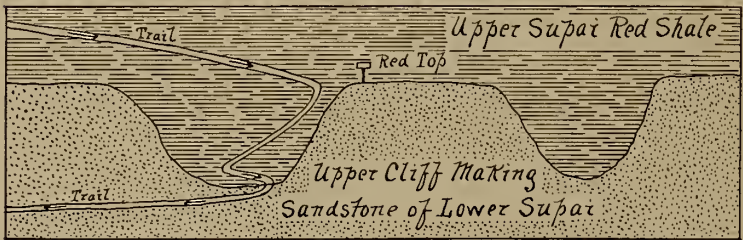


FIG. 3. Diagram to illustrate erosional contact between Upper and Lower Supai on Hermit trail. The fossils are from the beds on the lower turn of the trail. After L. F. Noble (unpublished MS. of the U. S. Geological Survey).

Pennsylvanian fossils have been secured. This will be explained further on. This line of erosion in the Upper Supai may therefore separate the Pennsylvanian from the Permian. Furthermore, there is another break or disconformity between the Upper Supai and the Coconino formations, and it lies in early Permian deposits. Which of the two breaks is the more important can not be answered from a study of the limited area about El Tovar, though to Doctor Noble, who has seen more of the Grand Canyon than any other geologist, the lower one is held to be of greater significance as a time break. In any event, the disconformity between the Upper and Lower Supai formations is of considerable importance in American stratigraphy and seemingly points the way for a satisfactory distinguishing between the records of Pennsylvanian and Permian time in the Cordilleran area.

*Lower Supai.*—The Lower Supai formation begins with a thick-bedded and cross-bedded cliff-making sandstone of about 150 feet in thickness. Beneath it are red sandy shales with two bands of sandstones that together have an estimated thickness of 200 feet. At the base of this zone is another horizon of thin flaggy beds with some sun-crack fillings and an abundance of rain-prints of the mammillary kind, interpreted as having been made by long-continued rain. Midribs of either ferns or cycadofilices were seen, and probably also indistinct feet imprints of amphibians. The trail runs along this zone for about 2 miles, and one has a fine opportunity to study the sediments and to note the abundance of rain-prints and a few rill-markings.

The next lower zone is a cliff-making sandstone about 50 feet in height. Then follows one of shales 100 feet thick, that near the top has beds of septaria-like limy concretions embedded in a dark purple sandy mud. No fossils were seen in them, and they give the impression of being caliche formations. Associated are also thin zones of intraformational conglomerates with flat and somewhat rounded small pebbles; the shale pieces have blackened surfaces.

Then follow the lower thick-bedded cliff-making Supai sandstones, again cross-bedded and, like the upper ones, about 150 feet in thickness. The top of this zone occurs at the sign post "Red Zigzags" and the whole is of a pink color.

The lowest zone of the Supai is about 250 feet in thickness and consists in the main of shales interbedded with many bands of sandstones. "Four Mile Camp" or "Point Lookout" is near the center of this zone and hereabouts occur pinkish arenaceous limestones with horizons of red cherts that may be of diagenetic origin rather than the result of weathering. Near the base of the Supai are again seen thin-bedded flaggy sandstones marked with rain-pittings and the fillings of sun-cracks; also the septaria-like limy concretions, up to 8 inches across, interbedded with thin zones of oölites. No fossils of any kind were seen. "Breezy Point" is near the base of the Supai formation.

In the field the writer got the impression that most or all of the Supai as developed along the Hermit trail is of fresh-water origin on a delta flood-plain of a river or rivers fronting the sea. The basal beds with the oölites

may have been formed under brackish water, but elsewhere the Supai is a typical series of continental flood-plain deposits accumulated on a subsiding area under a semi-arid climate. Whatever organisms were entombed were completely oxidized away. This is shown in the ferric condition of the included iron and the complete absence of actual fossils. The Supai formation, when compared with a typical intermontane continental deposit like the Newark formation of the Connecticut Valley, of Triassic age, is seen to be devoid of conglomerates, is more regularly bedded, and has a better assorting of the rock materials. From this the writer concludes that the Supai was laid down under greater and longer enduring sheets of seasonal waters, causing the materials to be more equally distributed than would be the case in meandering rivers of a narrower flood-plain. During the dry seasons the muds and sands were relieved of all organic materials by capillary action and the atmosphere.

*Age of Lower Supai.*—The Lower Supai rests upon the Redwall limestones. This contact may be studied just beneath the sign post "Cathedral Stairs," that stands on Supai strata. It is of the disconformable type and the Redwall is more or less eroded. Where the contact was studied this limestone-dolomite series terminates in thin-bedded deposits with the beds varying in thickness from 12 to 20 inches. The Supai begins at once with its characteristic sandy and rain-pitted shales and muddy sandstones. This disconformity has far greater significance than the physical phenomena as seen on the Hermit trail would seem to indicate, for the fossils of the Redwall are here all of early Mississippian age. Nothing of later Mississippian time is present here or elsewhere in Arizona, and the land interval preceding Supai deposition was certainly longer than all of Redwall time.

To fully understand this disconformity we must go farther northwest in the Grand Canyon, where Noble has fully studied the contact. In a letter to the writer dated May 10, 1916, he says:

"In the Kaibab division of the canyon there is evidence of a disconformity just at the top of the massive Redwall cliff, and it is possible that further study may show the break between the Pennsylvanian and Mississippian to be here, although it is commonly believed that the upper part of the Redwall is Pennsylvanian."

nian, and the lower part Mississippian. Gilbert<sup>8</sup> and Lee<sup>9</sup> report Pennsylvanian fossils from the upper beds of the Redwall. But Gilbert's 'Redwall group,' in the Kanab division, includes 500 feet, at least, of what I have been calling basal Supai in the Kaibab division. As one goes west, toward the region where Gilbert and Lee got the fossils, there is introduced more and more limestone in what I call basal Supai, and it is massive limestone like the Redwall. This Pennsylvanian limestone is *above* the horizon where the erosional break appears to be in the Kaibab division of the canyon.

"In Bass Canyon the lower 500 feet of the Supai are alternating massive blue crystalline limestone with bands and nodules of red chert, red shale, and red sandstone. In one limestone bed I saw sections of cup corals and brachiopods. This indicates that the basal Supai beds are in part marine in origin. Yet there is gypsum present, red shales with sun-cracking and ripple-marks, and maroon layers with septaria nodules. May we not have had here an alternating of marine and fresh-water flood-plain conditions?"

"The whole middle Supai—all the great cliff-makers—is made up of huge layers of fine cross-bedded sandstones with partings of red shale and red shaly sandstone. This part of the Supai, as you say, is certainly a unit. I noted the rain-prints, ripple-marks and sun-cracks. I also saw several horizons of intraformational conglomerates, one of them beyond a doubt a scoured and filled rain channel. I agree with you that this part of the Supai is a terrestrial deposit."

The fossils collected by Gilbert and Lee, and above referred to, have been examined by Girty,<sup>10</sup> who reports on them as follows:

"At Yampai . . . were obtained: *Derbya* (?), *Composita*, *Aviculopecten*, *Myalina* aff. *M. meliniformis* and *M. congeneris* and *Edmondia* (?). These fossils indicate a Pennsylvanian or 'Coal Measures' age."

That the earlier Pennsylvanian sea was widespread in the Colorado Plateau country is shown by its unmistakable presence in the San Juan area of southeastern Utah. Here between Goodridge and Bluff, Gregory<sup>11</sup> and Woodruff<sup>12</sup> report many local faunæ with *Myalina subquadrata*, *Spirifer rockymontanus*, *S. cameratus*, *Hustedia mormoni*, *Productus nebrascensis*, *P. cora*, *Marginifera muricata*, *M. wabashensis*, *Chonetes meso-*

<sup>8</sup> G. K. Gilbert, op. cit., p. 178.

<sup>9</sup> W. T. Lee, U. S. Geol. Survey, Bull. 352, p. 15, 1908.

<sup>10</sup> Noble, op. cit., p. 67.

<sup>11</sup> H. E. Gregory, U. S. Geol. Survey, Bull. 431, p. 19, 1911.

<sup>12</sup> E. G. Woodruff, *ibid.*, Bull. 471, pp. 83-85, 1912.

*lobus*, *Pugnax utah*, *Lophophyllum profundum*, *Fusulina*, etc., etc. From this we see that here the waters were more normally marine than in the area of the Grand Canyon.

#### REDWALL LIMESTONE.

The Redwall limestone beneath the Supai has a thickness of 550 feet and makes the most precipitous cliffs in this dry climate of the Grand Canyon. To the west the formation thickens and in the western part of the Shinumo quadrangle it is 700 feet thick. It consists of heavy-bedded, dense, hard and brittle limestone, with dolomites and sandstones toward the base. On fresh fracture, the limestones have in general a bluish gray or yellowish gray color. There are no shale partings and the Redwall therefore appears as one unbedded mass. Noble says, in the Bright Angel topographic sheet:<sup>13</sup> "Its face is recessed by niches and alcoves and is stained red by the wash from the Supai strata above." It is also much pitted through weathering and cuts fingers and clothing. Redwall is therefore a misnomer for this formation, which is the most difficult one of all in the Grand Canyon to understand from the historical standpoint. The overwash hides the very nature of the strata and the few fossils it has. These latter are casts of fossils in dolomites, occasionally an actual one in dense limestones that one can not get, and where there is chert they are poor siliceous pseudomorphs. The diagenetic changes and the dense limestone nature of the formation have apparently obliterated what organisms there may have been originally. To the south and southeast the Redwall becomes somewhat thinner bedded and introduces some shale and sandstone.

The base of the Redwall on the Hermit trail consists of three thick beds. The upper one is from 10 to 12 feet thick, and the lowest bed is 8 feet thick, of a vesicular gray dolomite with the cavities filled with calcite. The upper bed has *Syringopora* cf. *surcularia*. Between these two dolomite beds is a yellowish white sandstone, 4 feet thick.

The Redwall may be studied on the Hermit trail below the "Cathedral Stairs" but the sequence can not be made out with certainty because all of it has slumped and slid down in a huge landslide. The parts are mixed and even

<sup>13</sup> Noble, U. S. Geol. Survey, Bright Angel Topographic sheet, 1914.



some of the Supai is included with blocks of the Redwall. One entire day was devoted to collecting fossils from it, but the results were very unsatisfactory. Toward the middle of the Redwall were seen sections of a few corals, of *Menophyllum* and *Clisiophyllum*, and a number of crinoidal columnals, besides *Spirifer centronatus*. Of the few fossils taken away, there is a *Syringopora* like *S. surcularia* Girty, *Menophyllum excavatum* Girty, *Fenestella* and *Polypora* in several species, and a finely striate *Spirifer*.

These fossils are seen to belong to the same fauna as those identified by Girty<sup>14</sup> from near Nelson, Arizona, and collected by W. T. Lee. The time indicated by them is that of the Madison limestone so widely distributed in the Rocky Mountain country, or of the older half of the Mississippian of the Mississippi valley.

*Devono-Cambrian contact.*—The Redwall usually reposes disconformably on the Muav member of the Tonto formation of Cambrian age, but in many places in the Grand Canyon from El Tovar Hotel west far into the Shinumo quadrangle Noble has found remnants of the Upper Devonian “preserved in hollows eroded in the upper part of the Tonto formation.” These Devonian hollows are in depth up to 80 feet and were first noted by Walcott in 1880.<sup>15</sup> Throughout the Grand Canyon area no one has found a trace of the Ordovician or Silurian and none of the Lower and Middle Devonian. In 1916 Noble informed the writer that in the basal conglomerates of one of these eroded hollows in Sapphire Canyon he found an abundance of fish remains that have been identified by Mr. J. W. Gidley as scales of *Holoptychius* and plates of *Bothriolepis* nearest to *B. nitidens* of the Catskill formation of New York. The only hollow with Upper Devonian sediments seen by the writer was high above the Hermit trail on Cope Butte, where the formation consists of a twisted and gnarled, mottled yellow and pink, fine-grained calcareous sandstone that appears to be somewhat worm bored. It is an odd deposit and probably is of fresh-water origin. The disconformity between the Tonto and the succeeding Upper Devonian or Redwall is therefore very marked and is the most significant one in the Paleozoic of the Grand Canyon.

<sup>14</sup> Girty, loc. cit.

<sup>15</sup> C. D. Walcott, this Journal, (3), vol. 20, p. 224, 1880.

ART. XXIII.—*The Cambrian of the Grand Canyon of Arizona*; by CHARLES SCHUCHERT.

[Contributions from the Paleontological Laboratory, Peabody Museum, Yale University, New Haven, Connecticut, U. S. A.]

In the month of September, 1915, the writer had the great advantage of spending four days studying the Cambrian of the Grand Canyon of Arizona in the vicinity of El Tovar. One day was devoted to the Bright Angel trail and the others to the depths of the canyon about Hermit camp. The purpose of this article is not to describe the Cambrian of this wonderland in all of its manifestations throughout the Grand Canyon, for that will be done by Doctor Levi F. Noble for the United States Geological Survey. What is intended is to bring out certain physical features of the deposits, showing the shallowness of the seas of Cambrian time in the El Tovar region of Arizona, the abundance of life in those seas, though little of it is now preserved, and what is known here of the fossils proving that their age is Middle and Upper Cambrian.

*Absence of Lower Cambrian.*—No Lower Cambrian strata are known in the Grand Canyon area and for that matter anywhere in Arizona or New Mexico. The nearest known deposits of this time occur to the southwest less than 200 miles in eastern California and again about 225 miles to the north and northwest in Utah and Nevada. In the Cordilleran geosyncline the Cambrian formations attain to over 12,000 feet in thickness and the Lower Cambrian is generally several thousands of feet thick. Against these great thicknesses within the trough, the Cambrian of the Grand Canyon area averages less than 1000 feet in depth. In this we see that Arizona lies to the east and outside of this great geosyncline and that it is on the western end of the vast neutrally isostatic area of North America.

The Lower Cambrian waters were restricted in the Cordillera to the geosyncline, and a wider transgression did not take place until Middle Cambrian time. This spreading over the low neutral area, however, was still very limited, but in the Upper Cambrian the marine flood transgressed widely over the United States and far to the east of the Mississippi valley. The sediments of the

Cambrian of Arizona appear to have come from the east (New Mexico, etc.) and from the south and southeast (Mexico). As the epeiric sea advanced over the ancient peneplain, it first gathered into the basal member of the Middle Cambrian the old regolith which lay on the plain and which was essentially one of quartz sands and pebbles. Succeeding this introductory deposit, the rivers brought at first much mud and less fine sand, and finally less and less of muds and the finest of sands but more and more of solution materials. From this we learn that the lands furnishing the sediments were low and that the rivers probably were more or less long, for they brought only finer sediments and solution materials. Throughout Cambrian time none of the lands to the east and southeast of the Grand Canyon area appear to have undergone crustal movement other than warping. To the west of the Cordilleran geosyncline the story is a different one, but as it is outside of our area of description and did not furnish sediments to it, it need not be considered.

*Contact with the Vishnu.*—The contact between the Cambrian and the Archean is to be seen very clearly on Hermit Creek just below the camp site (see figs. 4 and 5). The Archean gneiss is much folded and contorted and the planes of gneissoid banding appear to dip nearly vertically. The gneiss is cut by dikes of pegmatite and by large bodies of granite. On these ancient rocks rests the Cambrian series in nearly horizontal strata, and the sea invaded the land over an almost plane surface. In a distance of several hundred feet the plane of the transgressing sea does not have hollows in it of more than 3 feet (fig. 5). In a long distance view, however, one can see places where the Vishnu rises sharply above the peneplain and seemingly sometimes several hundred feet. These monadnocks made islands in the sea of earlier Middle Cambrian time. Elsewhere this peneplain as it extends over the Proterozoic strata (Grand Canyon series) also has its monadnocks and ridges of quartzites trending northwest and southeast, and they protrude even higher into the Cambrian than do those of the Vishnu, up to 700 feet Noble<sup>1</sup> describes this peneplain as follows:

<sup>1</sup>L. F. Noble, this Journal, (4), vol. 29, p. 527, 1910.

The Cambrian sea "transgressed a surface which strongly resembled the present surface of the great Laurentian peneplain of Canada with its broad areas of crystalline rocks in which are inset occasional blocks of Paleozoic strata, and above which stand occasional monadnocks of quartzite. . . . When the Tonto sea came in over the surface of the ancient peneplain the monadnocks stood out as islands which were gradually overwhelmed and buried in the sands of the deepening sea. . . . These monad-

FIG. 4.



FIG. 4. General view of Grand Canyon from Tonto Platform east of Cope Butte, looking west. I, Lower Supai; II, Redwall limestone; III, Muav formation; IV, Bright Angel shale; V, Tapeats sandstone; VI, Vishnu series.

nocks of the Cambrian plain may be compared with the Baraboo ridges of Huronian quartzite [in Wisconsin] which by virtue of their homogeneity and hardness still stand as prominences which have weathered repeated cycles of erosion."

*Subdivisions and Character of the Middle Cambrian Series.*—According to Doctor Noble,<sup>2</sup> the basal member of the Cambrian series is the Tapeats sandstone with a

<sup>2</sup>L. F. Noble, *Geol. Hist., Bright Angel Quadrangle, U. S. Geol. Survey, 1914.*

thickness near Hermit camp of about 200 feet (fig. 4). Elsewhere it varies between 100 and 250 feet. Within the inner gorge it is a cliff maker and especially so in its lower two thirds; otherwise it determines the floor of the Tonto platform. The lower 150 feet consists of coarse, brownish, much cross-bedded sandstones that are often slightly glauconitic, followed by 25 feet of finer grained brown and glauconitic sandstones with shale

FIG. 5.

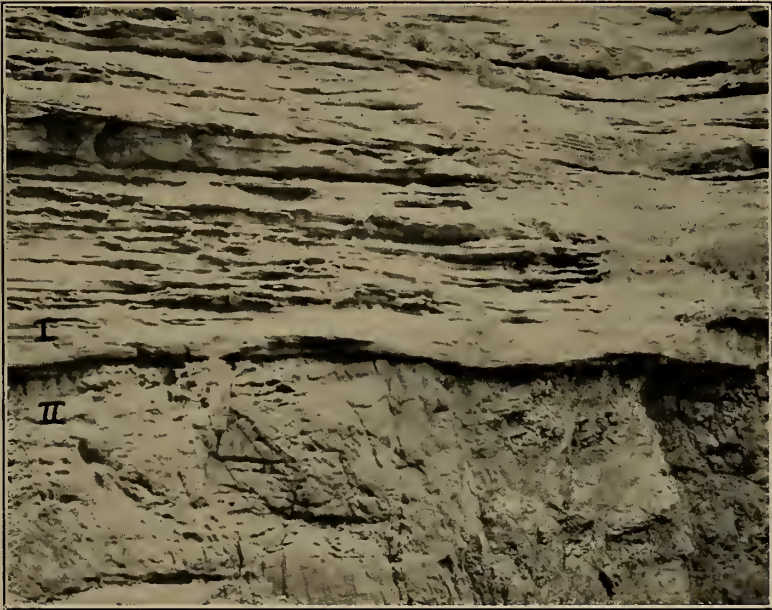


FIG. 5. Contact between Tapeats sandstone (I) and Vishnu series (II) near Hermit camp. Distance along contact about 40 feet.

beds. At the top is a white cross-bedded sandstone about 25 feet thick, and here was seen very rarely a fragment of an obolid shell.

The basal bed of the Tapeats, about 1 foot in thickness, has many slightly worn subangular pieces of quartz averaging about an inch across. The stratum is, however, a jumble of small and large pieces of the Vishnu up to one foot in length, consisting of hard and soft rocks lying in the shallow depressions of the ancient peneplain.

The material is of the rocks immediately beneath and the old regolith has had but little transportation and assorting.

The character of the basal 35 feet of the Tapeats shows little assorting and the thick beds are composed of decidedly cross-bedded fine-grained conglomerates with sub-angular pebbles up to 10 mm. across. In these strata are also interbedded short lenses up to 4 inches thick of maroon colored shale. The material of these basal strata is essentially the Vishnu, fragmented, with many pebbles of red jasper (the red jasper probably came from some nearby outcrop of Unkar), the whole being of a blotchy maroon-yellowish color. Then comes 10 feet of conglomerate, maroon in color. Higher, the coarse sandstone with layers of conglomerate is more evenly bedded in beds from 1 to 2 feet thick, separated by irregular layers of dark green shale. As one rises through the Tapeats it is seen that the material becomes finer grained and is better assorted, and that the shale zones become more and more prominent, though the muds do not dominate the Tapeats member until near the top and then the whole changes over into a deep blue shale that weathers an olive-green. These data show that the greater part of the Tapeats is a delta deposit on the land side rather than on that under the influence of the invading sea.

The Tapeats sandstone passes gradually into the Bright Angel formation of fine sandy soft shales with interbedded shaly sandstones, here 332 feet thick according to Noble's measurements (fig. 4). Everywhere it makes gentle slopes and little cliffs where the sandstones are. On the weathered surface it is in general olive-green in color, but on fresh fracture is a bluish micaceous (muscovite) shale, interbedded with many thin and thick beds of dark or brownish cross-bedded sandstones, many of which are highly glauconitic. When the sandstones have obolid shells, then they become more or less calcareous or even arenaceous glauconitic limestones. These sediments show clearly that the sea was not deep, but that it probably covered wide flats to a depth of less than 150 feet, not many tens of miles from the shore. Deposition was fairly rapid. When the waters were fairly clear and were depositing sandstones, glauconite was forming and there were incursions of inarticulate brachi-

opods. These sands were constantly reworked by the waves, washing the shells out of the holes and breaking them into pieces. When the sandy muds were forming, seaweeds (*Palæophycus*) were common, along with a great abundance of burrowing annelids. Trailings and fucoidal casts are nearly always to be seen and also the vertical burrowings of worms like *Arenicolites*. One of the most striking features of the Bright Angel formation is that nearly all of the sandstones are full of glauconite.

In spite of the fact that almost no good fossils are to be had in the Bright Angel formation, yet the physical phenomena show that the epeiric sea of this time must have been rich in life. This is proved by the abundance of fucoidal casts, trailings, and annelid burrows. Further, in some of the sandstones obolid fragments teem and at times their shells make up one third of a stratum. When the obolid shells are prevalent, glauconite is also common, and the formation of this mineral is probably conditioned by the decomposition of the organic remains. On the other hand, there are entire beds of glauconite up to a few inches thick that are almost devoid of fossils. When glauconite is very abundant, there are also apt to be thin beds and even zones a few feet thick of low grade iron-ore.

*Fossils of the Middle Cambrian.*—*Palæophycus* casts are very common and well preserved at 15 feet above the Tapeats sandstone, and 150 feet higher is a glauconitic sandstone replete with the brachiopods *Micromitra* (*Iphidella*) *pannula* (White) and *Obolus* (*Westonia*) *chuaensis*. Ten feet higher occur abundantly in thin-bedded sandstones *Obolus zetus* and rarely *Obolus* (*Westonia*) *themis* and *Lingulella acutangula*.

The most prominent horizon for fossils, consisting almost entirely of obolids, is the one just mentioned which occurs from 150 to 170 feet above the base of the Bright Angel formation and is at the same time a general level for thin-bedded sandstones. At about this same general level Walcott<sup>3</sup> has elsewhere collected in the Grand Canyon, besides those mentioned above, *Obolus* (*Westonia*) *euglyphus*, *Lingulella perattenuata*, *L. lineolata*, *Micromitra pealei*, *M. crenistria*, and *M. superba*.

On the Bright Angel trail at 100 to 120 feet above the

<sup>3</sup> C. D. Walcott, U. S. Geol. Survey, Mon. 51, 1912.

Tapeats sandstone Walcott<sup>4</sup> has gotten *Obolus chuarensis* and the trilobites *Alokistocare althea*, *Dolichometopus productus* and *D. tontoensis*. The two last named trilobites are typical Middle Cambrian forms of the Cordilleran province, and as guide fossils have far more value than any of the brachiopods.

*Upper Cambrian Series.*—The top member of the Tonto series is Noble's Muav limestone (fig. 4). To the west in the Shinumo area the Upper Cambrian series is more calcareous than in that of the Bright Angel and therefore it can there be properly referred to as a limestone formation.<sup>5</sup> About El Tovar, however, the series is best referred to as the Muav formation. In the Hermit camp area the thickness is, according to Noble, 425 feet, though in his *Geologic History of the Bright Angel Quadrangle*, 1914, it is given as 380 feet. The thinning, Doctor Noble writes me, is not due to erosion, but to actual shrinkage in the thickness of the beds as they are traced from west to east. Throughout the Grand Canyon region occur many isolated hollows eroded into the Muav, in which are preserved fresh-water sandy limestones up to 100 feet in thickness, bearing locally fish remains of Upper Devonian age. Above the Hermit trail in Cope Butte there is such a hollow, 80 feet deep, inset into the Upper Cambrian formation. The Muav makes steep slopes in the lower half and cliffs above, due to the protecting hard limestones of the Redwall, which are of early Mississippian age (fig. 4).

In general the Muav formation about El Tovar may be defined as a buff colored series of decidedly variable calcareous strata, or as a series of impure micaceous (muscovite) shaly and sandy limestones (70%), calcareous shales (18%), and calcareous sandstones (12%). It is only in the uppermost 50 feet that the strata may be regarded as more or less pure limestones. Where the calcareous materials become more dominant the beds are completely riddled with vertical and anastomosing worm burrows. These are usually filled with a very fine sand and it is this feature that gives so much of the Muav its mottled appearance and that led Gilbert many years ago to call the formation in the western part of the Grand Canyon the "Mottled limestone." Throughout the mid-

<sup>4</sup> Walcott, *Smithson. Misc. Coll.*, vol. 64, pp. 369-374, 184, 1916.

<sup>5</sup> L. F. Noble, *U. S. Geol. Survey, Bull.* 549, p. 64, 1914.



dle third of the Muav many of the shaly limestones are intraformational conglomerates with the pebbles small, flat, and more or less rounded on the edges. It is an interesting shallow-water, near-shore, marine deposit. This is shown in the great abundance of annelid burrows, in the intraformational conglomerates, and in the variable nature of the calcareous deposits.

As to whether there is a break in sedimentation between the Muav and Bright Angel formations, or, in other words, between the Middle and Upper Cambrian, the writer could not determine in his limited time. In any event, one has no difficulty in the field in drawing the line of separation between the blue-green shales at the top of the Bright Angel formation and the thinly laminated calcareous shales and impure limestones at the base of the Muav. Doctor Noble in a letter to the writer states that he had even less difficulty in laying the line of separation between these formations to the west in the Shinumo quadrangle, for here the change in lithology is sharper than about El Tovar and to the eastward.

*Fossils of the Muav.*—While recognizable fossils are extremely rare in the Muav formation, yet annelids were exceedingly common. The writer has not seen a Paleozoic marine deposit more bored into and consumed by mud eaters than this one, and these burrows are most prevalent in the calcareous zones. Worm castings are often well preserved in the thin-bedded shale zones, and occur as little confused heaps or in circular sausage-like strings.

At about 200 feet above the base of the Muav Noble collected and Kirk identified the brachiopod genus *Syn-trophia* and, through fragments, the following trilobite genera: *Finkelnburgia*, *Pagodia*, *Anomocarella* and *Ptychoparia*. About 50 feet lower the writer found pygidia of *Saukia* and cf. *Neolenus*. Near the top were found by Walcott two large orthids of *Jamesella* ? and *Billingsella*. These fossils, and more especially the trilobites, show that the Muav is of Upper Cambrian age.

ART. XXIV.—*The Gravimetric and Volumetric Determination of Fluorine Precipitated as Thorium Fluoride*; by F. A. GOOCH and MATSUSUKE KOBAYASHI.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccc.]

The work of which an account is here given is the result of an attempt to base a volumetric method for the determination of fluorine upon the recent method of Pisani<sup>1</sup> for the gravimetric determination of that element by precipitation as hydrous thorium fluoride and the conversion of the last to thorium oxide by ignition. Incidentally, it became necessary to modify somewhat the procedure of Pisani when applied either gravimetrically or as preliminary step in the volumetric determination of fluorine.

According to the procedure of Pisani, thorium nitrate is added gradually in limited amounts to the solution of an alkali fluoride slightly acidulated with acetic acid, or even with nitric acid, and the heavy gelatinous precipitate allowed to settle after every small partial precipitation before the addition of more of the precipitant. When the precipitate is considerable enough water must be added to permit the decanting of a large portion of the clear liquid into a conical vessel for further treatment with the precipitant, to make it sure that no further precipitation will take place. If necessary, the deposition is allowed to continue for some hours and too great an excess of the precipitant must not be added at once, because, in a concentrated liquid, thorium nitrate may dissolve a little of the precipitate. When, however, the content in fluorine is known approximately, the necessary quantity of thorium nitrate may be added at the beginning in sufficiently large amount to complete the action at once. The delicacy of the reaction is very great, permitting the recognition of as little as one part of fluorine in ten thousand parts of the liquid. In the washing many decantations are employed and the clear liquid is decanted into a large vessel and allowed to stand for some time before filtering, to prevent the small amount of suspended material from passing the filter. The precipitate of hydrous thorium fluoride,  $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ ,

<sup>1</sup> *Compt. rend.*, 162, 791, 1916.

is ignited with the paper filter and the fluorine present is calculated from the weight of the residual thorium oxide,  $\text{ThO}_2$ .

In preliminary experiments upon this method it became plain that the precautions relating to acidity and excess of the precipitant must be more accurately defined and later it was found that the tedious succession of partial precipitations when unknown amounts of fluoride are to be titrated may be obviated by a simple modification of method.

The experiments to be discussed were made with a solution of thorium nitrate made by dissolving 10 gm. of the hydrous salt,  $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ , in a liter of cold water acidulated with 1  $\text{cm}^3$  of glacial acetic acid, and with a nearly N/10 solution of sodium fluoride made by dissolving about 4.2 gm. of that salt in a liter of cold water containing a small amount (0.5 gm. to 1 gm.) of sodium carbonate, to insure alkalinity of the solution. The exact strength of the thorium nitrate solution was determined by precipitating the thorium as oxalate and weighing the ignited thorium oxide. The fluoride solution was standardized by precipitation as calcium fluoride and treatment, according to the common procedure<sup>2</sup> and also by the more recent procedure of Dinwiddie.<sup>3</sup> Portions of these solutions were measured from burettes for the experiments to be detailed, correction being made for temperature variations.

In the following table are given the results found in a series of experiments made to determine approximately the effect of thorium nitrate when added in excess to the solution of the fluoride slightly acidulated with acetic acid, the effect of varying amounts of acetic acid, and the effects of free nitric acid and free sulphuric acid.

The results of Table I show, first, that great care must be taken in respect to the excess of thorium nitrate, used as the precipitating reagent, and that the precipitate will probably be sufficiently insoluble for the purpose of a quantitative determination, if the excess of the thorium salt does not exceed by more than 50% the amount theoretically needed in the metathesis.

Furthermore, it is plain that free nitric acid, even in very small amount, exerts a strong and inadmissible sol-

<sup>2</sup> Treadwell-Hall; Analytical Chemistry, 4th ed., vol. 2, 471.

<sup>3</sup> This Journal, (4), 42, 421, 1916.

TABLE I.

*Conditions Affecting the Precipitation of Thorium Fluoride.*

## A.

## Effect of Varying Amounts of Thorium Nitrate.

Weight of ThO <sub>2</sub> corresponding to fluoride taken gram.	Variation in amounts of reagents	Weight of ThO <sub>2</sub> found gram.	Error gram.	Total volume cm <sup>3</sup>
0.0688	Thorium nitrate } 50% in excess	0.0687	-0.0001	80
0.0688	Thorium nitrate } 100% in excess	0.0646	-0.0042	90
0.0688	Thorium nitrate } 200% in excess	0.0462	-0.0226	100

## B.

Effect of Varying Amounts of Nitric Acid and Sulphuric Acid:  
Thorium Nitrate 50% in Excess.

0.0679	HNO <sub>3</sub> -conc.	0.02 cm <sup>3</sup>	0.0622	-0.0057	30
0.0679	"	0.1 "	0.0584	-0.0095	30
0.0679	"	0.4 "	0.0564	-0.0115	30
0.0679	H <sub>2</sub> SO <sub>4</sub> -	1.02 "	0.0711	+0.0032	30
0.0679	"	1.27 "	0.0681	+0.0002	30
0.0679	"	1.52 "	0.0639	-0.0040	30

## C.

Effect of Varying Amounts of Acetic Acid:  
Thorium Nitrate 50% in Excess.

0.0679	Acetic acid: 0.01 N	0.0727	+0.0048	30
	0.018 gram.			
0.0679	Acetic acid: 0.02 N	0.0675	-0.0004	30
	0.036 gram.			
0.0679	Acetic acid: 0.06 N	0.0676	-0.0003	30
	0.108 gram.			
0.0679	Acetic acid: 0.13 N	0.0673	-0.0006	30
	0.234 gram.			
0.0679	Acetic acid: 0.26 N	0.0664	-0.0005	30
	0.468 gram.			
0.0679	Acetic acid: 2.75 N	0.0658	-0.0021	30
	4.95 gram.			

vent action upon the precipitate, while the action of sulphuric acid is considerable. On the other hand, the action of acetic acid in properly regulated proportion is not only permissible but necessary to secure a proper acidity of the solution. From the figures given, it appears that the amounts of acetic acid may vary between about

0.04 grm. and 0.4 grm., in a volume of 30 cm<sup>3</sup>, or that the concentrations of the solution in respect to free acetic acid may be between the limits of about 0.02 N and 0.2 N acid. In the work to be further described these conditions of acidity were preserved.

In putting this general procedure to the test, portions of the fluoride solution were measured exactly from a burette and in some cases the portions were further diluted with water. Enough acetic acid was added to make the acidity of the solution in respect to that acid lie between the limits of about 0.02 N and 0.2 N—amounting to a content of about 0.12 grm. and 1.2 grm. of free acetic acid in 100 cm<sup>3</sup> of solution. The thorium nitrate solution was run in slowly in amounts about 25% in excess of that theoretically required in the reaction, with constant stirring. The mixture was allowed to stand for a few hours and the precipitate after several washings by decantation with cold water containing a drop of glacial acetic acid in 25 cm<sup>3</sup>, was filtered off upon ashless paper supported by a perforated platinum cone so that suction might be applied at the end of this washing, washed, and ignited in platinum. The weight of thorium oxide, ThO<sub>2</sub>, remaining was taken as the gravimetric measure of fluorine precipitated as thorium fluoride, ThF<sub>4</sub>·4H<sub>2</sub>O.

The filtrate containing the excess remaining from the known amount of thorium nitrate taken was poured into a measured amount of a solution of oxalic acid containing a few drops of concentrated sulphuric acid and allowed to stand on the steam bath for a period of from fifteen to twenty minutes. The precipitated thorium oxalate was filtered off on asbestos in a perforated crucible, washed with cold water containing one drop of concentrated sulphuric acid in every 25 cm<sup>3</sup>, and oxidized by standard permanganate according to the method previously described<sup>4</sup> for the volumetric determination of thorium precipitated as the oxalate. The difference between the amount of thorium originally present and that found in the filtrate was taken as the measure of fluorine by the volumetric process.

It was found that the addition of an emulsion of asbestos to the liquid containing thorium fluoride in suspension obviates the necessity of several decantations and

<sup>4</sup> Gooch and Kobayashi; this Journal, 45, 227.

aids greatly in the filtration and washing if only a volumetric determination is to be made, but this device can not be applied when the gravimetric determination of the ignited thorium oxide is desired.

In Table II are recorded the details of experiments made according to the procedure outlined.

TABLE II.

## Gravimetric and Volumetric Determinations of Fluorine Precipitated as Thorium Fluoride.

Fluorine taken gram.	Fluorine found:		Error		Total volume of liquid cm <sup>3</sup>	Acidity of acetic acid N.
	Gravimetrically gram.	Volumetrically gram.	Gravimetrically gram.	Volumetrically gram.		
A.						
<i>Filtration after one decantation.</i>						
0.0391	0.0404	0.0412	+0.0013	+0.0021	86	0.06
0.0588	0.0610	0.0617	+0.0022	+0.0029	109	0.07
B.						
<i>Filtration after two decantations.</i>						
0.0196	0.0202	0.0202	+0.0006	+0.0006	29	0.05
0.0196	0.0190	0.0193	-0.0006	-0.0003	79	0.04
0.0391	0.0405	0.0409	+0.0014	+0.0018	76	0.05
0.0391	0.0398	0.0403	+0.0007	+0.0012	77	0.10
C.						
<i>Filtration after several decantations.</i>						
0.0196	0.0198	0.0198	+0.0002	+0.0002	39	0.02
0.0196	0.0196	0.0198	0.0000	+0.0002	39	0.05
0.0196	0.0200	0.0199	+0.0004	+0.0003	39	0.07
0.0196	0.0197	0.0197	+0.0001	+0.0001	39	0.09
0.0196	0.0191	0.0190	-0.0005	-0.0006	38	0.05
0.0196	0.0197	0.0195	+0.0001	-0.0001	28	0.06
0.0391	0.0398	0.0399	+0.0007	+0.0008	76	0.06
0.0391	0.0391	0.0389	0.0000	-0.0002	56	0.06
0.0588	0.0598	0.0598	+0.0010	+0.0010	114	0.07
0.0588	0.0590	0.0591	+0.0002	+0.0003	114	0.05
0.0789	0.0763	0.0774	-0.0021	-0.0010	152	0.05
0.0980	0.0960	0.0974	-0.0020	-0.0006	191	0.06
D.						
<i>Filtration after addition of asbestos, without decantation.</i>						
0.0196	.....	0.0200	.....	+0.0004	38	0.05
0.0196	.....	0.0195	.....	-0.0001	38	0.05

The adjustments of the amounts of thorium nitrate necessary and permissible in precipitating unknown amounts of fluoride by means of a series of partial precipitations and decantations, as described by Pisani, is a

very tedious and troublesome matter. It has been found, however, that the difficulty may be obviated, at least for solutions of moderate dilution, by the simple procedure to be described. In this procedure, a small measured amount of the fluoride solution was made barely acid to litmus with acetic, nitric, or sulphuric acid and then added drop by drop, with stirring, to a small measured amount (a few  $\text{cm}^3$ ) of the standard thorium nitrate solution (10 grms. of the hydrous nitrate in one liter) until a *distinct turbidity* was produced. Under the conditions of dilution described the development of the distinct turbidity, which marks the beginning of immediate precipitation, indicated a relation between the thorium nitrate and the fluoride which was sufficiently definite to serve as a basis for the easy calculation of the amount of thorium nitrate required for complete precipitation of the fluoride. The determinations of Table III show that turbidity is produced upon addition of the fluoride solution to the excess of thorium nitrate solution when the amount of the latter is about two and a half times as much as would be required theoretically for the precipitation of the amount of fluoride used and this amount is about twice as much as may be used with safety if the precipitation is to be complete.

TABLE III.

The Point of Incipient Precipitation when the Fluoride is added to an Excess of Thorium Nitrate.

Fluoride solution N/10 $\text{cm}^3$	Thorium nitrate solution* $\text{cm}^3$	Water added $\text{cm}^3$	$\text{ThO}_2$ equivalent to fluoride gm.	$\text{ThO}_2$ contained in thorium nitrate used gm.	Ratio of $\text{ThO}_2$ used to $\text{ThO}_2$ equivalent to fluoride gm.
0.52	2	0	0.0036	0.0094	2.6 : 1
0.54	2	2	0.0037	0.0094	2.5 : 1
0.80	3	0	0.0055	0.0141	2.6 : 1
0.81	3	3	0.0056	0.0141	2.5 : 1
0.82	3	0	0.0057	0.0141	2.5 : 1
0.83	3	0	0.0057	0.0141	2.5 : 1
0.84	3	0	0.0058	0.0141	2.4 : 1
1.35	5	0	0.0093	0.0235	2.5 : 1
2.70	10	0	0.0186	0.0470	2.5 : 1

\* 10 gm. of the hydrous salt in 1 liter.

According to this procedure, directions for the precipitation of the hydrous thorium fluoride,  $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ , from a fluoride solution of unknown concentration may be summarized as follows:

The approximately measured solution of alkali fluoride is made barely acid with acetic acid and a small amount of this solution is taken in a convenient graduate. From a burette filled with the standard thorium nitrate solution a small portion (a few cubic centimeters) of the solution is drawn into a small beaker. To this small portion of the thorium nitrate solution the fluoride solution is added from the graduate, drop by drop, with stirring, until a faint but *distinct* turbidity is formed immediately. The amount of fluoride solution required to bring about the immediate turbidity in the measured amount of thorium nitrate solution is noted and from the relation of these amounts of the solutions of fluoride and thorium nitrate thus used is calculated the amount of thorium nitrate solution which should stand in similar relation to the entire amount of the fluoride solution. One half of the amount of thorium nitrate thus calculated, which will be about 25% more than is theoretically required and well within the limit of safety in respect to an excess, will be the proper amount to bring about the complete precipitation of all the fluoride.

The unused portion of the solution is acidified with acetic acid until the acidity falls within the limits of about 0.02 N and 0.2 N—amounting to a content of about 0.12 gm. to 1.2 gm. of free acetic acid in every 100 cm<sup>3</sup> of solution—and the small portion of the fluoride solution used in the test is returned to the unused solution. The calculated proper amount of thorium nitrate solution (taking into account the amount of it already added in the preliminary test) is added to the entire fluoride solution and the mixture is allowed to stand a few hours. From this point the procedure for the determination of fluorine gravimetrically or volumetrically is that previously described.



ART. XXV.—*Eruptive Rocks at Cuttingsville, Vermont*;<sup>\*</sup>  
by JULIUS WOOSTER EGGLESTON.

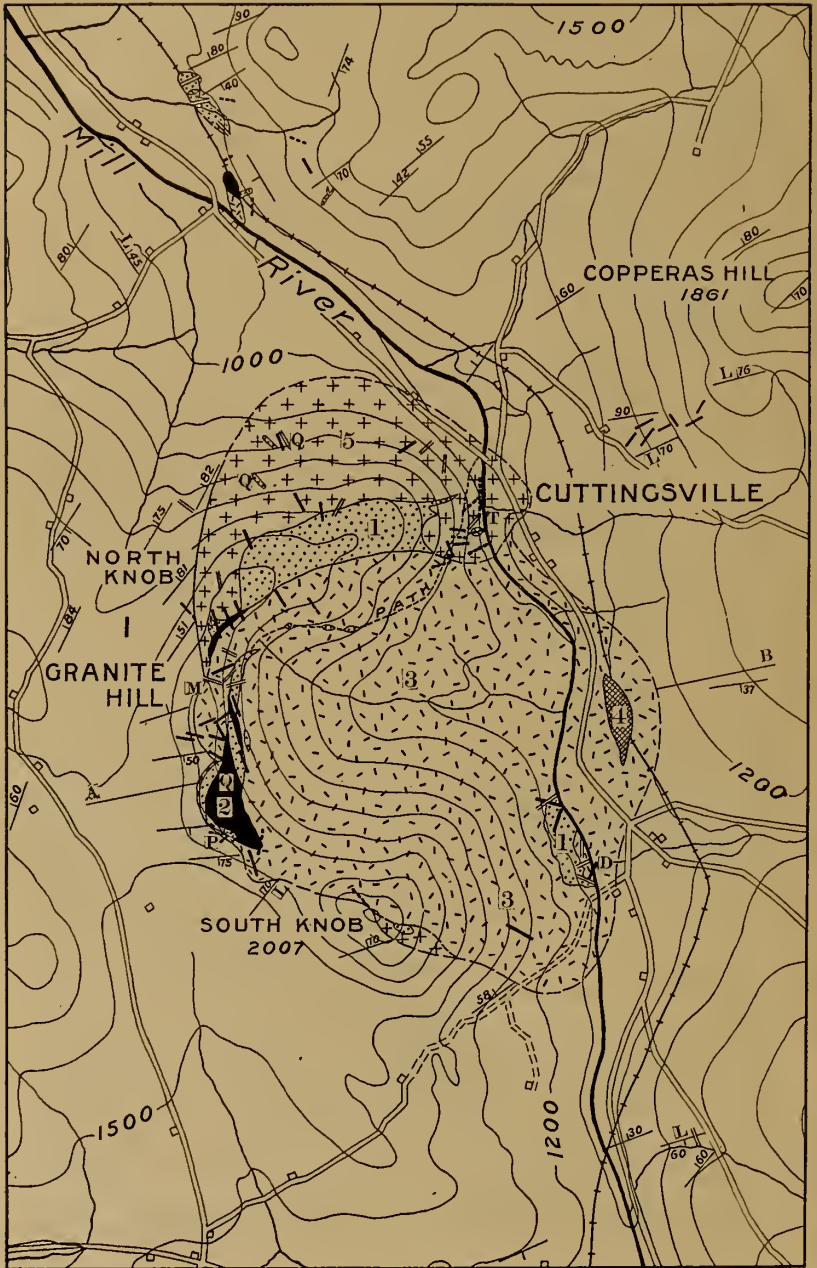
- Introduction.
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    - Gneisses.
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    - Quartzite.
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  - Stock rocks.
    - Essexite.
    - Hornblende-biotite syenite.
    - Pulaskite.
    - Sodalite-nephelite syenite.
    - Augite syenite (nordmarkite).
  - Dike rocks.
    - Essexite porphyry.
    - Nephelite syenite.
    - Syenite porphyry.
    - Zircon-rich pulaskite porphyry.
    - Aplite.
    - Tinguaite.
    - Camptonite.
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- List of chemical analyses.

## INTRODUCTION.

Under the name "granite" the eruptive body at Cuttingsville, on the west slope of the Green Mountains and 10 miles southeast of Rutland, Vermont, was noted in E. Hitchcock's geological report on Vermont (map and vol. 2, p. 742, 1861). In 1892 and 1894 Mr. C. L. Whittle, with an assistant, studied the Cuttingsville area for the U. S. Geological Survey, but the results of this work have not been published. In the years 1906 to 1909 the

<sup>\*</sup> Shaler Memorial Investigation No. 9. The cost of publication of this paper has been defrayed by the Shaler Memorial Fund, Harvard University.

FIG. 1.



writer carried on intermittent, detailed work in the area. A summary of results was given before the Geological Society of America at Cambridge, Mass., December, 1909. An abstract was printed in the Proceedings of that meeting (vol. 21, p. 785, 1910).

In connection with the present paper, acknowledgments are due to Dr. Charles Palache, who first called the writer's attention to the Cuttingsville rocks; to Professor Wolff, under whose direction this study was undertaken; to Mr. C. L. Whittle for the use of his reconnaissance map and collections; to Professor R. A. Daly, who

FIG. 2.



FIG 2. Section along line A-B in fig. 1. Natural scale, 1: 28,000.

has assisted in the preparation of the manuscript. Special thanks are due to Dr. H. E. Merwin, now of the Carnegie Geophysical Laboratory at Washington, D. C., and to Professor C. D. Test, of the Department of Chemistry of the Colorado School of Mines, who made the excellent chemical analyses accompanying this paper.

### TOPOGRAPHY.

Cuttingsville lies in the valley of Mill River on the Rutland railroad, about 1,000 feet above sea (fig. 1). The main eruptive body, 1.7 square miles (4 sq. km.) in area, is largely confined to Granite Hill (2,007 feet, fig. 3), so named from its quarries of syenite, popularly called

FIG. 1 (p. 378). Geological map of Cuttingsville district. Scale, 1: 28,000. Standard orientation.

*Stock rocks*—1, Essexite; 2, hornblende-biotite syenite; 3, pulaskite; 4, sodalite-nephelite syenite; 5, nordmarkite.

*Dike rocks*—Dotted line, essexite porphyry. Heavy broken line, syenite porphyry. Heavy full line, tinguaite. Double line, camptonite.

*Country rocks*—except limestone (L), not distinguished.

A-B, line of section. D, dike of type tinguaite. M, open cut for molybdenite. P, pit. Q, quarry. T, tunnel.

“granite.” This hill is crescentic in form, with a knob towards either end of the crescent, the south knob rising about 250 feet higher than the north knob (fig. 4). The shape of the hill is very suggestive of a low glacial cirque tributary to the glaciated valley of Mill Creek.

Two smaller eruptive bodies lie on the northeast side of Mill River (fig. 1), and, still farther north, a mass of breccia occupies the eastern half of a 1,400-foot hill north of Mill Creek (fig. 4). Including the breccia, the bodies extend along a line nearly  $3\frac{1}{2}$  miles long. The accompanying geological maps are based upon an enlargement of adjoining parts of the Wallingford and Rutland, Vt., sheets of the topographic map of the United States.

### CONDITIONS OF EXPOSURE.

Much of Granite Hill, particularly the north and east slopes of the two knobs, is thickly wooded. The bowl, crest, and west slope are fairly free from trees, but the bowl is heavily drift-covered. Along the crest, on the slopes of the north knob, and also at the east foot of each knob, where Mill Creek is actively eroding, exposures are especially numerous; those on the south knob much fewer. Three small abandoned quarries, several test pits, a prospect cut, a tunnel and a railroad cut south of Cuttingsville (see fig. 1) furnish fresh rock. Ledges and open cuts along a pyrrhotite deposit on the lower southwest slope of Copperas Hill expose a group of dikes presumably connected with the main eruptive body (fig. 5).

Excepting along the crest of the middle part of Granite Hill and for a short stretch along the crest of the south knob, contacts are rarely exposed. As mapped they are accordingly for the most part only approximate.

### OUTLINE OF FIELD RELATIONS.

#### COUNTRY ROCKS.

The country rocks are all metamorphic—chiefly hornblende-pyroxene and mica gneisses, with considerable limestone, and quite subordinate chloritic schists and quartzite. In a zone a score or two feet wide along the only visible contact, on the west side of the main eruptive body, they show some contact metamorphism besides moderate brecciation, diking, and impregnation by eruptive rocks.

Strikes and dips of the country rocks are indicated upon the accompanying map. The strikes are commonly northeasterly, in accord with the usual Appalachian trend and run at high angles to the axis of the eruptive bodies.

Structural relations among the members of the country-rock series are obscure. The hornblendic gneisses commonly strike at an angle to the other members and are probably intrusive into them. The structural complexity makes it difficult to state the nature of the rocks beneath those actually visible. Quartzite and less certain dolomite xenoliths in the essexite of one of the northern eruptive bodies may have been derived wholly from beds formerly overlying the visible country rocks, although some may have come from beneath.

Whittle\* refers the country rocks to the Algonkian and places them in a system named by him the Mount Holly, from a neighboring hill and village.

#### ERUPTIVE ROCKS.

The eruptive rocks include essexite, hornblende-biotite syenite, pulaskite, nephelite syenite, sodalite-nephelite syenite, nordmarkite, essexite porphyry, tinguaita, camp-tonite, and an eruptive breccia. Some of the eruptives have locally suffered slight faulting and possibly very limited crushing and shearing along certain contacts, as a result of successive intrusions and later movements; but all these rocks are entirely free from anything at all comparable to the effects of regional metamorphism displayed by the country rocks.

*Composite stock.*—Cross-cutting relations to the country rocks, combined with high outward dips of the contact where observable, nearly vertical flow lines, and small areal extent of the intrusive mass, indicate that the main body is a stock. In any case a laccolithic origin cannot be assumed. The composite character of the body is revealed by the distribution and structural relations of its rocks. The chief types are arranged in a roughly concentric manner (see fig. 1), essexite being partly surmounted by pulaskite and both being probably cut by the nordmarkite body.

\* C. L. Whittle, The Occurrence of Algonkian Rocks in Vermont and the Evidence for their Subdivision, Jour. Geology, vol. 2, p. 396, 1894.

*Essexite* composes nearly one-quarter of the total area of the eruptives. In practically all of its occurrences it is cut by syenite or syenite porphyry, the smaller masses apparently being completely inclosed. Evidently the *essexite* represents an older body, probably a stock, which has been invaded and largely engulfed by the later intrusions. Nearly vertical contacts and occasional nearly vertical flow lines, in the *essexite* and some of the syenite, suggest that the whole forms a composite stock.

FIG. 3.



FIG. 3. Granite Hill, looking southwest.

The *pulaskite*, especially well shown on the north slopes of the bowl, constitutes about two-thirds of the main eruptive body. It clearly penetrates the *essexite* and gneisses. In places it extends west of the crest of the middle part of Granite Hill (fig. 3), forming, where *essexite* is present, a band of no great width between the *essexite* and gneisses.

Between flanking lenses of *essexite* and occupying the crest of the middle part of Granite Hill, is an area of *hornblende-biotite syenite*, upwards of 1,000 feet long and half as wide. It appears again, in a much narrower band, near the crest of the north knob. Its total areal extent is believed to be least of all the chief types of rock exposed on Granite Hill. Its structural relations to both the *essexite* and the *pulaskite* are somewhat obscure, due to the failure of sharp contacts. A point bearing upon this question, however, is the very common development of a *biotite-hornblende* phase of the *pulaskite* on the side towards the *essexite*. These border phases frequently

resemble very closely the type hornblende-biotite syenite in the quarry near the crest of the middle part of Granite Hill.

These facts might be explained on the assumption that the hornblende-biotite syenite is a sort of hybrid, having resulted from the assimilation of essexite by pulaskite. This view accords with the usual absence of sharp contacts between pulaskite and essexite, the one gradually passing into the other, as illustrated in a narrow band near the crest of the north knob.

However, in the quarry the hornblende-biotite syenite itself is cut by an apophysis or irregular dike of syenite porphyry merging into porphyritic syenite. If it is a tongue from the main mass of pulaskite, the view that the hornblende-syenite is a hybrid of essexite and pulaskite must be relinquished in favor of early differentiation and intrusion coincidentally with or immediately succeeding the essexite, but preceding the pulaskite.

The *nordmarkite* is clearly intrusive into the essexite, cutting it freely and inclosing fragments, as well shown in the contact zone of essexite and nordmarkite on the north knob. Its relations to the other syenites are obscure. On the lower southeast slope of the north knob, the path to the quarry has been cut in bedrock which shows quartz-syenite dikes penetrating a pulaskitic type.

A similar combination, with gneiss fragments also included, is shown in excavated blocks at the edge of Mill River just below. This is the only recorded evidence that nordmarkite intrudes eruptives other than essexite, and it is not conclusive. The nordmarkite along Mill River, at the east foot of the north knob of Granite Hill, is cut by several large dikes of syenite porphyry.

These may possibly be apophyses from the pulaskite, though there are certain field, lithological, and chemical reasons for believing these syenite-porphry dikes to be intrusions later than both nordmarkite and pulaskite, and connected with the nephelite syenite.

The *sodalite-nephelite syenite* in the railroad cut is probably considerably less extensive than any type on Granite Hill. Very similar rock exposed on the lower east slope of the south knob, in a small detached outcrop, on the west shore of Mill River, may indicate that the area extends into Granite Hill. The structural relations are completely hidden. The rock is either a sodalite-

bearing phase of the pulaskite and contemporaneous with it, or, as just suggested, a distinctly later intrusion.

*Smaller igneous-rock areas.*—The two smaller areas north of Granite Hill appear to be parts of one irregular, composite intrusion, fed from the same magma reservoir as the main body. It is quite possible that the northern areas are continuous with the Granite Hill mass, beneath the cover of drift and alluvium in Mill River Valley. If so, this would increase the length of the area of the Granite Hill stock by about three-quarters of a mile, and give it a pronounced northward elongation.

The northern eruptives, where exposed, are much more involved with the country rocks than is the case on Granite Hill. Contorted and brecciated gneisses frequently alternate with eruptives along the railroad, and flank them on the northwest. The geological map, owing to the limitations of its scale, gives a quite inadequate impression of the intricate relations between eruptives and country rock, especially in the case of the more northern area.

The rocks of the northern areas resemble those on Granite Hill, but nordmarkite and the more basic phases of essexite are absent. Thick dikes of camptonite with numerous inclusions are the more impressive features in the northern areas.

Although not so well shown as on Granite Hill, the syenite of the northern areas is nevertheless clearly intrusive into the essexite, probably vertically, judging from limited contacts and nearly vertical flow lines in some of the syenite. The essexite carries occasional xenoliths of quartzite, hornblende gneiss, and possibly of dolomite, and is probably a quite irregular intrusion. The syenite, although not chemically or microscopically studied, is regarded as partly pulaskite and partly biotite syenite (with some hornblende). The latter has been mapped under the same symbol (2, fig. 1) as the hornblende-biotite syenite of Granite Hill, which rock it most resembles.

*Breccia mass.*—About three quarters of a mile north of the small areas of eruptive rock just described, there is a body of breccia, shown in fig. 4. Though not closely studied it appears to represent shattering by faults. The constituent fragments, never more than a few centimeters in diameter, are composed of quartzite, with subordinate schist and gneiss. In its southern part the



breccia is intimately injected by a trappean rock, possibly an essexite porphyry. The exposures indicate an elongate mass, about half a mile long and 500 feet wide, lying *en axe* with the eruptive bodies. The eruptive rocks of the small areas farther south are bordered by, and alternate with, brecciated country rock. All the breccias may form a single band, the most northerly mass being not so much injected by igneous rock because of greater distance from the eruptive center.

FIG. 4.



FIG. 4. Area of breccia, two miles northwest of Cuttingsville. Standard orientation. Scale, 1:21,000. Area shown is nearly continuous with that of figure 1. B, breccia. L, limestone. Other rocks not distinguished.

*Dikes.*—Associated with the plutonic rocks are numerous dikes, both aschistic and diaschistic. They comprise, in the inferred order of intrusion, essexite porphyry, nephelite syenite, syenite porphyry, aplite tinguaitite, and camptonite.

As a whole the dikes have not been thoroughly diagnosed. Two, a syenite-porphry dike and a tinguaitite dike, mapped respectively at *T* and *D*, fig. 1, have been chemically studied. Classification of the other dikes is tentative. Some mapped as tinguaitite may, upon further study, prove to be fine-textured phases of syenite porphyry, or possibly bostonite. Others mapped as

camptonite may prove to be fine-textured essexite porphyries.

The dikes range in thickness from a fraction of an inch to 25 feet, with an average of about one foot. The dikes are most numerous in or near eruptive areas. They rarely occur more than half a mile distant. In the eruptive areas they are not confined to any particular kind of plutonic rock, though they seem to be more numerous near contacts of the syenites with essexite.

#### DATE OF ERUPTIVITY.

There is little direct evidence bearing upon the exact geological age of the eruptives. They are clearly of later date than the gneisses and limestone of supposed Algonkian age. Their freedom from marked crushing and shearing suggests that the intrusions did not consolidate until after the strong deformation of the country rocks had been accomplished. Assuming that the last of these could not have been earlier than late Carboniferous times, when the whole Appalachian province was greatly disturbed, it may be inferred that the Cuttingsville eruptives do not antedate the close of the Carboniferous period. Similar intrusions, at Ascutney Mountain, not more than 25 miles distant, are regarded as probably of post-Carboniferous and pre-Cretaceous age.<sup>1</sup>

#### PETROGRAPHY.

##### COUNTRY ROCKS.

*Gneisses.*—The gneisses are of two kinds, a basic hornblende-pyroxene gneiss and a mica gneiss which is more or less granitic. The former is the more abundant in the immediate neighborhood of the eruptives, and more study has been devoted to it on that account. It is typically a heavy, rather dense, fine- to medium-grained, black rock, weathering a streaked or speckled brownish gray. The thin section shows about equal amounts of olive-brown to green hornblende and pale greenish pyroxene. In addition there is subordinate brown biotite and plagioclase with some orthoclase and doubtful quartz. Magnetite and apatite are accessory. The rock is

<sup>1</sup> R. A. Daly, U. S. Geol. Surv., Bull. 209, p. 21, 1903.

inferred to be a metamorphosed eruptive of gabbroid, diabasic, or basaltic character.

*Limestone.*—The limestone (L, figs. 1 and 4) varies considerably in texture, mineral content, and degree of metamorphism. It is quite subordinate to the gneisses as a member of the country rock series. It crops out at four localities about the main eruptive body and also about one-half mile west of the area of breccia shown in fig. 4.

The limestone on the southwest slope of Granite Hill and on Mill River varies in color from bluish gray through cream to white. It is fine-grained although the sparkle of the calcite cleavage is distinctly visible. It effervesces freely with dilute hydrochloric acid. Under a hand lens grains of quartz and particles which are probably graphite are noticeable.

On the southwest slope of Copperas Hill (fig. 1) one or more bands of crystalline limestone follow the easterly to northeasterly strike and high dips of the enclosing gneisses. One of the bands has an exposed width of 20 feet. In working the pyrrhotite bodies which replace the limestone along the belt of tinguaitite dikes on this slope of Copperas Hill (fig. 1) cuts have been made in masses of limestone 5 to 15 feet thick associated with hornblende gneiss. This limestone is light bluish gray to white in color, fairly coarse-grained, and distinctly metamorphic. The metamorphism is presumably due to regional rather than igneous contact action. Hand specimens show, besides calcite, generally considerable muscovite or sericite, and more locally, abundant flakes of graphite. Some bands carry much tremolite or wollastonite developed in short prisms and fibers along the planes of schistosity. All samples effervesce freely with dilute hydrochloric acid.

One half-mile southeast of the Granite Hill eruptive a bed of coarsely crystalline tremolitic limestone about 15 feet thick is associated with quartzite and hornblende and mica gneisses, and is cut by a dike of camptonite or essexite-porphyr.

The limestone indicated in fig. 4 varies from light gray and medium-grained, with occasional graphite flakes, to cream white and decidedly coarse-grained, with quartz veins and considerable muscovite. There is a notable amount of limestone altogether, although it soon passes into sericitic schist.

*Quartzite.*—Micaceous quartzite forms a few thin beds or lenses in gneiss and limestone. Granular quartzite is relatively abundant as fragments in the breccia, and as xenoliths in the essexite of the northern eruptive area.

*Schists.*—Sericitic, chloritic, and tremolitic schists occur only as thin bands between much thicker beds of quartzose gneiss, hornblende gneiss, and crystalline limestone.

#### STOCK ROCKS.

The rocks of the stocks will be described in the order from oldest to youngest, which is also the order from basic to acid (1, figs. 1 and 2).—Fresh essexite is exposed in cuts on both sides of the crest of the central part of Granite Hill and along the path to the quarry, near the top of the hill. It varies from a nearly black, fairly uniform, medium- or coarse-grained gabbroid rock, to a gray, more or less porphyritic phase.

The *type phase* was taken for study from an open cut or pit (P, fig. 1) on the southwest side of the crest of the middle part of Granite Hill, less than 1,000 feet south of the hornblende-biotite syenite quarry (Q 2, fig. 1). The same phase has been freshly cut on the other side of the crest along the path near the quarry, and rock much like it is exposed by Mill River at the east foot of the south knob. It is dark-colored, sometimes almost black, and usually coarse-grained. Barkevikitic hornblende, showing luster-mottling, is generally prominent in the hand specimen.

Thin sections show coarse-grain and hypidiomorphic-granular texture. About 60 per cent of the rock is feldspar, mostly plagioclase, ranging from  $Ab_7 An_3$  to  $Ab_3 An_7$ . From 5 to 10 per cent of the rock is orthoclase, which appears in small- and medium-sized grains and irregular areas sometimes intergrown with, enclosing, or embaying the plagioclase. The other essentials are hornblende, pyroxene, and biotite, in nearly equal amounts.

Of the dark-colored minerals barkevikitic hornblende is most notable. Its optical properties are sensibly identical with those of the hornblende in the hornblende-biotite syenite, and will be stated at length in the description of that rock. The pleochroism of the hornblende of the essexite shows, however, more reddish or chestnut tints

in the darker colors. Poikilitic inclusions of pyroxene and, in less amount, biotite and olivine give rise to the luster-mottling visible in the hand specimen.

Pyroxene is represented by augite of two colors, pale green and pale brown. The colors appear separately or sometimes together in the same grain. A pale brown center may be bordered by pale green, with a zone of inclusions of magnetite and hornblende between the two colors. The differently colored parts are optically continuous and extinguish together. When occurring separately, a maximum extinction angle of 44° for the green and 37° for the brown was observed. The augite and hornblende are remarkably intergrown, the latter surrounding augite which in turn incloses grains of hornblende.

Biotite is in thick tables, besides forming striking intergrowths with hornblende. Its pleochroism ranges from pale yellow to chestnut and deep brown or nearly black.

Olivine in occasional large grains, partly serpentinized, enters the list of accessory minerals, which also includes magnetite, titanite, apatite, pyrite, and probably pyrrhotite.

One of the sections includes an irregular area of what is possibly cancrinite derived from original nephelite. This is the only suggestion of the presence of nephelite, indicating that it is seldom, if at all, a constituent.

Texture and mineralogical composition place the rock among the alkali-gabbros under the head of essexite. Chemical analysis supports this conclusion.

	I	II	III	IV	V	VI	VII
SiO <sub>2</sub>	46.47	46.99	48.85	44.00	49.96	47.90	48.64
TiO <sub>2</sub>	2.86	2.92	2.47	1.90	2.40	1.91	1.86
Al <sub>2</sub> O <sub>3</sub>	16.86	17.94	19.38	27.73	18.83	16.55	17.96
Fe <sub>2</sub> O <sub>3</sub>	3.21	2.56	4.29	2.36	2.52	5.67	4.31
FeO	7.72	7.56	4.94	3.90	6.64	7.50	5.58
MnO	0.23	Trace	0.19	0.08	0.20	0.60	0.19
MgO	5.16	3.22	2.00	2.30	3.52	4.44	4.00
CaO	9.45	7.85	7.98	13.94	7.42	9.35	8.89
Na <sub>2</sub> O	4.20	6.35	5.44	2.36	5.26	3.23	4.30
K <sub>2</sub> O	1.35	2.62	1.91	0.45	2.58	2.08	2.28
H <sub>2</sub> O+	0.45	0.65	0.68	0.80	0.07	0.20	1.34
H <sub>2</sub> O—	0.04				0.53		
P <sub>2</sub> O <sub>5</sub>	1.15	0.94	1.23	0.20	0.25	0.32	0.65
CO <sub>2</sub>	Trace						
ZrO <sub>2</sub>	None						
SO <sub>3</sub>	None		not det.				
Cl	0.06						

	I	II	III	IV	V	VI	VII
F	0.10						
Cr <sub>2</sub> O <sub>3</sub>	None						
BaO	Trace						
SrO	0.04						
FeS <sub>2</sub>	0.21						
Fe <sub>2</sub> S <sub>3</sub>	0.08						
Li <sub>2</sub> O	None						
Sum	99.64	99.60	99.36	100.01	100.18	99.75	100.00
Specific gravity		2.919					

I = Essexite, type phase (andose), Cuttingsville, Vt., H. E. Merwin, analyst.

II = Essexite (essexose), Salem Neck, Essex Co., Mass.

III = Normal essexite (andose), Mt. Johnson, Quebec.

IV = Essexite (hesose), Brome Mt., Quebec.

V = Essexite (salemore), St. Hilaire Mt., Quebec.

VI = Essexite (camptonose), Tofteholmen, Norway.

VII = Essexite (average of 20 analyses, R. A. Daly, in "Igneous Rocks and Their Origin," 1914, p. 30).

The rock is an andose, allied to camptonose, with the following norm:

Orthoclase	7.78	Olivine	9.93
Albite	27.25	Magnetite	4.64
Anorthite	23.35	Ilmenite	5.47
Nephelite	4.54	Apatite	2.48
Diopside	13.07	Water, etc	.98
			99.49

Comparison of the Cuttingsville essexite shows its close similarity to the type from Essex County, Massachusetts, and to the varieties of essexite from the Montegregian Hills, Quebec. The likeness in chemical composition to the essexite from Tofteholmen, Norway, is but one example of a striking chemical similarity between the Cuttingsville rocks and some of those of southern Norway.<sup>2</sup> The table facilitates comparison with the average essexite as computed by Daly from twenty analyses.

One of the variations from the type phase apparently results from the local impregnation and partial assimilation of essexite by pulaskite. Hand specimens usually show dikelets and streamers of this syenite, traversing essexite. The color resulting from the combination of pulaskite with essexite is lighter and the grain less uniform than in simple essexite. Idiomorphic hornblende and more or less definitely bounded feldspars are sometimes noticeable. A characteristic feature is an abundance of titanite.

<sup>2</sup> Brögger, W. C., "Die Eruptivgesteine des Kristianiagebietes": Vidensk. Skrifter I, No. 4, 1894; No. 7, 1895; No. 6, 1897.

Sections show a greater proportion of feldspars than simple essexite. About 70 per cent is feldspar, of which approximately one-third is orthoclase and two-thirds plagioclase, of a composition intermediate between basic oligoclase and andesine. There is some microperthite, and possibly altered nephelite and cancrinite. The remaining chief constituents are: hornblende, sometimes surrounded by, and intergrown with, olive-brown biotite; and augite poikilitically inclosed in hornblende.

The rock may be regarded as a more acid essexite, which with the hornblende-biotite syenite itself occurs in the series between essexite and pulaskite.

On the north knob of Granite Hill an extremely *coarse-grained phase* of essexite is developed. It is largely composed of prisms of hornblende, some upwards of 2 inches in length. A little biotite is visible in the hand specimen. The amount of feldspar varies. Towards pulaskite contacts the proportion of feldspar increases, and the rock grades into a very coarse hornblende-biotite syenite. This gradation is quite clearly shown near the crest of Granite Hill, from the north knob to the molybdenite prospect (M, fig. 1).

*Porphyritic phases* form important parts of the more extensive essexite areas. They are also exposed as smaller masses which appear to be apophyses and detached portions of the main bodies. The groundmass varies from coarse to almost aphanitic. The phenocrysts are usually hornblende, commonly an inch or two in length, frequently much less, and sometimes very much greater. In one case the measured dimensions of a hornblende phenocryst were 15 by 8 inches. Biotite appears, with or without hornblende, usually in the groundmass.

The porphyritic phases quite generally carry large and small inclusions, apparently of the coarse phases of essexite and hornblende-biotite syenite. These inclusions are not always so sharply defined as accompanying inclusions of the country rocks, but they seem to demonstrate an intrusion of porphyritic essexite into an earlier intrusion of more uniformly coarse-grained essexite and possibly syenite. The blurred outlines of the inclusions suggest that the interval between the earlier and the later intrusion was comparatively short.

*Hornblende-biotite Syenite* (2, figs. 1 and 2). Hornblende-biotite syenite is of smaller total area than most of the other plutonic types. Its principal exposures are near the crest of the central part of Granite Hill, where a small quarry was opened about 25 years ago.

The *type* phase, taken from the quarry (Q 2, fig. 1), is moderately coarse-grained, almost white in ground color, and abundantly specked with black amphibole and mica. Occasionally a slightly darker-colored, finer-grained, indistinct patch or schlier, a few centimeters in dimensions, appears in the hand specimen.

In thin section the hornblende-biotite syenite shows a hypidiomorphic, medium to coarse granular texture. Eighty per cent or more is feldspar, of which the bulk is plagioclase, in composition intermediate between basic oligoclase and andesine. About one-third of the feldspar is orthoclase, some of which is intergrown with plagioclase.

After the feldspars, amphibole is most notable. It appears in well-defined prisms, commonly twinned. The pleochroism is distinctive, green to greenish brown in the direction of the *c* axis; dark greenish brown to almost black parallel to the *b* axis; and pale yellow parallel to the *a* axis. The absorption scheme is  $b > (\text{nearly } =) c > a$ . The extinction angle on (110) cleavage pieces is  $12^\circ$ .  $2E = 70^\circ - 80^\circ$  or less. A calculation of the angle of extinction on (010) gave  $8^\circ$ . The specific gravity, by pycnometer, at  $20^\circ\text{C}$ ., is 3.518. These characteristics taken together indicate a soda-amphibole near barkevikite.

In order to check the optical determination of the amphibole, a chemical analysis of the amphibole was made by Professor C. D. Test of the Department of Chemistry of the Colorado School of Mines. Good material was obtained by the usual modes of separation from the rock powder. The analysis resulted in the values given in Column I of the following table, in which those for related amphiboles are also entered:

	I	II	III	IV	V	VI
SiO <sub>2</sub>	38.04	38.633	40.10	42.46	42.27	38.41
TiO <sub>2</sub>	1.06	5.035	4.35	(In SiO <sub>2</sub> )	1.01	1.26
Al <sub>2</sub> O <sub>3</sub>	13.50	11.974	10.88	11.45	6.31	16.39
Fe <sub>2</sub> O <sub>3</sub>	6.21	3.903	7.81	6.18	6.62	3.75
FeO	15.85	11.523	9.66	19.93	21.72	21.75
MnO	1.21	0.729	0.15	0.75	1.13	0.15



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	I	II	III	IV	V	VI
MgO	7.26	10.200	9.74	1.11	3.62	2.54
CaO	12.42	12.807	12.60	10.24	9.68	10.52
Na <sub>2</sub> O	3.21	3.139	3.18	6.08	3.14	2.95
K <sub>2</sub> O	1.68	1.489	1.60	1.44	2.65	1.95
H <sub>2</sub> O (by ignition)	0.48	0.330	0.00		0.48	0.24
F			0.31			
P <sub>2</sub> O <sub>5</sub>			0.63			
Sum	100.92	99.762	101.01	99.64	98.63	99.96

I = Hornblende from Cuttingsville hornblende-biotite syenite, C. D. Test, analyst.

II = Hornblende from Mt. Johnson, Quebec, essexite, F. D. Adams, Jour. Geology, vol. 11, p. 260, 1903.

III = Hornblende from Heum, Norway, heumite, J. P. Iddings, "Rock Minerals," 1906, p. 338.

IV = Barkevikite from Barkevik, Norway, nephelite syenite, *ibid.*, p. 339.

V = Barkevikite from Barkevik, Norway, syenite, *ibid.*, p. 339.

VI = Barkevikitic hornblende from Square Butte, Mont., sodalite syenite, L. V. Pirsson, U. S. Geol. Surv., Bull. 237, p. 67, 1905.

Chemically, as well as optically, this Cuttingsville amphibole is seen to be a barkevikitic hornblende.

Chief among the remaining minerals, in thin sections of the type phase of the Cuttingsville hornblende-biotite syenite, is brown biotite which is present in amount nearly equal to hornblende. There are occasional triangular and irregular areas, filled with alteration products probably derived from nephelite, which is not otherwise represented in the type phase of the syenite, though visible to the naked eye in coarser-grained segregations to be described hereafter.

Apatite, titanite, magnetite, zircon, and pyrite are accessory.

The abundant plagioclase allies it to monzonite, but the ratio of dark silicates to feldspar warrants the designation of the rock as a hornblende-biotite syenite. Its analysis is given in the succeeding table (column I), which introduces relevant analyses from similar rock bodies and also the average analysis of laurvikite:

	I	II	III	IV	V	VI	VII
SiO <sub>2</sub>	57.44	57.44	59.96	59.01	56.85	57.12	57.45
TiO <sub>2</sub>	0.69	1.97	0.66	0.81			
Al <sub>2</sub> O <sub>3</sub>	21.60	19.43	19.12	18.18	21.56	21.69	21.11
Fe <sub>2</sub> O <sub>3</sub>	0.20	1.69	1.85	1.63	3.44	1.63	2.89
FeO	2.62	2.70	1.73	3.65	1.14	3.65	2.39
MnO	0.14	0.25	0.49	0.03			
MgO	1.09	1.16	0.65	1.05	0.85	1.55	1.06
CaO	2.90	2.66	2.24	2.40	5.26	4.03	4.10
Na <sub>2</sub> O	7.36	6.48	6.98	7.03	6.07	5.93	5.89
K <sub>2</sub> O	4.12	4.28	4.91	5.34	3.66	3.48	3.87

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	I	II	III	IV	V	VI	VII
H <sub>2</sub> O+	0.58	1.03	1.10	0.50	0.52	0.58	0.70
H <sub>2</sub> O—	0.03			0.15			
P <sub>2</sub> O <sub>5</sub>	0.38	0.60	0.14	Trace			0.54
CO <sub>2</sub>	0.39						
ZrO <sub>2</sub>	0.02						
SO <sub>3</sub>	None	not det.	0.08				
Cl	0.07	Trace	0.14	0.12			
F	0.05						
Cr <sub>2</sub> O <sub>3</sub>	None						
BaO	0.26	not det.	0.12	0.08			
SrO	0.04						
FeS <sub>2</sub>	0.15						
Fe <sub>7</sub> S <sub>8</sub>	0.14						
Li <sub>2</sub> O	None						
Sum	100.27	99.69	100.17	99.98	99.35	99.66	100.00

I = Hornblende-biotite syenite, type phase (laurvikose), Cuttingsville, Vt., H. E. Merwin, analyst.

II = Pulaskite (laurvikose), Mt. Johnson, Quebec.

III = Pulaskite (laurvikose), Shefford Mt., Quebec.

IV = Umptekite (umptekose), Red Hill, Moltonboro, N. H.

V = Laurvikite (laurvikose), Notterö, Norway.

VI = Laurvikite (laurvikose), Frederiksvärn, Norway.

VII = Laurvikite (average of 3 analyses, R. A. Daly).

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- II, III Quoted from F. D. Adams, *Jour. Geology*, vol. 11, p. 271, 1903.  
 IV, V, VI “ “ Washington, H. S., “*Chemical Analyses of Igneous Rocks*”: U. S. Geol. Surv., Prof. Paper 14, pp. 253, 203, 1903.  
 VII “ “ Daly, R. A., “*Igneous Rocks and Their Origin*,” p. 23.

The norm (laurvikose) was calculated to be:

Orthoclase .....	24.46	Ilmenite .....	1.36
Albite .....	44.01	Magnetite .....	0.23
Nephelite .....	9.94	Corundum .....	0.31
Anorthite .....	12.81	Apatite .....	0.93
Olivine .....	4.75	Water, etc. ....	1.47

100.27

A coarse-grained phase of this syenite is best shown in a narrow belt between essexite and pulaskite, extending for a part of the distance between the summit of the north knob and the molybdenite prospect (M, fig. 1) near the crest of Granite Hill. Hornblende in prisms, occasionally upwards of 2 inches in length, is the most prominent constituent. Flakes of biotite, sometimes half an inch across, are sparsely scattered through the rock. Titanite and pyrite are visible without a lense. As the

proportion of feldspar, much of which is plagioclase, diminishes, the rock becomes dark-colored and gabbroid, and grades into coarse-grained essexite.

A strongly *biotitic* phase of medium grain, and with a somewhat greater proportion of dark silicates than in the type phase, is exposed along the railroad in the first small eruptive area north of the Granite Hill area (fig. 1).

In the hornblende-biotite syenite of the quarry on Granite Hill (Q 2, fig. 1), *foyaitic schliers* are not uncommon. Some appear to be segregations. Others are more sharply defined, elongate, and dike-like. They are usually small, but may attain a width of several inches and a length of 2 or 3 feet. The larger are coarse-grained, with gray nephelite, sometimes an inch or more in diameter, white or pearl-gray feldspars, and an occasional biotite flake or hornblende prism. Thin sections of these schliers show microperthite, some plagioclase, nephelite, colorless sodalite, hornblende, titanite, and magnetite. In the finer-grained rock there also appear olive-brown biotite, pyrite, and possibly cancrinite and zircon as subordinate accessories.

*Pulaskite* (3, fig. 1).—This rock is usually coarse-grained and much weathered. The *type phase* is essentially a coarse-grained aggregate of hypidiomorphic, gray-white feldspars, which weather cream-white, yellowish, or brownish. Biotite is generally present, becoming abundant in some varieties.

A thin section of comparatively fresh rock from the exposure along Mill River at the east foot of the south knob of Granite Hill shows the rock to be composed chiefly of microperthitic feldspar with a little orthoclase. One area probably represents cancrinite derived from original nephelite. A little nephelite is almost certainly present in some other hand specimens. Titanite, magnetite, pyrrhotite, apatite, and zircon are accessory; the sulphides and titanite are sometimes macroscopically visible.

Some of the weathered rock from the upper southward slope of the north knob of Granite Hill appears to carry a little augite, as well as some biotite. If so, it approaches augite syenite in composition, but is decidedly more feldspathic and coarser-grained than the typical augite syenite or nordmarkite (5, fig. 1) of the northward slope of the north knob. It has been a difficult matter to

draw a line between the two in mapping their respective areas. It is possible that there is no such line, and that the pulaskite and nordmarkite are really one body, more augitic and nordmarkitic on the north and more feldspathic and pulaskitic on the south.

*Coarse-grained phases* of pulaskite are very strikingly developed near the crest of the middle part of Granite Hill. It occurs as ill-defined apparently northward-trending streaks or schliers, about a foot wide, in syenite not quite so coarse. The rock is practically all feldspar, in chunks or rough crystals, some upwards of 2 inches in length.

A noteworthy point about some of the coarse-grained phases of the Cuttingsville eruptives is their proximity to eruptive contacts, suggesting that their coarseness of grain is partly due to the action of gases emanating at contacts.

*Biotitic phases* of the pulaskite develop near contacts with essexite. This is notably the case on the north knob of Granite Hill, and in the exposures along Mill River at the east foot of the south knob.

A peculiar coarse biotitic phase is developed in small amount between essexite and normal pulaskite in the pit (P, fig. 1) south of the quarry. Similar rock, with the same association of essexite and normal pulaskite and in limited amounts, is exposed on the path near the quarry. Penetrating the usual coarse, hypidiomorphic gray-white feldspars are skeleton flakes of biotite up to one inch in diameter. The flakes are quite numerous and lie in various attitudes. Consequently a broken surface of the rock shows a number of roughly radiating black lines, which are the traces of the wide flakes broken across. Besides these, some flakes, luster-mottled as a result of their skeletal structure, appear full face.

Fine-grained and *porphyritic phases* of pulaskite appear frequently along contacts.

The pulaskite of the two small eruptive areas (fig. 1) north of the Granite Hill area is mostly medium grained.

*Sodalite-nephelite Syenite* (4, fig. 1).—The sodalite-nephelite syenite at the railroad cut is a holocrystalline, moderately coarse-grained aggregate of light-gray feldspar of tabular habit, rather frequently in Carlsbad twins, with interstitial black pyroxene and brownish

nephelite. Minute grains and small masses of pyrite are disseminated through the rock. Blue sodalite is rarely discernible in the hand specimen.

Thin sections show about 90 per cent feldspar, of which upwards of one-half is microperthite, orthoclase, and microcline. Both the orthoclase and microcline are somewhat microperthitic. Some form of microperthite is thus the chief feldspar. A part is possibly anorthoclase. The plagioclase is near albite in composition. Colorless sodalite forms angular and veinlike areas between and penetrating the feldspars. The chemical analysis indicates its amount as about 3 per cent. The nephelite, with nearly equal abundance, is in various stages of alteration, to cancrinite, zeolites, and muscovite. Pyroxene is next to the feldspars in abundance. It is a pleochroic variety, the color ranging from pale yellowish green through olive-green to green. Extinction angles indicate an ægirite-augite somewhat nearer ægirite than augite. There is some biotite bordering, penetrating, and included in the ægirite-augite.

The order of crystallization is given in the following list, which shows also the nature of the accessories: (1) apatite; (2) magnetite, titanite, and possibly pyrite; (3) biotite; (4) ægirite-augite; (5) plagioclase; (6) sodalite, nephelite, and most of the feldspars.

The chemical analysis (column I of the following table) agrees with the mineralogical composition in referring the rock to the sodalite-nephelite syenites. For convenience the analyses of other types are also entered:

	I	II	III	IV	V	VI
SiO <sub>2</sub>	60.88	56.45	60.20	60.13	58.61	61.86
TiO <sub>2</sub>	0.35	0.29	0.14	1.15	1.10	0.15
Al <sub>2</sub> O <sub>3</sub>	20.75	20.08	20.40	20.03	21.12	19.07
Fe <sub>2</sub> O <sub>3</sub>	0.63	1.31	1.74	2.36	2.62	2.65
FeO	1.13	4.39	1.88	1.33	1.14	1.49
MnO	0.22	0.09	Trace	Trace	Trace	0.01
MgO	0.17	0.63	1.04	0.76	0.79	0.55
CaO	1.08	2.14	2.00	0.87	0.62	1.47
Na <sub>2</sub> O	6.35	5.61	6.30	6.30	7.85	6.45
K <sub>2</sub> O	5.57	7.13	6.07	5.97	5.93	5.75
H <sub>2</sub> O +	0.88	1.51	0.23	1.41	1.01	0.47
H <sub>2</sub> O -	0.03	0.26	0.10	0.16		
P <sub>2</sub> O <sub>5</sub>	Trace	0.13	0.15	0.06	Trace	0.08
CO <sub>2</sub>	0.61		None	None		
ZrO <sub>2</sub>	Trace		Trace	0.05		
SO <sub>3</sub>	None		0.13	0.14		
Cl	0.18	0.43	0.09			

	I	II	III	IV	V	VI
F	0.05					
Cr <sub>2</sub> O <sub>3</sub>	None					
BaO	0.02					
SrO	Trace					
FeS <sub>2</sub>	0.61					
Fe <sub>7</sub> S <sub>3</sub>	0.13					
Li <sub>2</sub> O	None					
Sum	99.64	100.45	100.47	100.72	100.79	100.00

I = Sodalite-nephelite syenite, type phase (nordmarkose), Cuttingsville, Vt., H. E. Merwin, analyst.

II = Sodalite syenite (pulaskose), Square Butte, Mont.

III = Pulaskite (pulaskose), Fourche Mts., Ark.

IV = Foyaite (phlegrose), Fourche Mts., Ark.

V = Aegirite—kataforite foyaite (miaskose), Heum, Norway.

VI = Pulaskite (average of 5 analyses, R. A. Daly).

II, III, IV, V Quoted from Washington, H. S., U. S. Geol. Surv., Prof. Paper 14, pp. 201, 199, 195, 211, 1903.

VI “ “ Daly, R. A., “Igneous Rocks and Their Origin,” p. 22.

The rock is a nordmarkose, near phlegrose, with the following norm:

Orthoclase .....	32.80	Magnetite .....	.93
Albite .....	53.45	Ilmenite .....	.61
Anorthite .....	5.28	Corundum .....	2.35
Hypersthene .....	1.72	Water, etc. ....	2.51
			99.65

A comparison of columns I, III, and VI tends to support the view that the sodalite-nephelite syenite is a phase of the Cuttingsville pulaskite.

*Augite Syenite (Nordmarkite)* (5, fig. 1).—In the middle of the last century, during the construction of the railroad, openings were made in the north end of Granite Hill, and a considerable amount of stone quarried for bridge foundations. This stone is popularly known as green granite from its light olive-green color. The grain is usually medium, but there are fine-grained and decidedly coarse-grained phases. In total areal extent it is probably second only to the pulaskite.

The *type phase* is a medium-grained aggregate largely of hypidiomorphic feldspar. Grains of black augite and occasional small grains of quartz are usually discernible.

The rock on the fresh fracture is bluish gray to gray-green in color. This color changes in a few weeks indoors to olive or brownish green.<sup>3</sup> The change is pre-

<sup>3</sup> This remarkable behavior is paralleled in the case of the nordmarkite of Asectney Mountain. (See R. A. Daly, U. S. Geol. Surv. Bull. 209, p. 51, 1903.)

sumably due to the oxidization of iron sulphide or some other substance disseminated through the feldspar. The rock yields a strong sulphurous odor while being broken. Out-door weathering rusts the rock surface, finally changing the color to pale buff or very light brown.

In thin section the texture is holocrystalline, hypidiorhombic granular. Seventy-five per cent or more is feldspar, of which microperthite is most notable and is accompanied by microcline, probably anorthoclase, orthoclase, and a little albite. Green augite, locally rimmed with green hornblende, is chief of the remaining minerals. With it there is some ægirite-augite whose extinction angle approaches that of ægirite. An occasional large grain of olivine (fayalite?), more or less serpentinized, and a little primary quartz, in distinct grains, are usually present. Magnetite, possibly some ilmenite, zircon, and apatite are accessory. A single, large crystal, possibly allanite, was noted in one section.

The mineralogical composition indicates that the rock is an augite syenite of the nordmarkite group, a conclusion borne out by a comparison of its chemical analysis (column I of the following table) with other nordmarkitic types and with average nordmarkite (column VII).

	I	II	III	IV	V	VI	VII
SiO <sub>2</sub>	67.30	65.43	65.43	60.45	66.13	67.99	64.36
TiO <sub>2</sub>	0.17	0.16	0.50		0.74		0.45
Al <sub>2</sub> O <sub>3</sub>	17.44	16.96	16.11	20.14	17.40	17.54	16.81
Fe <sub>2</sub> O <sub>3</sub>	1.56	1.55	1.15	3.80	2.19	1.17	1.08
FeO	1.76	1.53	2.85	not det.	not det.	0.82	2.71
MnO	0.16	0.40	0.23		0.13		0.15
MgO	0.14	0.22	0.40	1.27	0.04	0.13	0.72
CaO	1.00	1.36	1.49	1.68	0.81	1.44	1.55
Na <sub>2</sub> O	7.08	5.95	5.00	7.23	5.28	4.92	5.76
K <sub>2</sub> O	4.78	5.36	5.97	5.12	5.60	5.78	5.62
H <sub>2</sub> O +	0.05	0.82	0.39	0.71	1.22	0.05	0.70
H <sub>2</sub> O -	0.05		0.19				
P <sub>2</sub> O <sub>5</sub>	0.04	0.02	0.13				0.09
CO <sub>2</sub>		None	Trace?				
ZrO <sub>2</sub>	0.08		0.11				
SO <sub>3</sub>	None	0.06	None				
Cl		0.04	0.05				
F			0.08				
BaO		None	0.03				
SrO			Trace				
FeS <sub>2</sub>			0.07				
Li <sub>2</sub> O			Strong trace				
Sum	101.61	99.86	100.18	100.40	99.54	99.84	100.00
Specific gravity			2.659				

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- I = Augite syenite, nordmarkite, type phase (nordmarkose), Cuttingsville, Vt., C. D. Test, analyst.  
 II = Nordmarkite (nordmarkose), Shefford Mountain, Quebec.  
 III = Hornblende-biotite nordmarkite (phlegrose), Ascutney Mountain, Vt.  
 IV = Nordmarkite (laurvikose), Annerød, Norway.  
 V = Akerite (phlegrose), between Thinghoid and Fjelcbua, Norway.  
 VI = Quartz nordmarkite (toscanose), Halasag, Ditro, Siebenbürgen, Hungary.  
 VII = Nordmarkite (average of 7 analyses, R. A. Daly).

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II Quoted from Dresser, J. A., Amer. Geologist, vol. 28, p. 209, 1901.  
 III “ “ Daly, R. A., U. S. Geol. Surv., Bull. 209, p. 59, 1903.  
 IV, V, VI “ “ Washington, H. S., U. S. Geol. Surv., Prof. Paper 14, pp. 171, 195, 203.  
 VII “ “ Daly, R. A., “Igneous Rocks and Their Origin”, p. 22.

The rock is nordmarkose, with the following norm:

Quartz .....	5.40	Hypersthene .....	.79
Orthoclase .....	28.36	Magnetite .....	2.32
Albite .....	59.74	Ilmenite .....	.30
Anorthite .....	1.67	Water, etc. ....	.22
Diopside .....	2.85		
			101.65

Hand specimens of the Cuttingsville augite syenite and the Ascutney Mountain nordmarkite very closely resemble each other and the Shefford Mountain nordmarkite. The resemblance is so close that hand specimens of the three are practically indistinguishable. Although the Cuttingsville rock contains the highest per cent of silica, thin sections of the Ascutney rock seem to show the most quartz, and thin sections of the Cuttingsville rock the most augite. The Shefford Mountain rock, judged in this manner, appears to be intermediate between the other two.

The Cuttingsville augite syenite has a *quartz-bearing phase*. It is apparently quite subordinate to the type phase, and occupies no well-defined area. Generally it is developed as a selvage, a few feet in width, along the contact of the augite syenite and the country rocks. It is usually finer-grained than the type phase, but the quartz is always distinctly visible, sometimes forming a considerable part of the rock. With diminution of the proportion of dark silicates, the finer-grained rock becomes quite aplitic. Some of it, of aplitic or paisanitic habit, occurs



in narrow dikelets and streamers cutting the type and coarser phases.

Green hornblende, with accessory quartz, is notable in certain thin sections. Part of the hornblende is probably secondary. The presence of hornblende and quartz allies this phase to the Ascutney Mountain nordmarkite, and less closely to the Shefford Mountain nordmarkite.

Near the summit of the south knob of Granite Hill a *porphyritic* syenite, tentatively mapped as nordmarkite (5, fig. 1), is closely associated with essexite not far from the country-rock contact. Apparently it is a border development of the eruptive body, and of small extent.

In the zone between nordmarkite and essexite, on the upper north slope of the north knob of Granite Hill, the nordmarkite becomes increasingly biotitic. Some of it also carries roughly idiomorphic hornblende and plagioclase, which are sometimes arranged in flow lines. The rock grades from medium-grained to fairly fine, and from granitic to porphyritic. It becomes so much like the adjoining essexite that the actual contact is somewhat indistinct. The contact rock is perhaps best classified as an essexite-nordmarkite hybrid.

#### DIKE ROCKS.

*Essexite porphyry*.—The apophyses from the essexite are generally porphyritic. Petrographically this essexite porphyry has no special peculiarities worthy of detailed statement. Hornblende and biotite, alone or together, are the chief phenocrysts.

*Nephelite syenite*.—As already noted, nephelite syenite forms dike-like bodies in the hornblende-biotite syenite of the quarry (Q 2, fig. 1).

*Syenite porphyry*.—Pulaskite porphyry and nordmarkite porphyry are developed at the borders of both the pulaskite and nordmarkite masses. An account of porphyritic phases of pulaskite and nordmarkite has been given. These phases pass into pulaskite porphyry and nordmarkite porphyry, at contacts and in apophyses, by increase of groundmass.

Some of the pulaskite porphyry is apophysal from the main pulaskite body, but other masses form dikes which seem to be distinctly later intrusions. Two or more of

these later dikes are exposed in the pit (P, in fig. 1) south of the quarry (Q 2, fig. 1). They appear to cut essexite and probably also biotitic pulaskite.

*Zircon-rich pulaskite porphyry.*—At the foot of the eastern slope of the north end of Granite Hill, about 200 feet downstream from a short tunnel (T, fig. 1), a dike of coarse trachytic rock is exposed from the bank of Mill River 40 feet up the steep slope. The dike cuts green, quartz-bearing augite syenite, which is brecciated at the lower contact and receives branch dikelets. The main dike has a thickness of approximately 12 feet, and dips about 50° S. E. About 125 feet upstream an irregular dike of similar rock, with a maximum width of 15 feet, extends 10 feet up the slope. Downstream from the main dike, near a dam, similar rock is again exposed. All three of these exposures may belong to the same dike.

The rock of the main dike shows strong contact chilling. The sections studied are of the coarse-grained, middle phase. These specimens show broad, half-inch tablets of gray feldspar, slender prisms and small grains of black pyroxene, and less frequent, small, hexagonal and irregular flakes of black mica, in a fine to medium-grained mass of feldspar, black pyroxene, and black mica. Feldspar greatly predominates, giving the rock its light gray color.

Thin sections show roughly idiomorphic feldspar and pyroxene in a granular mass, including feldspars, pyroxene, biotite, magnetite, zircon, titanite, apatite, little hornblende, and possibly nephelite (or sodalite), corundum, and fluorite. About 90 per cent of the rock is feldspar, chiefly anorthoclase, with orthoclase, microperthite, and subordinate oligoclase ( $Ab_6An_1$ ). Between and penetrating the feldspar are irregular areas of zeolites or other secondary minerals, which may have been derived from nephelite or sodalite. Augite, occasionally with outer zones of ægirite-augite, or ægirite, is the principal colored mineral.

Mineralogically the rock is a zircon-rich pulaskite porphyry. Its complete chemical analysis was not attempted. Dr. H. E. Merwin, however, tested it for zirconia in order to check the microscopic evidence of abundant zircon. He found sufficient zirconia for at least 1 per cent of zircon. He also determined the percentages of soda and potash, as, respectively, 7.32 and 4.81.

*Aplite.*—Narrow aplitic dikes of paisanitic quality cut the coarse and medium phases of the augite syenite. They also penetrate, for short distances, the country gneisses to the west.

*Tinguaite.*—The locations of tinguaite dikes are shown in fig. 1. At the foot of the eastern slope of the south knob of Granite Hill, along the bank of Mill River, a complex of syenitic and essexitic phases is cut by numerous narrow dikes of syenite-porphry, tinguaite, and camptonite. A tinguaite dike (D, fig. 1) towards the upstream end of the exposure carries remarkably fresh rock, selected for chemical analysis. The dike, about one foot wide, dips 80° N. N. W.

The hand specimen has a medium-gray color, a dense, fine-grained texture, and a superficial resemblance to blue quartzite, though of duller luster. A few, small phenocrystic laths of feldspar are discernible. In the groundmass, nephelite is sufficiently abundant to yield much gelatinous silica when the powdered rock is treated with hydrochloric acid.

The thin section shows well-formed phenocrysts of anorthoclase and micropertthite in a fine, granular groundmass. The groundmass carries some fairly distinct laths of feldspar and prisms of pyroxene. The remaining feldspar, pyroxene, and most of the other minerals are allotriomorphic. Orthoclase and nephelite appear in roughly equal amounts, with plagioclase (albite) apparently somewhat less than either. Reckoning groundmass and phenocrysts together, 90 per cent or more of the rock is feldspar and nephelite. The nephelite is seen to enclose minute orthoclase crystals. There are occasional grains of cancrinite. A colorless mineral in irregular and veinlike patches is probably sodalite; a little chlorine reported in the analysis may thus be accounted for. Pyroxene is represented by two varieties. One is pleochroic, in colors from yellowish or brownish to green. Extinction angles run up to 20°. These characters, together with the proper elongation, indicate an ægirite-augite. The other, less abundant, is a very pale or colorless variety, apparently diopside. The accessories are magnetite, titanite, zircon and rare apatite.

The chemical analysis of this tinguaite (miaskose) and its parallels are stated in the accompanying table:

	I	II	III	IV	V	VI	VII
SiO <sub>2</sub>	57.64	55.68	54.22	55.06	55.46	56.58	55.02
TiO <sub>2</sub>	0.15	0.60	0.38		0.20		0.36
Al <sub>2</sub> O <sub>3</sub>	23.31	20.39	20.20	23.29	24.49	19.89	20.42
Fe <sub>2</sub> O <sub>3</sub>	1.22	2.10	2.35	3.29	2.63	3.18	3.06
FeO	0.55	1.95	1.02	not det.	1.06	0.56	1.82
MnO	0.10	0.31	0.19		Trace	0.47	0.22
MgO	0.22	0.80	0.29	Trace	0.05	0.13	0.59
CaO	0.67	1.92	0.70	1.46	0.92	1.10	1.67
Na <sub>2</sub> O	10.48	9.18	9.44	6.76	9.78	10.72	8.63
K <sub>2</sub> O	5.09	5.34	4.85	8.86	5.16	5.43	5.38
H <sub>2</sub> O +	0.24	1.50	5.57	1.08	0.07	1.77	2.77
H <sub>2</sub> O —	0.02		0.42				
P <sub>2</sub> O <sub>5</sub>	Trace	0.06	0.11		Trace		0.06
CO <sub>2</sub>	None		Trace				
ZrO <sub>2</sub>	0.12						
SO <sub>3</sub>	Trace		None				
Cl	0.02		Trace				
F	0.06		Trace				
Cr <sub>2</sub> O <sub>3</sub>	None						
BaO	None		Trace				
SrO	Trace						
FeS <sub>2</sub>	0.08						
Fe <sub>7</sub> S <sub>8</sub>	0.05						
Li <sub>2</sub> O	None						
Sum	100.02	99.83	99.74	99.80	99.82	99.83	100.00

I = Tinguaitite, type phase (miaskose), Cuttingsville, Vt., H. E. Merwin, analyst.

II = Tinguaitite (laurdalose), Brome Mt., Quebec.

III = Aegirite tinguaitite (miaskose), Southboro, Mass.

IV = Leucite tinguaitite (beemerose), Serra de Tingua, Brazil.

V = Tinguaitite (miaskose), Gy. Szt. Miklos, Czanod, Siebenbürgen.

VI = Tinguaitite (laurdalose), Hedrum, Norway.

VII = Tinguaitite (average of 15 analyses, R. A. Daly).

II	Quoted from	Dresser, J. A., this Journal, vol. 17, p. 355, 1904.
III	“	Clarke, F. W., U. S. Geol. Surv. Bull. 591, p. 35, 1915.
IV, V, VI	“	Washington, H. S., U. S. Geol. Surv., Prof. Paper 14, pp. 207, 213, 295.
VII	“	Daly, R. A., “Igneous Rocks and Their Origin,” p. 35.

The rock is a miaskose, with the following norm:

Orthoclase	30.02	Diopside	1.08
Albite	36.68	Magnetite	1.86
Anorthite	1.96	Ilmenite	.30
Nephelite	27.55	Water, etc.	.59

100.04

Comparison with the Brome Mountain tinguaitite shows one more proof of general chemical similarity between the Monteregean eruptives and those at Cuttingsville.

The Southboro, Mass., tinguaitite (also miaskose) contains ægirite, while the Cuttingsville rock carries ægirite-augite. The Brazilian tinguaitite is the classic example from Serra de Tingua, the type locality. It differs from the Cuttingsville rock in bearing leucite.

*Camptonite.*—Camptonite dikes, not quite as numerous as the tinguaitite dikes (fig. 1), are associated most closely with essexite and nordmarkite.

Perhaps the most typical camptonite occurs in a dike a foot thick, exposed in the wall of a small, abandoned nordmarkite quarry (Q 5, fig. 1) on the lower north slope of Granite Hill. The rock is black and porphyritic, with a few scattered, flashing crystals of black hornblende, and more numerous, smaller tablets and masses of gray-white feldspar. One of the hornblendes is 2 centimeters long. An occasional grain of olivine also contrasts with the black, fine-grained groundmass. The thin section shows phenocrysts of augite, moderately basic plagioclase, brown hornblende, and serpentinized olivine. The groundmass is an aggregate of brown hornblende, plagioclase, augite, magnetite, and some pyrite.

In the more northerly of the two small eruptive areas north of Granite Hill (fig. 1) three camptonite dikes cut essexite or the country gneisses. One of the dikes, about 25 feet wide, carries many inclusions of gneiss, quartzite, syenite, and probably essexite. They are generally angular in shape and less than 1 cm. in diameter. The camptonite is porphyritic. The phenocrysts are brilliant, black hornblendes. They are usually under 2 cm. in length, though some reach 8 or 10 cm. A single large grain of serpentinized olivine appears in one specimen. The groundmass is dark gray, fine-grained, and dense.

Thin sections show the phenocrysts to be brown hornblende and, in smaller amount, zoned plagioclase, andesine to basic labradorite. There is some kaolinized orthoclase or micropertthite, probably xenolithic. Green pyroxene, more or less altered to actinolite and chlorite, also appears among the phenocrysts. The groundmass is chiefly composed of plagioclase laths, small prisms of hornblende and actinolite, and chlorite. Brown biotite, magnetite, apatite, titanite, ilmenite, and pyrite are accessory.

### MINERAL DEPOSITS.

On Copperas Hill (fig. 5) large bodies of pyrrhotite, once mined as a source of copperas, have replaced limestone cut by tinguaitic dikes which appear to have played a determining part in the ore deposition. In this connection, the presence of pyrrhotite, as an accessory min-

FIG. 5.



FIG. 5. Copperas Hill, looking northeast. Dumps from open cuts in pyrrhotite deposit at right center.

eral in several of the rocks which have been described, is worth noting.

Molybdenite (M, fig. 1) occurs in syenite at its contact with gneiss on the crest of Granite Hill, a quarter of a mile north of the hornblende-syenite quarry. The molybdenite scales are of medium size, often thickly powdered, like the inclosing syenite, with yellow molybdenite. Apparently the deposit is too limited to warrant development.

### GENERAL CONCLUSIONS

*Emplacement of Eruptives.*—Cross-cutting relations of the main eruptive body to the country rocks, the oval surface plan, and high contact dips, indicate that the

main eruptive body is a composite stock. It is certainly not a laccolith and probably not a chonolith. The two small eruptive areas north of the main body seem to be parts of a single, small, satellitic stock or chonolith, if not simply a northward prolongation of the main body, now separated in outcrop by fluvial and glacial deposits.

*Comparison with other areas.*—The general structure is comparable to that of Ascutney Mountain, not more than 25 miles distant, which is also a composite stock. There biotite granite and diorite appear in addition to types which almost duplicate certain of the Cuttingsville rocks.

Though the main Cuttingsville body has a rough concentric structure, its relations to country rock recall those of at least four stocks of the Monteregian Hills, Quebec, namely, St. Hilaire, Rougemont, Johnson (a neck?), and Yamaska Mountains. Of the other Monteregian masses, Shefford, Brome, and St. Bruno (Montarville) are composite and have been described as laccoliths, without compelling evidence.

In all of these hills, essexite is represented. In six (perhaps all) of them the essexite is associated with syenite. This association, combined with close mineralogical and chemical similarity to the Ascutney and Cuttingsville eruptives, renders the comparison doubly impressive.

Red Hill, N. H., a neighboring New England locality, furnishes another example of a small, composite syenite stock, described by Pirsson.<sup>4</sup> The country rock is a granitic gneiss, and the eruptives include, in the order of eruption, nephelite syenite (umpteckite, foyaite), aplite, paisanite, bostonite, syenite porphyry, and camptonite. Chemical similarity of the Red Hill umpteckite and the Cuttingsville, Vt., hornblende-biotite syenite has been noted.

Essex county, Mass., the type locality for essexite, and Southboro, Mass, a tinguaitite locality, are other examples of New England areas containing eruptives chemically related to certain of the Cuttingsville rocks.

The Cuttingsville area thus takes its place as one more of the known number of small alkaline intrusive bodies in the New England-Quebec region. Most of the Monte-

<sup>4</sup>L. V. Pirsson, this Journal, vol. 23, p. 257, 1907.

regian Hills lie west of the limit of Appalachian deformation, their intrusions penetrating practically undisturbed beds. The Cuttingsville and other New England examples are located in disturbed rocks, although themselves not notably affected by deformation.

Reference has already been made to the similarity of the Cuttingsville rocks to certain eruptive rocks of southern Norway.

*Order of Eruption.*—Field observation indicates that eruption of the plutonic types proceeded in the order usual with alkaline intrusions, namely from basic to acidic. Essexite was plainly the earliest intrusion. The syenites followed essexite in a succession not entirely clear. Nordmarkite was apparently the last. Hornblende-biotite syenite, with pulaskite, nephelite syenite (foyaite) and sodalite-nephelite syenite, probably came between essexite and nordmarkite in about the order given.

On the other hand, the syenites possibly constitute a single eruption, rather than a succession of intrusions. If the hornblende-biotite syenite is a simple differentiate, rather than a hybrid, it was the first of the syenites to separate.

The apophysal dikes conform, in a general way, to the same order of basic to acidic intrusions. Essexite porphyries were the earliest, some of them apparently truly apophysal from the essexite body, and others intrusive into it. Aplite was later than the nordmarkite. The syenite porphyries presumably came between essexite porphyry and aplite. Some of the pulaskite-porphyry dikes, however, cut nordmarkite, and may be even younger than aplite.

With the "complementary" dikes the order was reversed, the tinguaitite dikes, which are relatively acidic, preceding the relatively basic camptonite dikes. Some of the tinguaitite dikes are probably younger than all the plutonic types and the truly apophysal dikes. Others are possibly only tinguaitic phases of pulaskite porphyry and nordmarkite porphyry. The camptonite dikes may not all be of the same age. Some of them are the latest of all the intrusions.

*Origin of the Magmas.*—The Cuttingsville eruptives are clearly consanguineous; it may be reasonably inferred that all have come from a single parent magma.



No subalkaline rocks have been noted in association with the Cuttingsville eruptives. Yet that fact does not necessarily invalidate the hypothesis that the alkaline rocks are differentiates from modified subalkaline magmas. It might be assumed that an originally subalkaline magma was modified by desilication to produce the alkaline parent magma. The desilication may have resulted from the assimilation of limestone which outcrops in at least four different localities about the main eruptive body. More limestone may have been stopped from overlying beds since removed by erosion. Assimilation of hornblende gneiss, so abundant in the country rock series, may have increased the desilicating effect.

That syntexis of country rock has played a part in magmatic changes is to some extent supported by the frequent development of a quartzose selvage of syenite in contact with quartzose country rock, and by the occurrence of apparently primary calcite in certain of the dike rocks.

A highly important factor in the problem of the origin of the magma is the stock structure of the eruptive body. This structure implies a body of magma very much greater than that corresponding to the rocks directly visible at the present erosion surface. Stocks are generally assumed to be small projections from greater batholithic bodies. In any case, the exposed part of a stock is only a transverse section high up in the magma chamber. This condition renders assumptions regarding the nature of the original magma, before assimilation and gravitative differentiation had set in, highly speculative.

The exposed rocks of the stock have an average composition not far from that of a typical laurvikose. It is not unlikely that, owing to gravitative differentiation, the deeper rocks are more basic and mafic. This of course would increase the basicity of the stock as a whole and necessitate the assumption of a parent magma more basic than laurvikose. The essexite may represent nearly the chemical nature of the parent magma, suggesting, further, that the original, unmodified subalkaline magma was truly basaltic.

This view has much in its favor. It explains the eruption of essexite first as an extravasation of parent magma before very marked differentiation had set in. The succeeding, increasingly feldspathic eruptions mark

stages in the advance of differentiation, possibly interrupted, and again renewed, by further assimilation of country rock.

## LIST OF CHEMICAL ANALYSES.

	I	II	III	IV	V	VI	VII	
SiO <sub>2</sub>	57.44	46.47	60.88	57.64		67.30	38.04	
Al <sub>2</sub> O <sub>3</sub>	21.60	16.86	20.75	23.31		17.44	13.50	
Fe <sub>2</sub> O <sub>3</sub>	.20	3.21	.63	1.22		1.56	6.21	
FeO	2.62	7.72	1.13	.55		1.76	15.85	
MgO	1.09	5.16	.17	.22		0.14	7.26	
CaO	2.90	9.45	1.08	.67		1.00	12.42	
Na <sub>2</sub> O	7.36	4.20	6.35	10.48		7.08	3.21	
K <sub>2</sub> O	4.12	1.35	5.57	5.09	7.32	4.78	1.68	
H <sub>2</sub> O +	.58	.45	.88	.24		0.05	0.48	
H <sub>2</sub> O —	.03	.04	.03	.02		0.05		
CO <sub>2</sub>	.39	Trace	.61	None				
TiO <sub>2</sub>	.69	2.86	.35	.15		0.17	1.06	
ZrO <sub>2</sub>	.02	None	Trace	.12		0.08		
P <sub>2</sub> O <sub>5</sub>	.38	1.15	Trace	Trace		0.04		
SO <sub>3</sub>	None	None	None	Trace		None		
Cl	.07	.06	.18	.02				
F	.05	.10	.05	.06				
Cr <sub>2</sub> O <sub>3</sub>	None	None	None	None				
MnO	.14	.23	.22	.10		0.16	1.21	
BaO	.26	Trace	.02	None				
SrO	.04	.04	Trace	Trace				
FeS <sub>2</sub>	.15	.21	.61	.08				
Fe <sub>3</sub> S <sub>8</sub>	.14	.08	.13	.05				
Li <sub>2</sub> O	None	None	None	None				
Sum	100.27	99.64	99.64	100.02		101.61	100.92	
Specific gravity	—							3.518

- I = Hornblende-biotite syenite (laurvikose), H. E. Merwin, analyst.  
 II = Essexite (andose), H. E. Merwin, analyst.  
 III = Sodalite-nephelite syenite (nordmarkose), H. E. Merwin, analyst.  
 IV = Tinguaitite (miaskose), H. E. Merwin, analyst.  
 V (partial) = Zircon-rich pulaskite porphyry, H. E. Merwin analyst.  
 VI = Augite syenite (nordmarkite, nordmarkose), C. D. Test, analyst.  
 VII = Barkevikitic hornblende from hornblende-biotite syenite of analysis I, C. D. Test, analyst.

ART. XXVI.—*The Formation of Missouri Cherts;*  
by REGINALD S. DEAN.

A recent paper by Tarr<sup>1</sup> on the cherts of Missouri has made it seem that the views on this subject which have been developed during the last few years at the Missouri School of Mines might be profitably presented. A preliminary report was made in Bulletin No. 2, Missouri Mining Experiment Station, November, 1916, and although our work is not yet complete certain ideas have been developed which seem to be in advance of those previously presented.

The general occurrence and form of the chert nodules have been well described by Tarr. There are however a number of characteristic occurrences and forms which have a definite bearing on the origin which have not been sufficiently emphasized. Chert nodules occurring in a limestone formation which has small shale layers will nearly always have a greater number of nodules in the shale than in the surrounding limestone and there is usually a segregation of the chert along the bedding planes. In these cases the beds around the nodule are bowed out showing that the nodule has grown since the beds were consolidated. In the case of the Jefferson City formation the amount of the bowing of the beds from this cause is often sufficiently great to induce small faults of six inches to one foot in displacement. Although the general form of the nodules is that of a smooth ellipsoid a large number of the smaller nodules have protrusions which indicate that during formation the feeding of the nodules was not equal from all sides. The cherts are in general cryptocrystalline and compact but some show openings at the center which are filled with a tripili.

A fundamental question is the relative age of the chert and the surrounding rock. The bowing of the beds previously referred to seems to be irrefutable evidence in favor of the epigenetic origin of the chert since the beds could not have been distorted by the growing chert had they not been formed at the time; further evidence is found in the uneven growth of the chert mentioned. Tarr argues that since chert nodules are found in limestone at some distance from openings of any sort that the chert

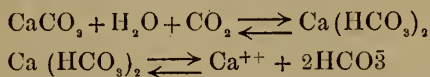
<sup>1</sup> This Journal, 44, 409, 1917.

must have been laid down with the rock and the argument seems well founded; the conclusion is however not without an alternative as will be discussed later. There are also many difficulties which confront a sea-bottom deposition. It is rather hard to conceive of so dilute a solution of silica being precipitated in such large masses and remaining intact sufficiently long to be transformed into chert (if indeed it ever would be). The experiments given by Tarr to show the precipitation of dilute silica hydrosol by the salts of the sea would have been more convincing if made with a pure dialized silica hydrosol which differs markedly in properties from the impure hydrosols used by Tarr and which more nearly approaches the natural waters. If, however, the silica is precipitated by the salts of the sea these salts or at least their cations should be the principal materials to be adsorbed by silica and would hence form the principal impurity in the chert. Since sodium chloride is the salt present in largest amount in the sea water we should expect to find a predominance of sodium in the chert; as a matter of fact the analyses show very little sodium and a decided predominance of calcium and magnesium carbonates.

The silica required for the epigenetic origin of the cherts may have been from different sources in different localities but its immediate source is unquestionably the ground water. In the rocks of Mississippian and Cambro-Ordovician age the silica was probably derived from the overlying carboniferous shales by the decomposition of silicates by carbon dioxide and water. The ground waters at present circulating in the Cambro-Ordovician limestones contain a notable quantity of silica as is evidenced by the replacement of certain limestone fragments in the top member of the Roubidoux Sandstone when this member is exposed to the ground waters, as for example in stream beds. Accordingly the formation of chert is probably going on at the present time.

The ground waters containing the silica hydrosol and carbon dioxide do not deposit the silica since carbonic acid is a weak electrolyte, *i. e.*, undergoes slight dissociation in water. But when water containing carbon dioxide comes in contact with carbonate rocks ordinarily limestone and

dolomite, an acid carbonate is formed which like all salts is more or less readily dissociated as shown:



The positive calcium ions so formed are very efficacious in precipitating colloidal silica, even more so than the small amount of hydrogen ions formed from the dissociation of carbonic acid, since the precipitating power increases with the valence. A colloidal silica solution prepared from water-glass and hydrochloric acid was purified by dialysis until free from chlorides. To test the effect of calcium carbonate on silica hydrosols and determine if the reaction was due to the presence of carbon dioxide, two samples of colloidal silica solution were taken, one was freed from carbon dioxide and the other saturated with it. To both solutions was added ground calcite with the result that the solution free from carbon dioxide remained stable for over a year while the one containing carbon dioxide had precipitated within an hour. This shows conclusively that silica hydrosols will be precipitated by calcium carbonate in the presence of carbon dioxide while in the absence of carbon dioxide the calcite acts as a remarkable stabilizer, since the original silica sol precipitated within a few weeks. Several ordinary dolomites and calcareous shales were tried in the same way both in powdered form and in coarse fragments, all of which produced the same results as the pure calcium carbonate. Doubtless if the solution were made very dilute and a long period of time allowed small pieces of limestone could be silicified as the silica is precipitated where the calcium carbonate goes into solution. This is probably the explanation of Church's experiment in which a coral was silicified. We have then an adequate explanation of the replacement of limestone as well as the precipitation of silica. It is of course true that this process would tend to localize the cherts along bedding planes and channels for the circulation of ground water, and they are found in this connection, but they are also found in the shale layers and in the solid limestone away from any fissures. Their occurrence in the shale bands is probably due to the fact that these shales are the local source of the silica. The occurrence of the nodules in

the solid rock results from the pores becoming filled with a silica hydrosol containing insufficient carbon dioxide to cause precipitation of the silica on coming in contact with the limestone. Precipitation may then start at a number of centers and nodules be built up around these neuclei. Why precipitation should start at these points cannot be said but neither can we say why crystallization starts at a given number of centers. A number of possible explanations can be thought of, *e. g.*, a small piece of pyrite might furnish enough sulphuric acid to start the precipitation at a given point and it is not uncommon to find particles of sulphides in chert nodules. The formation of chert after the exposure of a fresh face which has been noted by Lee<sup>2</sup> may be a similar phenomena; the rocks being saturated with silica hydrosol, which is actually stabilized by the calcium carbonate if no carbon dioxide is present, form chert nodules by taking up carbon dioxide from the air.

The dehydration of the silica to form chert has been tacitly evaded by all those who have previously considered the chert problem. Pressure has frequently been assigned to this difficult task but without reason or experimental evidence of the efficacy or presence of such pressure. O. Ruff<sup>3</sup> has shown that if colloidal iron oxide be subjected to high pressure (6000 to 10,000 atmospheres) it may be dehydrated to a very considerable extent if not entirely. This dehydration follows from the rule of LeChatelier since the volume of the iron oxide hydrates is less than the volume of the iron oxide and water in the gel. Similarly we would expect colloidal silica to be dehydrated since the volume of chert is less than the volume of the silica and water combined to form a gel. But how are we to obtain these pressures in nature? If we take the case of iron oxide we find that most of the dehydrated forms are results of alteration of sulphides and pseudomorphs of iron oxide after pyrite and marcasite are very common. That these pseudomorphs actually go down to near molecular dimensions can be seen from the preservation of very fine pyrite striae. If then the replacement is molecule by molecule as we have reason to suppose it is, 120 grams of pyrite or marcasite must give 80 grams of iron oxide and the

<sup>2</sup> Geology of the Rolla Quadrangle, Wallace Lee. Mo. Bureau of Geology and Mines.

<sup>3</sup> Berichte, 34, 3420, 1901.

density of the  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  which replaces the pyrite must be given by

$$\frac{120}{5} = \frac{80 + 18x}{d}$$

and hence  $d = 3.33 + \frac{3}{4}x$

if $x = 1$ (gothite)	$d = 4.08$ actual density	4.0 to 4.3
$x = 2$ (xanthosiderite)	$d = 4.83$	“ “ less than 4.0
$x = \frac{1}{2}$ (turgite)	$d = 3.70$	“ “ 4.2 to 4.6

From this it is seen that in order to fulfill the conditions the oxide must be very near gothite in composition. Analyses of pseudomorphs show that such is the case:

- (1) Pseudomorph from Germany, analysis from Rammelsberg  
 $\text{Fe}_2\text{O}_3$  90.02%,  $\text{H}_2\text{O}$  10.19%
- (2) Pseudomorph from Saxony, analysis from Kobell  
 $\text{Fe}_2\text{O}_3$  86.34%,  $\text{H}_2\text{O}$  11.60%
- (3) Pseudomorph from Rolla, Mo., analysis by the Author  
 $\text{Fe}_2\text{O}_3$  90.5%,  $\text{H}_2\text{O}$  9.5%
- (4) Pseudomorph from Missouri  
 $\text{Fe}_2\text{O}_3$  90.1%,  $\text{H}_2\text{O}$  9.9%

In these cases no pressure may have been actually exerted, the latent pressure, so to speak, being sufficient to prevent further hydration of the iron oxide.

In the case of silica replacing limestone no such calculations can be made since the amount of colloidal silica thrown down by a given volume of limestone varies greatly with the conditions. It is safe to say however that the volume of the silica would be very large in comparison to the limestone replaced and hence the replacement would take place under pressure and the silica would be largely dehydrated. That chert nodules have been formed under pressure is evident from the bowing up of the beds previously spoken of.

The formation of tripoli has been assumed to be due to the weathering of the chert and to the leaching out of some constituent of the chert. It seems more probable that it represents the deposition of silica in open spaces and not under pressure and hence in a hydrated form which on drying gives tripoli. This is confirmed by the presence of tripoli in the shrinkage cracks in the center of chert nodules where the pressure has been removed by arch action. Colloidal silica may then be thought of as capable of undergoing two modifications, the one to tripoli and the other to chert.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *A New Volumetric Method for Silver*.—LOUIS SCHNEIDER, of the Research Laboratory of the Eastman Kodak Company, has devised a method for titrating silver nitrate by means of a potassium iodide solution and the use of palladium nitrate as an internal indicator. His results show that the method is a very convenient and accurate one and that the presence of mercury does not interfere with it, as is the case with the well-known thiocyanate method. As soon as the silver is completely precipitated as iodide the reddish-brown color of palladium iodide makes its appearance. A very weak solution of palladium nitrate, containing 0.06% of the metal was employed, and of this dilute solution only about 1 cc in volumes up to 225 cc was found to be required. Larger quantities of the indicator gave a much slower establishment of equilibrium in the end-reaction.

The method was found to be particularly well adapted to the determination of very small quantities of silver. It was found also that the presence of a little gum arabic in the solutions titrated was advantageous in preventing the occlusion of silver nitrate and potassium iodide by the silver iodide precipitate.—*Jour. Amer. Chem. Soc.*, **40**, 583.

H. L. W.

2. *Potassium Iodate Titrations*.—GEORGE S. JAMIESON of the Bureau of Chemistry, U. S. Department of Agriculture, has applied L. W. Andrews' method of titration of strong hydrochloric acid (11-20%) solutions with potassium iodate, using a globule of chloroform as an indicator, to the determination of arsenic in various insecticides and fungicides. For this purpose the method has advantages over the usual iodimetric methods on account of the ease with which the volumetric solution can be prepared, its perfect stability on keeping, and particularly from the fact that the titration is not interfered with by ferric and cupric salts nor by most kinds of organic matter, so that in most cases the determination of arsenious oxide may be made directly by this method after dissolving the substance in hydrochloric acid. In cases where the arsenic was present, partly or wholly, as arsenic acid the process was applied, after distillation with cuprous chloride and strong hydrochloric acid, to the distillate. The results of many analyses showed excellent agreements with an official method.—*Jour. Indust. Eng. Chem.*, **10**, 290.

H. L. W.

3. *The Chemist's Pocket-Manual*, by RICHARD K. MEADE. 12 mo, pp. 530. Easton, Pa., 1918 (The Chemical Publishing Company).—This is the third edition of this useful handbook containing tables, formulas, calculations, information, and physical



and analytical methods for the use of chemists, chemical engineers, assayers, metallurgists, manufacturers and students. The first edition of the book which appeared in 1900 was intended particularly for the use of analysts, and while this feature is still prominent with many improvements, extensive additions have been made of data connected with chemical engineering, such as information and tables on fuels, boilers, engines and chimneys, drying and evaporation, fire-brick and refractories, heat-conductivity and resistivity, tanks, piping and pumps, belts, pulleys and shafting, elevators and conveyors, and tables of the heats of formation of chemical compounds.

A great many useful numerical tables are presented. There are tables relating to economic minerals, giving their compositions, uses, physical properties and a scheme for their determination. There is also a scheme for the general qualitative analysis of the common metals and acid radicals. Many methods of technical quantitative analysis are described, dealing with the examination of various ores, metals, slags, fuels, gases, waters, cements, limestones, clays, oils, soaps, pigments, fertilizers, etc., and the methods appear to be well-chosen and clearly described.

H. L. W.

4. *Chemical French*, by MAURICE L. DOLT. Svo, pp. 398. Easton, Pa., 1918 (The Chemical Publishing Co.).—This is a text-book of chemical French for the use of students. It is intended as an aid in overcoming the decided difficulties that are encountered by those who have had but a year or two of ordinary instruction in the French language, and it is so arranged that it can be used by beginners in the language with the help of a French grammar.

The first part, comprising about one-half of the text, is made up of graded exercises with which special vocabularies are given. These exercises not only supply a very large number of technical terms, but they give much interesting chemical information, so that the reader will not only learn French but also much chemistry by following this course. The last part of the text is made up of about a dozen important articles by eminent chemists. These have been well selected, and are exceedingly important and interesting. For instance, Moissan's article on fluorine is given, the famous reactions of Grignard and of Friedel and Crafts are described by their authors, and there are celebrated papers by Pasteur and by Mme. Curie. The only strictly grammatical part of the book consists of a table of the irregular verbs occupying 10 pages. At the end there is a convenient French-English general vocabulary.

The book appears to be a most excellent one for its purpose, and its collection of famous chemical contributions makes it interesting to students of chemistry who can already read French.

H. L. W.

5. *American Lubricants*, by L. B. LOCKHART. Svo, pp. 236. Easton, Pa., 1918 (The Chemical Publishing Company).—This book is intended particularly as an aid to users in the selection of lubricants. It gives interesting data in regard to the production and refining of petroleum, descriptions of the products, and the physical tests for examining them. Lubrication is discussed in a great variety of special cases, especially in connection with viscosity. Animal and vegetable fats and oils are also extensively discussed, and physical and chemical tests for them are given. A large number of copies of specifications for various commercial oils are given, and several tables relating to viscosity, specific gravity, temperatures, prices of oils and heavy chemicals, and petroleum statistics are appended. It should be said that the book is not wholly devoted to lubricants, for other petroleum products such as gasoline, fuel-oil and kerosene are dealt with. The book will be useful not only to those who are interested in machinery, but also to chemists who have occasion to examine oils, greases and other lubricants.

H. L. W.

6. *Prime Numbers*.—For obvious reasons, the last anniversary address of the President of the Royal Society, SIR J. J. THOMSON, contains practically nothing of interest for the physicist. His comments, however, on a certain investigation relative to a rule for prime numbers merit quotation. "If we take the numbers in order 1, 2, 3, . . . we see that there are some, such as 3, 5, 7, 11, which cannot be divided by any number smaller than themselves; these are called prime numbers; the number of such primes which are less than a given number is a matter of very considerable importance, and Gauss, many years ago, gave, without any rigorous proof, a rule about it. The rule was tested by actual trial for numbers up to a thousand millions, and, as it was found to be true over that immense range, it was accepted as universally correct in spite of the absence of a satisfactory proof. Quite recently, however, Mr. Littlewood, one of our Fellows, has shown that, in spite of this apparently overwhelming evidence in its favour, the result is not general, but the numbers for which it breaks down are so enormous that it would be quite beyond the powers of human endurance to detect its failure by actual trial. I may say, in passing, that, enormous as these numbers are, they are mere nothings, compared with what we have to deal with in many branches of Physics. Here, then, we have a result which has satisfied, and apparently always will satisfy, any direct test that can be applied to it, and yet is not generally true; there seems to me to be something of a tragedy, perhaps the suspicion of a sermon, in this investigation, which is in a paper of a highly technical character, quite unintelligible to anyone who was not an expert mathematician."—*Proc. Roy. Soc.*, 94A, 187, 1918.

H. S. U.

7. *Polarimetry. Second Edition*. Pp. 196, 12 figures. Washington, 1918 (Circular No. 44 of the Bureau of Stand-

ards).—In this circular a concise account of the basic principles of modern polarimetry is given. The new edition has been carefully revised and 43 pages of additional matter have been incorporated in the appendixes. The new material comprises 10 tables which include the new Bureau of Standards Baumé scale for liquids more dense than water, the results of recent researches, a consideration of the polarization of low-grade products, a résumé of the work of the International Commission for Uniform Methods of Sugar Analysis, and amendments to the United States Treasury Department Sugar Regulations. The volume undoubtedly constitutes an important and practically useful contribution to the subject.

H. S. U.

8. *Theories of Energy*; by HORACE PERRY. Pp. vii, 231. New York, 1918 (G. P. Putnam's Sons).—After devoting twenty years to pondering over the phenomena associated with energy the author has developed certain lines of argument which he now presents as "theories." Among other things he gives theories of energy, spectral lines, chemical reaction, gravity, magnetism, electricity, reflection of light, color, double refraction, polarization, diffraction, etc. The Preface closes with the following sentence: "It has been my aim to be explicit and concise, and in order to facilitate the treatment of the subject and make myself the better understood, I have found it necessary to make use of a number of new terms." Although these new terms are defined in a general way in the Notes which follow the text proper they do not seem to correspond unambiguously to ordinary scientific terms and hence they defeat their own end by making the book almost unintelligible to the trained physicist. This difficulty is increased by the entire absence of mathematical symbols and formulae.

The following typical quotations are made without comment in order to show the style and character of the text. "The ether is, in all probability, a homogeneous substance, not in the form of particles, as some consider, but unparticleate and continuous, and it is only reasonable to suppose that there is no cohesion between its parts, there being merely a togetherness without any forcible hold." "The occurrence of gravity in all matter and its incessant action indicate that it is the primary form of energy, and if through reciprocal gravitational energization other manners of energy arise, it would be the primary form." "As has already been said, electricity is supposed to be energy, mannerically the same as magnetism, chemicity, heat and light, . . ." "Under the theory here advanced light is supposed to be polarized when the densitional movements are not parallel with the lines of propagation, not normal to the densits. In other words, polarization is densitional denormalization, the denormalization being caused by densitie interseccion."

H. S. U.

9. *An Introduction to Science*; by BERTHA M. CLARK. Pp. 494, with 346 figures. New York, 1918 (American Book Co.).—“The aim of this book is to start young high school pupils on scientific projects which will influence for good their *present* lives, and which under different guise will equally influence for good their future lives.” Among the scientific projects presented to the pupils are those of the selection of economic menus of dietary standards; the selection of suitable paints, oils, and varnishes for actual daily use; the examination of different fuels, and their adaptability to furnaces and kitchen range; the investigation of home and school lighting and its influence on eyesight; the utilization of simple labor-saving devices to relieve physical exertion; the employment of chemical agents to transform useless waste products, such as grease and sewage, into useful products, such as soaps and fertilizers; and the application of hygienic facts and theories to school, home, and community sanitation.

The author's style is clear, simple, and scientifically accurate. The material for the text has been selected with care, the figures are all good and many of them are half-tone reproductions of photographs, and typographical errors are exceptionally rare. Not only is the book admirably adapted to the needs of the students for whom it was written but it contains a wealth of valuable information which would be very helpful to progressive housewives whose early scientific training may have been somewhat inadequate or perhaps entirely lacking. H. S. U.

10. *Laboratory Manual*; by BERTHA M. CLARK. Pp. 203. New York, 1918 (American Book Co.).—This book is a companion volume to “*An Introduction to Science*” by the same author (*vide supra*). It consists of perforated loose leaves, each record requiring one leaf. The student is expected to enter his experimental data and conclusions on the blank areas of each leaf and to hand in the finished record for examination. The statement of the problem, a list of the essential pieces of apparatus, a diagram of the assembled parts, and the directions, observations, conclusions, and discussion are printed on the first or front page of each sheet. When the exercise involves plotting, the coordinate cross-ruling is printed on the back or second page of the sheet. The pages are numbered consecutively and a list of the titles of the experiments is furnished so that, at the end of the course, the entire set of reports may be bound permanently in a systematic sequence. The number of experiments (about 100) is too great for one year's work, the underlying idea being to enable teachers in cities and in rural districts to omit the problems with which the students are already familiar because of their respective environments and every-day experiences. The problems suggested are interesting and instructive, and the same high standard of composition and typographical perfection, which enhances the attractiveness and value of the companion text, has been maintained. H. S. U.

## II. GEOLOGY.

1. *Thirty-eighth Annual Report of the Director of the United States Geological Survey*; by GEORGE OTIS SMITH, Director. Pp. 176, 2 pls., 1917.—The commanding position of the Geological Survey among organizations devoted to advancing science and developing the nation's resources is generally recognized; but to appreciate the variety of its activities and its influence on industry and in education, the annual reports should be read. A general view of the Survey is gained by a list of its largest items: 40,937 square miles of geologic survey, 32,245 square miles of topographic surveys, 18,000,000 acres of lands classified, 1,197 stream-gaging stations maintained, and collection of statistics from 90,000 producers. The Survey staff numbered 934 and the number of published works 203. Geologic work extended into every State, the Canal Zone, and the West Indies, and the Survey coöperated with 25 States in geologic or paleontologic studies. Assistance was also given to the Bureau of Mines, Bureau of Standards, Office of Public Roads, the Forest Service, the Indian Office, the War and Navy departments, the Land Office, and several other institutions. Although much of the regular geologic research has been carried on, the dominant feature since the declaration of war has been the greater concentration along economic lines and the scientific guidance of war activities; the search for potash in desert basins, in ancient salt and gypsum beds, in feldspar and sericite has been continued; special investigations of sources of graphite, platinum, vanadium, antimony have been undertaken; and the search for manganese has been comprehensive. Much attention has been given to coal and oil, and an interesting phase of the year's work is the demonstration that 40,000,000,000 barrels of petroleum are stored in the oil shales of Utah and Colorado—an astounding figure when compared with 3,500,000,000 barrels, the total amount yet produced within the United States. Special military maps, descriptive publications, and reports on camp water supplies have been prepared. The Survey has contributed 79 men to the Engineer Officers' Reserve Corps, 37 of whom were in France on October 1, 1917.

H. E. G.

2. *Annual Report, 1915, of the Iowa Geological Survey, with accompanying papers*; GEORGE F. KAY, State Geologist. Vol. 26, 1917. Pp. vii, 456, 25 pls., 63 figs.—This annual report of the Iowa Geological Survey contains three important papers on glacial geology: The Iowan Drift, a review of the evidences of the Iowan stage of glaciation, by William C. Alden and Morris M. Leighton (pp. 49-212); Pleistocene Deposits between Manilla and Coon Rapids, by George F. Kay (pp. 213-231); The Pleistocene Geology of Northwestern Iowa, by J. Ernest Carman.

Alden and Leighton reach the conclusion that a drift older than the Wisconsin and younger than the Illinoian is found in northeastern Iowa and that consequently the Iowan stage of glaciation should stand as a major subdivision. Dr. Kay describes unusually complete exposures of loess, Kansan gumbotil, Kansan drift, Nebraskan gumbotil, and Nebraskan drift along the newly graded Chicago, Milwaukee & St. Paul Railroad. Mr. Carman contributes a detailed description of the Pleistocene deposits of a part of Iowa which have been relatively little studied. A valuable investigation on the adaptability to industrial purposes of the river waters of Iowa has been undertaken by George A. Gabriel.

H. E. G.

3. *Western Australia Geological Survey*.—The activities of the West Australian Geological Survey are recorded in the Annual Progress Report for 1916, by A. GIBB MITTLAND, Government Geologist (pp. 32, 2 maps, 1917). In addition to economic investigations in the Yalgoo, Kendenup, Yilgarn, Comet Vale, and Murchison districts, studies were made of the great fault system of the Southwest Division and a reconnaissance survey carried over the little-known region between Laverton and the South Australian border. Sufficient exploration has now been completed to justify the preparation of a much desired geologic map of the State.

Two detailed reports on economic geology and one on paleontology have also been issued: The Geology and Ore Deposits of Meekatharra, Murchison Goldfield, by E. deC. Clarke, with chapters on Petrology, by R. A. Farquharson, and on Mineralogy and Ground Waters, by E. S. Simpson (Bulletin 68, pp. 342, 88 figs.; 25 pls. in separate volume, 1917); The Geology and Ore Deposits of Kalgoorlie, East Coolgardie Goldfield, Part III, by F. R. Feldtmann (pp. 152, 43 figs.; 14 pls. in separate volume, 1916); Paleontological Contributions to the Geology of Western Australia, Series VI, Nos. XI and XII, by F. Chapman and R. Etheridge, Jr. (Bulletin 72, pp. 59, 15 pls., 1 map, 1917). Mr. Chapman describes the Foraminifera and Ostracoda of the Gingin Chalk, a remarkable deposit "nearly equivalent in age, structure, and organic contents to the Chalk of Upper Cretaceous age in Europe and America" and probably laid down in "deep gulfs running into the Continent." Mr. Etheridge calls attention to the presence of *Girvanella* associated with *Salterella hardmani* in the Cambrian in the Kimberley region.

H. E. G.

4. *Annual Report of the Director of Mines and Government Geologist for 1916, South Australia*; by L. KEITH WARD. Pp. 18, 2 maps, 1917.—As in previous years the staff of the Government Geologist was largely concerned with the examination of and reports on actual and prospective mineral localities. (The results of these studies for 1916 are published separately under the title, "Review of Mining Operations.") The features of

the present report are: 78 analyses of clays by W. S. Chapman, a small-scale reproduction of the geologic map of the State, and a useful contour map on which isolyets are also shown. A comparison of this topographic map,—the first one issued for South Australia,—with the geologic map shows the profound denudation to which the country has been subjected. H. E. G.

5. *Eleventh Annual Report, Geological Survey of New Zealand*; P. G. MORGAN, Director. Pp. 18, 4 maps, 1 plan, 1917.—In most countries the great war has stimulated geologic research; in New Zealand the opposite effect has been produced. The Survey staff has been depleted, the facilities for publication decreased, and its appropriations cut to the point where "it is threatened with extinction." If this unsound policy is continued, science in general and New Zealand in particular will suffer great loss.

In spite of unfavorable conditions a number of areal and economic investigations have been made and are summarized in the Annual Report. Two important paleontologic bulletins were published during 1917: The Cretaceous Faunas of the North Eastern Part of the South Island of New Zealand, by Henry Woods (pp. 41, 20 pls. or figs.); New Tertiary Mollusca Occurring in New Zealand, Part I, by Henry Suter (pp. 93, 13 pls. or figs.). Studies of New Zealand Mesozoic fossils, by C. T. Trechmann, have appeared in the Geological Magazine for February and July, 1917. H. E. G.

6. *Popular Oil Geology*; by VICTOR ZIEGLER. Pp. 144, 62 figs. Golden, Colo., 1918 (C. H. Merrifield).—The demand for petroleum has resulted in a world-wide search for deposits and enlisted the services of professionals and amateurs, alike. The failures have outnumbered the successes because of the ignorance of the geologic principles involved in commercial exploitation. Professor Ziegler's well-written and well-illustrated book is designed to present these principles in terms intelligible to the layman and to serve as an introduction to the author's forthcoming "Principles of Oil Geology." The topics discussed include the origin, properties, and mode of accumulation of oil, the use of maps, methods of prospecting, and oil investments. H. E. G.

### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Soil Conditions and Plant Growth*; by EDWARD J. RUSSELL. Third edition. London and New York, 1917 (Longmans, Green and Co.). Pp. viii + 243. (Monographs on Biochemistry).—Three editions within five years testify to the usefulness of this well-written monograph. The innovations in the present edition include particularly a new chapter on the colloidal properties of the soil. The limitations of present-day soil analysis

and its interpretation are clearly set forth. The references to the new journal *Soil Science*, publication of which was only recently begun in this country, indicate the up-to-date character of the book. The non-agricultural student with some biochemical training as well as the specialist in plant growth will find this monograph readable and stimulating.

L. B. M.

2. *Agricultural Bacteriology*; by H. W. CONN. Third edition, revised by HAROLD JOEL CONN. Pp. x, 357. Philadelphia, 1918 (P. Blakiston's Son & Co.).—A timely revision of a popular textbook and laboratory manual prepared after the death of Professor H. W. Conn by his son, a bacteriologist at the New York Agricultural Experiment Station. As might be expected, a large part of the volume is still taken up with consideration of bacteria in dairy products—a field in which the senior author was particularly competent. Beside general considerations the problems of bacteria in soil and water, their parasitic aspects, and the relation of micro-organisms to various farm products are not overlooked. The inclusion of bacteriology more extensively among the disciplines of scientific agriculture, as exemplified by books like this one, marks a helpful step in advance.

L. B. M.

3. *The Linacre Lecture on the Law of the Heart*; given at Cambridge, 1915; by ERNEST H. STARLING. Paper covered. Pp. 27. London and New York, 1918 (Longmans, Green and Co.).—Mainly an interpretation of the researches, in Professor Starling's laboratory, upon the surviving heart-lung preparation. "The law of the heart is thus the same as the law of muscular tissue generally, that the energy of contraction, however measured, is a function of the length of the muscle fibre."

L. B. M.

4. *Index to the Philippine Journal of Science, vols. 1 to 10*.—The long series of publications of the Philippine Bureau of Science does honor to all the gentlemen who have been connected with its work (see this Journal **21**, 336, 408, 1906; **23**, 322, 1907). It is interesting now to note the issue of "Publication No. 8, Contents and Index of the Philippine Journal of Science, volumes 1 to 10." This is sent without charge to subscribers and exchanges that have received volumes **11** and **12** of the Journal; to others the price is \$2.00 United States currency.

#### OBITUARY.

PROFESSOR G. A. LEBOUR, who occupied for nearly forty years the chair of geology in the Royal School of Mines, London, died on February 7 in his seventy-first year.

PROFESSOR E. A. LETTS, the British Chemist, since 1879, of Queens College, Belfast, died on February 19 in his sixty-sixth year.



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ART XXVII.—*Generalized Relativity and Gravitation*;  
by E. WOOLARD.

The following sketch is decidedly non-mathematical; consequently, the reader must take for granted many of the statements; in this respect, the paper may be found unsatisfactory, but it may be taken as a fair summary of the present state of the more important aspects of the theory of relativity. We are all put at a disadvantage regarding recent progress in German scientific investigations because of the impossibility of obtaining German periodical and other literature.

## I. THE "OLDER" RELATIVITY.

1. Man, in his study of natural phenomena, is forced to devise some means of describing these phenomena; this he does by creating artificial frames of reference to which the position of points, and the equations expressing his observations and conclusions, may be referred. We are all familiar with Cartesian rectangular coördinates in space, and the transformations by which expressions referred to one set of axes may be changed to refer to other sets of axes, rectangular or oblique, which have been rotated or translated with respect to the original set; evidently there is an infinite number of possible systems of reference. It is perfectly clear that natural phenomena themselves are entirely independent of the reference systems; no matter what system of coördinates is used to describe it, a phenomenon itself

remains the same, and hence our equations regarding it should remain essentially the same in form.

2. From a consideration of Newton's law of gravitation, and of his three laws of motion, there may be formed certain well-known differential equations which describe the motion of bodies under the influence of forces.<sup>1</sup> In building up his system of mechanics, Newton postulated the existence of a definite frame of reference, fixed in space, to which motion might be referred. In practice, motion is usually measured relative to the earth considered as fixed; we know that the earth, as well as every other celestial body, is in motion in space; hence we can observe no absolute motion; Newton considered such as existing, however, even though unattainable. The Newtonian equations are invariant in form for any uniform translatory motion of the axes of reference.<sup>2</sup> If the same arbitrary velocity were suddenly added to every body in a system, it would be impossible to detect it. The frame of reference assumed at the beginning is not unique, but only one of an infinite number, all moving relative to one another with a constant velocity of translation without rotation. It is possible to detect relative motion only.

3. The introduction of the all-pervading luminiferous aether gave rise to many difficulties. It seems to be necessary to postulate, however, on account of aberration, etc., that the aether is not entrained by bodies moving through it.<sup>3</sup> Hence, if we could measure the velocity of

<sup>1</sup> See, for example, Dadourian, *Analytical Mechanics*, New York, 1913; Moulton, *Introduction to Celestial Mechanics*, New York, 1914; Jeans, *Theoretical Mechanics*, New York, 1907; Watson, *Theoretical Astronomy*, 1881.

<sup>2</sup> Jeans, *Theoretical Mechanics*, p. 33; Cunningham, *Relativity and the Electron Theory*, 1915, pp. 2-11; Watson, *Theoretical Astronomy*, sec. 10: the equations of motion referred to two systems of coördinates respectively,  $(x, y, z)$  and  $(x_0, y_0, z_0)$  moving relative to one another are:

$$\sum_m \left( x \frac{d^2 y}{dt^2} - y \frac{d^2 x}{dt^2} \right) - \sum_m (Yx - Xy) = 0$$

etc.,

and

$$\sum_m \left( x_0 \frac{d^2 y_0}{dt^2} - y_0 \frac{d^2 x_0}{dt^2} \right) - \sum_m (Yx_0 - Xy_0) = 0$$

illustrating what we mean when we say the form of equations remains unchanged.

<sup>3</sup> See, e. g., Cunningham, *Relativity and the Electron Theory*, pp. 12-16.

the earth relative to the aether, we should have measured the absolute velocity of Newtonian mechanics. There are several experiments which should enable us to do this quite easily, the most famous being the so-called Michelson-Morley experiment<sup>4</sup>; but in every one of the numerous instances in which these experiments have been accurately performed, they have failed to give the slightest evidence of the expected effects. Hence, the statement of the Principle of Relativity, that "it is impossible by means of physical experiments to determine the absolute velocity of a body through space."

4. The theory of electricity and magnetism, based upon experimental evidence, gives us a set of equations for the conditions existing in an electromagnetic field. Let the systems of rectangular coördinates  $(x, y, z, t)$  and  $(x', y', z', t')$ ,  $t$  referring to time, be moving relative to one another with a uniform motion of translation without rotation; let the origins of the two systems coincide at the initial epoch; then it is clear that

$$\left. \begin{aligned} x' &= x - at \\ y' &= y - \beta t \\ z' &= z - \gamma t \\ t' &= t \end{aligned} \right\} \quad (1)$$

According to what we said above, the Newtonian equations of motion are unchanged by a transformation of this type; when we try to extend electrodynamics to moving systems in this way, however, we find that the equations *are* changed fundamentally. It is found that they are unchanged by a transformation of the type

$$\left. \begin{aligned} x' &= \beta (x - vt) \\ y' &= y \\ z' &= z \\ t' &= \beta \left( t - v \frac{x}{c^2} \right) \\ \beta &= \left( 1 - \frac{v^2}{c^2} \right)^{-\frac{1}{2}} \end{aligned} \right\} \quad (2)$$

where  $v$  is the velocity of motion, and  $c$ , as always, is the velocity of light. Now, in order to explain the fact that we cannot detect the motion of the earth relative to the

<sup>4</sup> Cunningham, *Relativity and the Electron Theory*, pp. 16-21; Carmichael, *Theory of Relativity*, 1913, pp. 10-13.

aether, it is necessary to postulate that a body, when set in motion, automatically contracts in the direction of

motion in the ratio  $1 : (1 - \frac{v^2}{c^2})^{\frac{1}{2}}$ ; this masks all effects of

relative motion. From this, the transformation equations connecting the coördinates of two systems moving relative to one another can be deduced, and they are the same as (2); this transformation should replace (1); the physical phenomena really being the same in the two systems, our mathematical equations for the operations of nature should be invariant for the *Lorentz-transformation*, as (2) is called.<sup>5</sup> Lorentz showed that the above contraction would take place if the intermolecular forces were of electrical origin; such considerations gave rise to the electron theory of matter of to-day, before electrons themselves were dissembled and experimented upon.<sup>6</sup>

The Newtonian equations are not invariant for the Lorentz-transformation, and a new system of dynamics and mechanics was built up.

## II. "GENERALIZED" RELATIVITY.

5. Evidently, the Principle of Relativity in its purest and most general form would be: The mathematical equations expressing the laws of nature must be invariant for *all arbitrary transformations* of coördinates.<sup>7</sup> The new theory of general relativity satisfies this postulate. In this new theory, gravitation plays an important part. Gravitation is certainly different from everything else because of its absolute independence of distance, physical and chemical conditions, etc. Furthermore, all bodies fall with the same acceleration, and all inertial masses are gravitating masses. From these facts, Albert Einstein deduced his "Equivalence-Hypothesis":<sup>8</sup>

6. "Consider an observer situated in a closed lift, observer and lift being free from the attraction of gravitating matter. If the lift were in uniform motion there

<sup>5</sup> Campbell, *Modern Electrical Theory*, 2d ed., pp. 357-9, 376-7, 1913. Cunningham, *Relativity and the Electron Theory*, pp. 21-2, 31-34. Carmichael, *Theory of Relativity*, pp. 44-48.

<sup>6</sup> Bumstead, *Science*, N. S. 47, pp. 57-58, 1918.

<sup>7</sup> Fokker, *Phil. Mag.* (6), 29, art. 10, sec. 16, 1915.

<sup>8</sup> Einstein, *Annalen der Physik*, 35, pp. 898 et seq., 1911.

would be no pressure between the lift floor and the observer's feet; in fact, by a gentle spring the observer could 'float up' to the ceiling of the lift; bodies placed anywhere in the lift would remain there without support—in short, there would be no 'up' nor 'down'. If now the motion of the lift were accelerated, all the mechanical phenomena which we associate with a field of gravitation would supervene. If the acceleration is maintained in a direction which is 'upwards' (in the sense from feet to head), the lift floor would exert a pressure on the observer's feet in proportion to the magnitude of the continuous, uniform, acceleration; bodies would 'fall' (i. e., move towards the lift floor) with an acceleration *relative to the lift* equal in magnitude and opposite in direction to the acceleration of the lift."<sup>9</sup>

It would be impossible to distinguish between a system at rest in a homogeneous gravitation field, and a system in continuously accelerated motion in a space free from gravitation. The Equivalence-Hypothesis states that two such systems are completely equivalent for *all* phenomena. This assumption is an application of our postulate of general relativity<sup>10</sup>; for, since at a given point in any gravitation field, every material particle receives the same acceleration, if we introduce at this point a new system of coördinates which here has exactly this acceleration relative to the old system, then the material point subjected to gravitation would be at rest relative to the new coördinates, and, relative to them, apparently not subject to gravitation; but by the postulate of general relativity, these two systems must be equivalent.

7. One great result of the "older" relativity was Hermann Minkowski's dictum that "space and time each separately must vanish to shadows, and only a union of the two should preserve reality." Four-dimensional space and mathematics are accordingly used throughout the principle of relativity, time being treated as the fourth dimension; this is measured in such a way that the velocity of light in free space is unity. "If we choose a new axis of  $t$ , we must choose a new axis of  $x$ , just as if we choose a new axis of  $x$ , we must choose a new axis of  $y$ ;" and the new choices must be such that the

<sup>9</sup> Rice, Relativity and Gravitation, Sci. Amer. Sup., April 7, 1917.

<sup>10</sup> De Sitter, Monthly Not. R. A. S., vol. 76, No. 9, Sec. 3, 1916.

differential of arc is unchanged, i. e., such that our equations shall be invariant.

In ordinary Euclidean three-dimensional space, for two points very close together, analytic geometry gives as the differential of arc

$$ds^2 = dx^2 + dy^2 + dz^2 \quad (3)$$

In the four-dimensional space-time manifold of relativity, the differential of arc may be shown to be

$$ds^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2 \quad (4)$$

If on any system of coördinates  $(x, y, z, t)$  we execute any arbitrary transformation

$$\left. \begin{aligned} x' &= f_1(x, y, z, t) \\ y' &= f_2(x, y, z, t) \\ z' &= f_3(x, y, z, t) \\ t' &= f_4(x, y, z, t) \end{aligned} \right\} \quad (5)$$

where  $f_i$  is any function whatsoever, substitute in the formula for the differential of arc, and collect, we shall find that

$$\left. \begin{aligned} ds^2 &= g_{11} dx^2 + 2g_{12} dx dy + 2g_{13} dx dz + 2g_{14} dx dt \\ &\quad + g_{22} dy^2 + 2g_{23} dy dz + 2g_{24} dy dt \\ &\quad + g_{33} dz^2 + 2g_{34} dz dt \\ &\quad + g_{44} dt^2 \end{aligned} \right\} \quad (6)$$

where  $g_{ij}$  denotes a coefficient which depends for its value upon the values of the  $i$ th and  $j$ th coördinates; this may be concisely expressed as follows:

$$ds^2 = \sum_{ij} g_{ij} dx_i dx_j \quad (7)$$

8. In (7) there are ten coefficients, all of them functions of the coördinates. Since this is a perfectly general transformation, it includes all others, to any one of which it may be reduced by a proper choice of functions. We pointed out above that by a suitable transformation, a gravitation field could be got rid of; hence, these ten  $g_{ij}$  specify the gravitation field, since they show how it can be abolished; but they also determine the reference system of coördinates; in the new theory gravitation is inextricably mixed up with space and time, *the three forming an inseparable union.*



9. By the Equivalence-Hypothesis, if we take a system at rest in a gravitation-free space, exactly the same results will follow whether we introduce a homogeneous gravitation field, or whether we put the system into uniformly accelerated motion. In a system at rest in a gravitation-free space, a material particle would of course move in a straight line with uniform velocity. All of the equations expressing the motion and energy of such a particle can be contracted into the single equation:<sup>11</sup>

$$\delta \left\{ \int H d\tau \right\} = 0 \quad (8)$$

where

$$H = -m \sqrt{c^2 - \left(\frac{d\xi}{d\tau}\right)^2 - \left(\frac{dn}{d\tau}\right)^2 - \left(\frac{d\zeta}{d\tau}\right)^2} \quad (9)$$

$m$  being the mass. Omitting this, as it is constant, (9) becomes

$$H = \frac{ds}{d\tau}$$

and (8) is

$$\delta \left\{ \int ds \right\} = 0 \quad (10)$$

When translated from the language of the calculus of variations, this means simply that the differential of arc of a moving particle is a minimum, i. e., the particle takes the shortest possible path between two points of four-dimensional space, which agrees with our statement that it moves in a straight line.

10. It is possible to find the relations between the coördinates in a system at rest in a gravitation-free space, and those of the same system put into uniformly accelerated motion in the same space.<sup>12</sup> Transforming the equations of motion by means of these, we find, after various reductions, etc., that in this case also,

$$\delta \left\{ \int ds \right\} = 0 \quad (11)$$

<sup>11</sup> Einstein, *Annalen der Physik*, 38, p. 458, 1912.

<sup>12</sup> Lorentz, *Het Relativiteits-beginsel*. Drie voordrachten bewerkt door Dr. W. H. Keesom, 1913; De Erven Loosjes, Haarlem. Einstein, *Annalen der Physik*, 38, pp. 359, 444, 1912.

Therefore the differential of arc is unchanged by such a transformation; but by the equivalence hypothesis, such a transformation is the same as would be produced by the creation of an homogeneous gravitation field in the system. It is reasonable to assume that a free particle *always* takes the shortest possible track between two points, and that (11) is invariant for *any* arbitrary transformation corresponding to the creation of *any unhomogeneous* gravitation field. Executing the transformation (5) we see that the  $g_{ij}$  determine the gravitation field and all its characteristics.

The determining feature of a gravitation field is its strength, which is measured by the potential. The potential energy of a unit mass at any point is the gravitational potential at that point, and is equal to the work done in bringing the mass from infinity to that point; hence the gravitational potential always has a negative sign, since in being so moved, a body itself does work. In Newtonian mechanics we have only one potential, but in this new theory, there are, of course, ten potentials, one of which, under ordinary conditions, is closely approximate to the Newtonian potential.

11. The ten coefficients may be written

$$\left. \begin{array}{cccc} g_{11} & g_{12} & g_{13} & g_{14} \\ g_{21} & g_{22} & g_{23} & g_{24} \\ g_{31} & g_{32} & g_{33} & g_{34} \\ g_{41} & g_{42} & g_{43} & g_{44} \end{array} \right\} g_{ij} = g_{ji} \quad (12)$$

This puts them into the form of a mathematical operator, known as a *tensor*, by means of which our various transformations and operations may be performed. It is impossible in this paper to go into the complex mathematics of these tensors; the original papers may be consulted by those who have the necessary mathematical knowledge<sup>13</sup>; suffice it to say, that if a transformation of coördinates be executed upon a tensor, each component,  $g_j$  of the tensor transforms itself exactly as the corresponding component of the differential of arc,  $dx_i dx_j$ . Hence if we have any vector with components  $F_i$ , and any tensor with components  $T_i$ , and if it be true that

$$T_i = F_i \quad (13)$$

<sup>13</sup> Einstein and Grossmann, *Zeitschr. für Math. u. Physik*, 1914, Jan. Einstein, *Sitzungsber. Berlin*, 1914, Nov.; *ibid.*, 1915, Nov. 25.

then, no matter how we transform this equation, both sides will transform themselves alike, and the equations will persist in the form

$$T'_i = F'_i \quad (14)$$

Consequently, if we once succeed in expressing the laws of nature as linear relations between tensors and vectors, and between tensors and tensors, we shall have satisfied the postulate of general relativity.

The transformation-formulas for tensors are easily derived from those for the coördinates; "these transformation-formulas express the components of the transformed tensor as homogeneous linear functions of the components of the original tensor. Therefore, if for one system of coördinates a certain tensor is zero, it is zero for any system of coördinates. Consequently, if once we have expressed the laws of nature in the form of linear relations between tensors they will be invariant for all transformations." Einstein, with the aid of the calculus of tensors, assuming (11) to be invariant, and adopting the fundamental formula (7), has thus succeeded in satisfying his original postulate.

12. The invariant equations of motion turn out to be the ordinary well-known Newtonian equations with certain small terms added to make them invariant. Under ordinary conditions the two theories differ so little that the new theory is of little use to experimental science, the magnitude of the numerous indicated effects being so minute; however, the general relativity theory can hardly be called a pure mathematical speculation, as only physical lines of thought have been followed in its development. Possibly observable consequences are indicated which are of great importance to physics, mathematics, electromagnetism, molecular physics, astronomy, mechanics, etc.

13. The final equations cannot be given here on account of the extreme complexity of the notation necessary. Reference may be had to Dr. Fokker's paper<sup>14</sup> and that of de Sitter<sup>15</sup>, in which all subjects discussed in the second part of the present article will be found fully developed, with full references to the original

<sup>14</sup> Fokker, A Summary of Einstein and Grossmann's Theory of Gravitation. *Phil. Mag.* (6), vol. 29, pp. 77-96, 1915.

<sup>15</sup> De Sitter, On Einstein's Theory of Gravitation and its Astronomical Consequences. *Monthly Notices R. A. S.*, 76, No. 9, pp. 699-728, 1916.

literature. One remarkable result is that these final equations show that the gravitation field is created not only by the *matter* which is present, but also by the *stresses, momenta, and energy*.

Just as in Newtonian mechanics the field is determined by one equation, viz., Poisson's

$$\nabla^2 V = -4\pi\rho \quad (15)$$

so in the new theory, the field is determined by a set of ten equations. Only six of these are mutually independent, however, so that the  $g_{ij}$  and the field are not completely determined by them; for once all the  $g_{ij}$  are known, all the properties of the space as well as of the field are known (since the  $g_{ij}$  determine both), i. e., the reference system of coördinates is known; the postulate of general relativity requires that the reference frame be arbitrary, so that these ten equations, describing as they do all the phenomena of the system (since they depend upon the matter, motions, electromagnetic fields, energy, etc., of the system), must not also fix the reference system; four additional conditions must be introduced before we can derive the equations for any specific system of coördinates.

14. We shall now briefly consider the only three phenomena indicated by the general relativity theory which are of sufficient magnitude to render their observational detection and verification a possibility at the present time.

A fundamental assumption of the "older" relativity was that the velocity of light in free space is constant. In the general theory it is found that  $g_{44}$ , which is approximately the Newtonian potential, is, in a fairly homogeneous gravitation field, equal to the square of the velocity of light in that system; i. e., the velocity of light plays the rôle of a gravitation potential, and varies with the gravitation-field; evidently, only in a homogeneous gravitation field, or in the absence of gravitation, is the velocity of light constant; only in these cases is the "older" relativity valid, it becoming a special case under the general theory. If the gravitation field is not homogeneous, i. e., if it varies in strength from point to point, as actual fields do as the distance from the attracting body varies, then a ray of light traversing free space is continually changing its velocity; but if this happens, the wave-fronts must also change their *direction*. We

know, e. g., that light travels slower in glass than it does in air; when a ray of light enters glass, the wave-fronts are rotated, and the ray is bent, or refracted, as we say. As a matter of fact, if we apply our general equations to the computation of the sun's gravitation field and the phenomena therein, taking into account also the effect of the sun's axial rotation, we reach some startling results.

If there is a space without any gravitation, then the velocity of light is constant:

$$v = \frac{d\sigma}{dt} \quad \parallel \quad (16)$$

where  $\sigma$  is the differential of arc in ordinary three-dimensional space. In this case

$$\begin{aligned} ds^2 &= c^2 dt^2 - d\sigma^2 \\ &= \left(\frac{d\sigma}{dt}\right)^2 dt^2 - d\sigma^2 \\ &= 0 \end{aligned} \quad (17)$$

In a gravitation field also,  $ds$  being invariant

$$ds = 0 \quad (18)$$

In the general equations for the sun's gravitation-field, we get an expression for  $ds$ ; equating this to zero, and solving for the velocity of light, we find that the equation of a ray of light in the field shows that *the ray actually is curved*.<sup>16</sup>

A ray of light going from plus infinity to minus infinity and just grazing the sun should be bent from its course  $1''.75$ ; hence a star observed very near the sun's limb during the time of a total eclipse should be displaced from its true position on the celestial sphere by this amount. "Comprehensive arrangements have been made for submitting Einstein's theory to the acid test in connection with the total solar eclipse of June 8, 1918." The observational difficulties are very great, and the failure to find such a displacement may mean that it is not there, or that it has escaped detection. This eclipse is not a very favorable one, either, as there are few stars near the eclipsed sun.

15. We also find from our equations that at the surface of the sun

<sup>16</sup> For approximate concrete demonstrations of this and the following phenomenon, see the introduction to Fokker's paper, cited above.

$$\frac{dt}{ds} = \frac{1}{c}, \quad (19)$$

and that at infinity from the sun

$$\frac{dt}{ds} = \frac{1.0_0212}{c}, \quad (20)$$

which means of course, that the measure of time varies with the strength of the field; that is, events which occupy so much time at one place, will, if observed from another place, actually seem to occupy a different amount of time, the phenomena itself appearing the same, but its rate apparently changing. The atomic and electronic vibrations which produce light-waves will therefore vibrate slower in the sun as observed from the earth than they will on the earth as observed from the earth; the wave-lengths of the Fraunhofer lines of any element will be longer in the solar spectrum than those of the same lines from a terrestrial spectrum of the same element; the solar lines should all be displaced systematically towards the red. Some observers have claimed to have found such an effect, although the cause of it could not be safely placed<sup>17</sup>; but Dr. Chas. E. St. John, using the powerful instruments of the Mt. Wilson Solar Observatory, reaches the conclusion, after a careful investigation of the nitrogen (cyanogen) bands in the ultra-violet, that "within the limits of error there is no evidence in these observations of a displacement to longer wave-lengths, either at the center or at the limb of the sun, of the order of 0.008A, as required by the principle of relativity."<sup>18</sup>

16. When we apply our equations to the problem of finding the motions of the planets in the sun's field, we get equations which show that the orbits are ellipses with moving perihelia. The fact is well known that the perihelion of Mercury refuses to obey the Newtonian theory, moving 40" per century too fast. Many causes have been assigned, but none have been entirely satisfactory, and in 1895 Newcomb adopted as the most probable of all, the hypothesis that the Newtonian law is not quite

<sup>17</sup> Freundlich, *Phys. Zeitschr.*, 15, p. 369, 1914. Evershed and Royds, *Bull.* 39, Kodaikanal Observatory.

<sup>18</sup> St. John, *Astrophysical Journal*, 46, pp. 249-265, 1917; *Proc. Nat. Acad. Sci.*, 3, pp. 450-452, 1917.

exact.<sup>19</sup> The fact which has, more than anything else, drawn attention to the general relativity theory is that the motion of Mercury's perihelion predicted by it agrees almost exactly with the actual motion.

17. The truth of the postulate of general relativity probably cannot be questioned<sup>20</sup>; as to whether the invariant equations derived by Einstein are *the* ones or not, future observations alone can tell. The agreement in the case of Mercury "may conceivably be due to accident and, in any case, its evidence is too slender to be regarded as establishing the theory. But we must face the distinct possibility of its ultimate success."<sup>21</sup>

Boulder, Colorado.

January 24, 1918.

<sup>19</sup> Newcomb, *Astronomical Constants*, 1895. In connection with relativity suggestions, see *Nature*, 99, pp. 412-3, 1917, and 100, pp. 33, 1917.

<sup>20</sup> Bumstead (*Science*, N. S. 47, pp. 59-60, 1918) says, however: "There can be little doubt of its correctness when applied to motions of translation; speaking in terms of the ether, we may be reasonably confident that it is impossible to detect the effects of uniform translation relative to the ether. But little has been accomplished in extending the theory to motions of rotation; indeed, rotation has always been a stumbling-block to a purely relative theory of motion, as soon as dynamical considerations are introduced." See his remarks following this, and also "On the Relativity of Rotation in Einstein's theory," *Sci. Amer. Sup.*, Aug. 18, 1917. In addition see Walker, *Proc. Roy. Soc., A*, 93, p. 448, 1917.

<sup>21</sup> Bumstead, cited above. As to both the relativity theories, see Einstein, *Scientia*, May, 1914; and *Tagesfragen aus den Gebieten der Naturwissenschaften und der Technik*, Heft 38, *Über die spezielle und die allgemeine Relativitätstheorie?* (Gemeinverständlich), 70 pp.

ART. XXVIII.—*An Unusual Mastodon*; by F. B. LOOMIS.

In 1869 Dr. C. U. Shepard, Jr., collected two imperfect skeletons of mastodons from the beds overlying the phosphate deposits of South Carolina. These have been in the collections at Amherst College since then, but on account of their fragmentary condition were not exhibited. Recently on trying to fit together some of the parts it was found that of one specimen the greater part of a skeleton could be assembled. This is the one used as the basis of this article. It also developed that there were several unusual characters about both of the specimens which makes it advisable to put them on record.

The first individual came from the marl at the head of Hilton Harbor on St. Helena Island, being found<sup>1</sup> "nearly at low water. One thigh bone projected for say two feet out of the sand and had been used by boatmen to tie their boats to." This is the better preserved specimen, over half of the skeleton being present and almost every bone represented on either one or the other side. Fig. 1 shows the skeleton as restored, the portions shaded dark being the parts preserved, the lighter areas being the restored portions. The lower jaw, however, belongs to the second individual. The cranium seems to have weathered to bits, though the upper dentition is preserved, and probably the lower was also originally, but as Dr. Shepard says, Captain B—— who helped dig out the specimen "retained some teeth" and of these there is now no trace.

The second specimen came from Nine Mile Bottom, *i. e.*, nine miles above Charleston. It was found while stripping to get to the phosphate deposit "in the black earth 3 to 4° feet from the surface." This specimen is about five per cent larger than the one from St. Helena Island, but is in a very poor state of preservation. The parts which were in a good state were the two lower jaws with their complete dentition including the tusks, and some of the foot bones and vertebræ.

Both individuals are of unusually large size; both have two tusks in the lower jaws, both have the last molars composed of five transverse ridges and a heel, whereas the usual number is four and a heel. It was a temptation to

<sup>1</sup> From a letter from Dr. C. U. Shepard of date March 6, 1913.



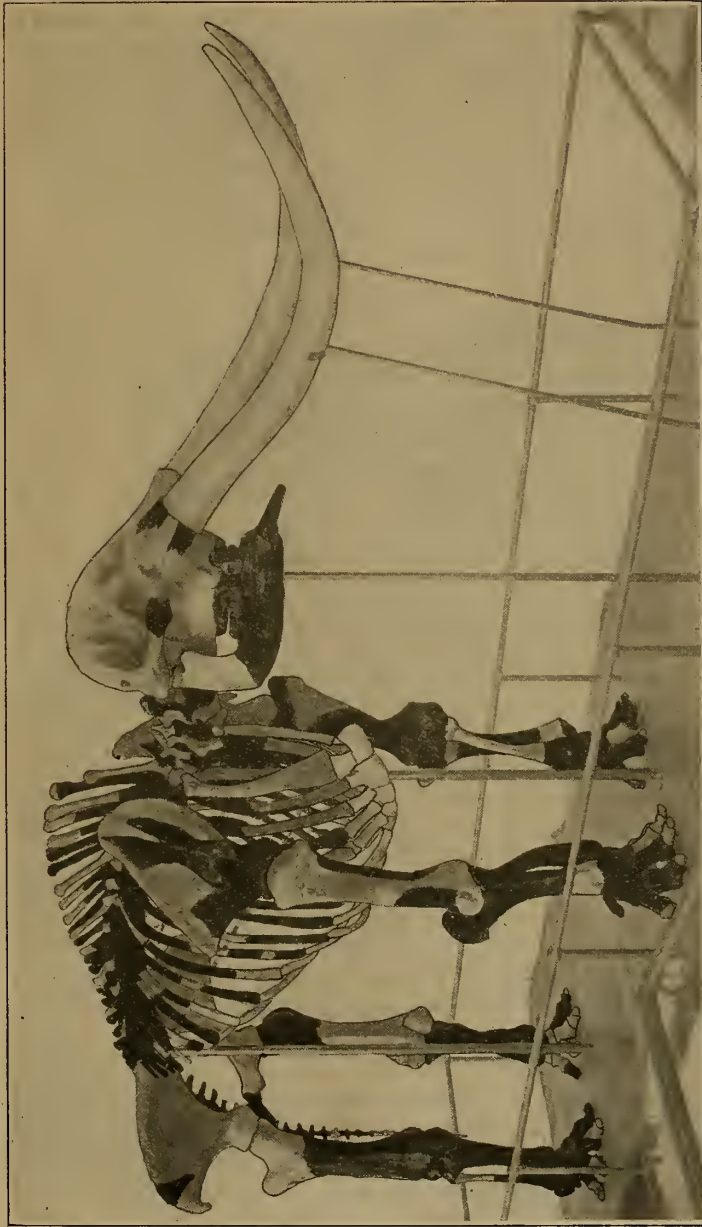


FIG. 1. *Mastodon americanus*, skeleton found at St. Helena Island, So. Carolina. Shaded areas show parts actually found, lighter areas indicate restoration.

distinguish these two specimens as a new species, distinguished from the American mastodon by the features above mentioned, but the large number of known specimens indicate that there is considerable range of variation in the mastodons, not only on account of age and sex, but also individual. As far as I can find from studying the reports of mastodons over the country, those from the south seem to range larger in general, and more frequently to show the more complicated molars.

The most striking feature is the presence of the well-developed tusks in the lower jaws which at once revives the *Tetracaulodon* discussion started by Godman in 1830<sup>2</sup> when he gave the name *Tetracaulodon* to a specimen which he found with a small tusk in the lower jaw. This specimen came from Newburg, N. Y., and had a small tusk four inches in length, together with the alveolus for its mate. Hays<sup>3</sup> confirmed the feature and cited three other specimens, presumably from Big Bone Lick, which either had lower tusks or alveoli for them. He further showed that some young had the tusks and some no trace of them. The tusks referred to by Hays are much larger, one of them being 11 inches long and two inches in diameter. In 1852 Warren<sup>4</sup> in his classic memoir described the skeleton of his big mastodon from Newburg, N. Y., which to date has been the largest recorded mastodon. This had one tusk present in the lower jaw and the alveolus for the other partly filled with bone. He examined sixteen lower jaws, in nine of which tusks or alveoli for them were present. He found that the skeletal portions of those with tusks and those without were similar and concluded that the lower tusk is not a specific, but a sexual character; the tetracaulodon forms representing the males, those without the tusks the females. Warren's position has since then been generally accepted. Cope in 1889 says<sup>5</sup> "mandibular tusks are present in the young and occasionally retained to maturity." And Matthew<sup>6</sup> uses the presence or absence of mandibular tusks to determine the sex, the tusk being the mark of the male. In the St. Helena specimen under discussion there were two lower tusks, each 10½ inches long and 2¼

<sup>2</sup> Trans. Amer. Phil. Soc., 1830, new series, Vol. 3, p. 478.

<sup>3</sup> Trans. Amer. Phil. Soc., new series, Vol. 4, 1834, p. 317.

<sup>4</sup> The *Mastodon giganteus* of North America.

<sup>5</sup> American Naturalist, vol. 23, p. 197.

<sup>6</sup> Mammoths and Mastodons, Amer. Museum Guide Leaflet 43, 1915.

inches in diameter. This individual was an adult which had recently reached maturity as shown by the fact that the last molars are in place and worn, and the epiphyses of the bones are fused to their shafts, except in a few cases those of the vertebræ are still free from the centra. The Nine Mile Bottom individual was older, the last molars being more worn and there being no free epiphyses. This latter individual had longer and larger tusks, the larger one being 14 inches long and  $2\frac{1}{2}$  inches

FIG. 2.

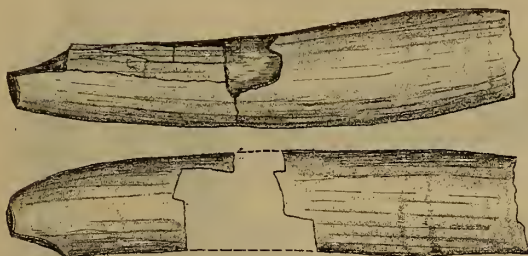


FIG. 2. The lower tusks of the St. Helena Island individual.  $\frac{1}{4}$  nat. size.

*This explanation belongs to fig. 3*

in diameter, and at that the tip is fractured, so that it must in life have been even longer, though not much. These are the largest tusks recorded from the lower jaws.

Each tusk is completely surrounded by a thick layer of enamel clear to the tip. The ends show hard wear, the enamel being worn through and the tips blunt. On both sets, the outer sides are chipped off and worn smooth, so that this was done during the life of the animals. At the base of each is a wide conical cavity showing that the tusks grew continuously. The large size and extensive wear on the ends indicate that these tusks were of considerable functional use to the animals in life, being more worn on the ends than is the case in the upper tusks.

The St. Helena Island specimen has the last two (fifth and sixth) molars in place in the upper jaw. The fifth is the usual six-point tooth, the points being united by transverse ridges. There are no intermediate cusps and the tooth differs in no way except its large size from the usual American mastodon. It is  $4\frac{3}{4}$  inches (118 mm.) long by  $3\frac{5}{8}$  inches (87 mm.) wide as compared with 101 mm. by 77 mm. in the Warren mastodon. The sixth

FIG. 3.

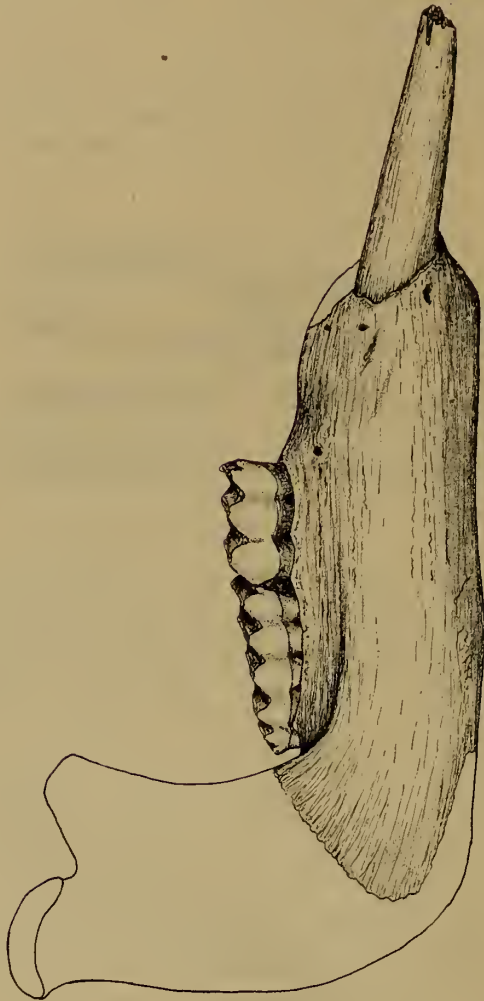


FIG. 3. The lower jaw, showing the two lower tusks in place. From Nine Mile Bottom, So. Carolina.  $\frac{1}{8}$  nat. size. *This belongs to fig. 2*

upper molar has five transverse ridges and a talon, whereas the usual number is four and a talon. The extra ridge is unusual, but has been noted in the case of a couple of specimens from Big Bone Lick, from one found in Virginia, and in the case of the specimen described by Holmes<sup>7</sup> from South Carolina. It seems to go with the southern and larger forms.

The lower jaws on the mounted skeleton are from the Nine Mile Bottom individual. The fifth and sixth molars are present on both sides. The fifth has three transverse

FIG. 4.



FIG. 4. The upper molars to show the five and the small talon.  $\frac{1}{4}$  nat. size.

ridges, and is 104 mm. long by 88 mm. wide as compared with 101 mm. by 77 mm. in the Warren mastodon. The last lower molar is 191 mm. long by 94 wide, while that of the Warren mastodon is 193 mm. long and 77 mm. wide. The Amherst tooth then is not quite so long but considerably wider than in the Warren mastodon. However, the Amherst mastodon is marked by having five transverse ridges and a talon, against four and a talon on the Warren tooth. This is the same increase in complexity characteristic of the upper jaw.

In general such a difference indicates a separate species, but the mastodon had very wide range and I do not favor splitting up the species unless there are several characters differing, for wherever large series of individuals have been studied dental variation of larger amount than here found often appears, as in the case of the skulls of the saber-toothed tigers from Rancho Le Brea. This extra ridge is not a sexual feature, for some of the tusked forms have only four; nor does it depend entirely on size, for the Warren mastodon has only four and is nearly as large. It looks like a meristic variation which appears frequently among the American mastodons.

<sup>7</sup> Post Pleiocene Fossils of South Carolina, 1860, p. 108, fig. 1, pl. 18.

The teeth I have described are the largest cited except one described by Hays (op. cit.), a fifth lower tooth; which is 5.8 inches long, and the sixth is 8.1 inches long. These are in the Wistar Institute, and are the largest mastodon teeth recorded.

The skeleton of the St. Helena mastodon has the usual characters of the American mastodons except that it is of unusually large size. The Nine Mile Bottom individual was slightly larger, about five per cent. The following measurements give a fair idea of the variation in size of the larger mastodons. The Warren mastodon was presumably a male. The same is true of the St. Helena Island individual. The Cambridge mastodon was presumably a female, as was also the one from Crawford County, Ohio.<sup>8</sup>

	St. Helen Is.	Warren	Cambridge	Crawford Co.
Humerus, total length....	39	39	30½	29
smallest circumference				
of shaft .....	19½	18	14	
Radius, length .....	29¼	29	23½	23
breadth at carpal end	7½	6½	6	
Ulna, length .....	34	34	27	25½
least circumference of				
shaft .....	15	14	10½	
Femur, length .....	43	43	36	35
circumference of head	23	22	18	
least circumference of				
shaft .....	18¼	17	13	
circumference of lower				
end .....	34½	34		
Tibia, length .....	28	28	20½	22
circumference at upper				
end .....	31¾	30		
least circumference of				
shaft .....	14	13½		

From the foregoing it will appear that in the case of these two mastodons from South Carolina, we are dealing with individuals of unusually heavy build, even more so than in the case of the Warren specimen. I feel that this is a feature not only of the males but a tendency of the southern individuals, which will appear more clearly as soon as comparative measurements of a considerable number from the south are available.

<sup>8</sup> Horner and Hays, Trans. Amer. Phil. Soc., 1842, new series, vol. 8.

ART. XXIX. — *A Restoration of Neocalamites*; by  
EDWARD W. BERRY.

Evidence is gradually being accumulated that the break between the floras of the Paleozoic and the earlier Mesozoic was not nearly so marked as the older students imagined, and that a considerable number of the plant types that have always been regarded as distinctly Paleozoic were represented by Mesozoic descendants, which in several instances, as in the case of *Calamites*, *Sigillaria* and *Cordaites*, were not very different from their Paleozoic ancestors.

The genus *Neocalamites* furnishes a striking illustration of this dictum. It was proposed by Halle<sup>1</sup> in 1908 for certain forms from the upper Triassic that had previously been referred to the illy understood genus *Schizoneura* of Schimper and Mougeot.<sup>2</sup> The species that are referred to *Neocalamites* at the present time, with their occurrences, are as follows:

*Neocalamites meriani* Brongniart, Keuper of Europe (Bavaria, Baden, Switzerland).

*Neocalamites hoerensis* Schimper, Rhætic of Europe (Baden, Hanover, Sweden). Also recorded from the lower Gresten sandstone of northern Hungary on the boundary between the Rhætic and lower Lias.

*Neocalamites carrerei* Zeiller, Rhætic of Tonkin, South Africa and Sonora, Mexico.

*Neocalamites virginiensis* Fontaine, Keuper of Virginia.

*Neocalamites knowltoni* Berry, Keuper of Virginia.

The most Calamite-like of these species of *Neocalamites* is undoubtedly the one described by the writer<sup>3</sup> from the Triassic of the Richmond basin in Virginia as *Neocalamites knowltoni*. This is strongly suggestive of the *Annularia* type of Paleozoic Calamite foliage, as for example, the widespread type known as *Annularia sphenophylloides*. It differs from *Annularia* in having all the leaves of a whorl similar in size and probably free to the base.

<sup>1</sup> Halle, T. G., Zur Kenntniss der Mesozoischen Equisetales Schwedens. Kgl. Svensk. Vetensk.-Akad. Handl., 43, p. 56, 1908.

<sup>2</sup> Schimper and Mougeot, Mon. Pl. foss. Grès bigarre Vosges, p. 48. 1844.

<sup>3</sup> Berry, E. W., American Triassic *Neocalamites*, Botanical Gazette, 53, pp. 174-180, pl. 17, 1912.

That the restoration presented herewith does not depart from the facts and is not influenced by the resemblance to *Annularia* beyond what these facts warrant may be seen from the photograph of a branch which was reproduced in the paper just cited.

*Neocalamites knowltoni* was a large plant and it seems

FIG. 1.



FIG. 1. Restoration of *Neocalamites knowltoni* Berry. 1/20 natural size.

probable that some of the fragments of large stems, 10 cm. to 12 cm. in diameter, which are abundant in the same deposits as the type, represent the main axis of this same plant. The axis of the type specimen with its leaf-bearing subordinate branches is interpreted as a lateral



FIG. 2.

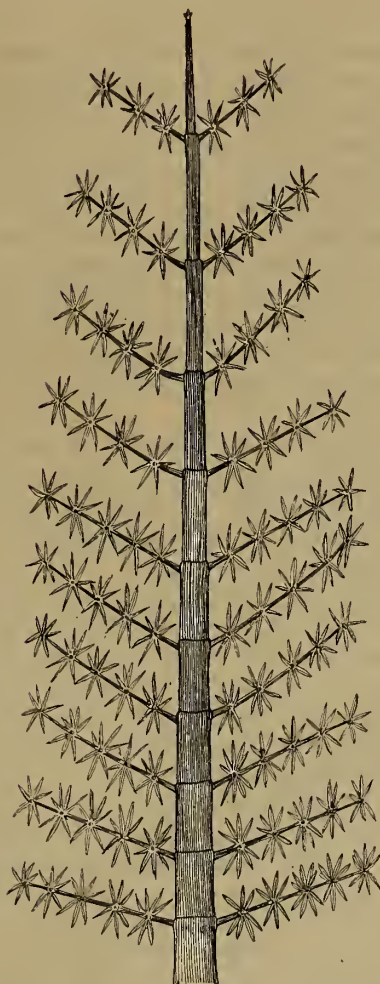


FIG. 2. Restoration of a primary lateral branch of *Neocalamites knowltoni* Berry.  $\frac{5}{12}$  natural size.

branch which was distinctly bifacial in habit. It is impossible to account for the uniform orientation of the numerous whorls of leaves on these distichous branches by appealing to compression during fossilization, which would not act with such uniformity, in fact the similar condition of preservation among the vastly more abundant materials of Paleozoic *Annularias* has led most students to insist that in the latter the plane of the verticils was oblique to the axis in life.

The internodes of *Neocalamites knowltoni* were short; the vascular strands did not alternate at the nodes—a much less important feature than was formerly supposed to be the case; the leaf-bearing branches were normally opposite and superposed, so that the lateral branches were bifacial. Ancestrally the leaf-bearing branches must have been in whorls, but these, except the lateral ones, were apparently gradually suppressed and rarely if ever functionally developed. The leaf-bearing ultimate branchlets were opposite laterals of the whorls of primary laterals of the main stem; they were slender with short internodes and bore whorls of nine or ten, superposed, apparently free, linear-lanceolate, equisized, thick, uninerved leaves.

The restoration of the complete plant shown one-twentieth natural size in fig. 1 represents a plant that would have looked familiar in a Carboniferous swamp environment, in fact the restoration is scarcely to be distinguished from various restorations that have been attempted of the true *Calamites* of the Paleozoic which had the *Annularia* type of foliage. A restoration of a primary lateral branch is shown five-twelfths natural size in fig. 2. This is somewhat more distinctive and brings out clearly the bifacial character of these lateral branches with their crowded leaf-bearing branchlets, although for ease of depiction these are shown in a somewhat less crowded condition than they were in life.

It should perhaps be pointed out that *Neocalamites knowltoni* had shorter internodes, less numerous and relatively very much shorter and broader leaves than the other upper Triassic species that have been referred to the genus *Neocalamites*.

ART. XXX.—*The Origin of Chert*;<sup>\*</sup> by FRANCIS M.  
VAN TUYL.

## INTRODUCTION.

In a recent issue of this Journal<sup>1</sup> there appeared a paper by W. A. Tarr, entitled "Origin of the Chert in the Burlington Limestone." This was based on a careful study of the exposures of this chert in the vicinity of Columbia, Missouri. In this paper Tarr summarizes briefly the prevalent theories of chert formation and concludes that these are inadequate to explain the Burlington chert, the occurrence of which is described in detail. He then introduces a new primary theory of colloidal deposition of this chert, and presents a large body of data in its support. Finally he discusses the possibility of the application of his theory to other cherts and concludes as follows:

"Though the theory advanced to explain the origin of the chert in the Burlington formation has many points in its favor, and would appear to have a wide application, it cannot be taken as explaining all occurrences of chert. More detailed studies of each formation which contains chert are necessary to determine its more general application. The evidence, as gathered from the literature, appears to be favorable to the theory, however.

The notable features of the theory are its explanation of the minor features of the chert as it occurs in the Burlington limestone and its application to the larger occurrences of chert as a rock in the formations from the Cambrian to the Cretaceous. The theory, if its application to those points is correct, should be found applicable to other deposits of chert."

On pages 443 to 449, Tarr presents an array of evidence opposed to the replacement theory of the origin of the Burlington chert, and it would appear that he attributes little importance to this possible mode of chert formation in general.

The writer's experience with cherts has led him to believe that many of them may be most satisfactorily explained upon the basis of replacement, although it is by

<sup>\*</sup> Published with the permission of the Director of the Iowa Geological Survey.

<sup>1</sup> This Journal, vol. 44, pp. 409-452, December, 1917.

no means intended to imply that all occurrences are of this origin. Let us consider certain facts which lend support to this view.

#### EVIDENCES OF REPLACEMENT.

The following features may be listed as favoring the replacement theory:

(1) the occurrence of chert along fissures in limestone; (2) the very irregular shape of some chert nodules; (3) the presence of irregular patches of limestone in some chert masses; (4) the association of silicified fossils and chert in some limestones; (5) the presence of replaced fossils in some cherts; (6) the preservation of structures and textures in some cherts; (7) the failure of some cherts to follow definite zones in limestone formations; (8) the occurrence of silicified oölites formed by the replacement of calcareous ones.

*Chert along fissures in limestone.*—Chert with this relationship has been noted by the writer in the St. Louis limestone in the government quarry at Little Rock, Missouri. In this limestone most of the chert is dark in color, and occurs in the form of nodules and small lenses, but a pinkish variety occurs in a bed 14 feet in thickness, near the top of the formation. This is usually in the form of nodules, but it occasionally follows small fractures for several feet. Frequently these are nearly vertical.

Very similar relations are shown by the pink chert of the St. Genevieve limestone in the exposures between Little Rock and the town of St. Genevieve.

In the Beekmantown dolomite at Ft. Ticonderoga, New York, chert not only traverses the dolomite along fracture lines and bedding planes, but also follows facoidal markings in such a way as to suggest selective replacement.

*Irregular shape of some chert nodules.*—Most chert nodules are rounded or elliptical in shape, and more or less symmetrically developed, but occasionally they are extremely irregular. The most irregular nodule yet encountered by the writer was collected from the Galena dolomite near Galena, Illinois. This is composed of branching and reuniting, rounded pipes of chert with the interstices filled with brownish dolomite. That this was formed by primary deposition seems improbable.

Other irregular masses of chert have been observed in the Mississippian limestones of Iowa, especially in the Montrose chert, which has formerly been referred to the Upper Burlington, but which is clearly basal Keokuk, as indicated by its fauna. This has been carefully studied by the writer in the excavation below the bed of the Mississippi River for the dam at Keokuk, Iowa. The accompanying section will give the reader an idea of the character of the chert at this place. Conditions were exceptionally favorable to the study of the chert here, because weathering had not obscured the original relationships of this material and the limestone.

Section of Montrose Chert in Excavation below bed of Mississippi River at Keokuk, Iowa.

	Thickness		Approximate per-centage of chert
	Ft.	In.	
13. Limestone, dark gray, impregnated with small, irregular patches of chert and chalcedony, and containing small, imperfect calcareous geodes....		8	50
12. Limestone, ash-colored, impure, very fine-grained. Chert correspondingly fine-grained, and occurring as discontinuous seams which usually run parallel to the bedding.....	3	8	30
11. Chert, white, gray, and bluish, dense, with discontinuous bands and irregular pockets of dark gray crinoidal limestone. Occasional geodic cavities in the chert are lined with drusy quartz studded with rhombs of calcite.....	1	3	75
10. Limestone, dark gray, crinoidal, fine-grained, almost entirely replaced by dark gray chert locally.....	1	9	50-75
9. Limestone, impure, very fine-grained, ash colored, with pockets and patches of bluish to whitish chert....	5		33
8. Limestone, dark gray, crinoidal cherty .....		9	33
7. Limestone, dark gray, bearing small crinoid stems, with whitish chert band in middle .....	2		50
6. Limestone, very fine-grained, ash colored, bearing irregular patches of whitish chert .....	1	2	25

	Thickness		Approximate per- centage of chert
	Ft.	In.	
5. Chert, in the form of a layer about 7 inches thick which locally grades into gray crinoidal limestone..		7	25
4. Limestone, fine-grained, with seams and nodules of bluish and whitish chert .....	1	5	25
3. Limestone, gray, bearing whitish fossiliferous chert as large, irregular patches, and irregular discontinuous bands .....		3	50
2. Limestone, fine-grained, with nodules of white and dark colored chert..		1	30
1. Limestone, dark gray, crinoidal, becoming lighter colored, and purer downward; in layers 6 to 22 inches thick, bearing fossiliferous chert in the form of bands, lenses and nodules ....		8	30

The chert of this horizon also outcrops about one-fourth mile northeast of Augusta, Iowa. At this place most of the chert masses are lenticular in shape, but many are very irregular. Furthermore, some of the bands and lenses of chert branch and reunite, and occasionally two lenses are joined by vertical columns.

Somewhat similar relations are shown by the Montrose chert in an exposure in the bank of Lost Creek, about two and one-half miles southeast of Denmark, Iowa, and again in exposures along the small creeks two miles northwest of the same town.

*Patches of limestone in chert.*—The presence of small patches of limestone in chert masses furnishes strong evidence of the replacement origin of all cherts showing them. Many of these are irregular in outline, and their relationship clearly favors the view that they represent residual masses of the limestone which for some unknown reason were not replaced at the time of the surrounding material was silicified. Such limestone patches are most abundant in the larger masses and bands of chert, and have been found in nearly all important chert deposits which have been examined by the writer. They have been observed in the Montrose chert of southeastern Iowa near Augusta; at Keokuk; two miles northwest of Denmark; and at nearly all other localities where this formation has been studied. Such inclusions occur also in the chert beds of the Galena dolomite on the

south side of Eighth Street, a short distance above Bluff Street, at Dubuque, Iowa; in the Fort Atkinson dolomite of Maquokata age, at Fort Atkinson, Iowa; and in the Niagaran chert at Hopkinton, Iowa.

In his description of the Longfellow limestone, of Ordovician age, in the Clifton-Morenci district of Arizona, Lindgren<sup>2</sup> describes microscopic grains of calcite which show a similar relationship. He remarks on the occurrence of chert in that formation as follows:

“The chert occurs in irregular bands or nodules, which under the microscope appear as an aggregate of greatly varying grain. Some of it consists of irregular quartz grains, while other parts contain much cryptocrystalline and fibrous chalcedonic material. Ragged calcite grains lie embedded in this mass, giving distinct evidence of the metasomatic origin of the chert by replacement of calcite by siliceous waters. The normal rocks contain no pyrite, nor other sulphides. The Longfellow limestone, is, as a rule, too siliceous to be used for quicklime or smelting flux.”

*Association of silicified fossils and cherts.*—The presence of an abundance of silicified fossils in the limestone layers associated with chert would appear to furnish strong evidence of the replacement origin of such chert. Such an association has been observed in several Paleozoic formations. For example, it is common in the cherty horizons of the Niagaran dolomite of Iowa. Calvin, long ago, mentioned the relationship of chert and silicified corals in this formation, in Delaware county.<sup>3</sup> In discussing the fauna of the formation and the favorable localities for collecting, he says:

“One of the best known localities in the county is that along Prairie creek, in section 28, of Coffins Grove township. Residual clays and cherts have in places a thickness of several feet, and these are rich in beautifully preserved specimens of silicified corals.”

Again, in his discussion of the cherty phase of the same formation in the vicinity of the town of Hopkinton in the same county, Calvin makes the following statement:<sup>4</sup>

“While there are few rock exposures that do not show more or less of chert, the most remarkable beds of this

<sup>2</sup> U. S. Geol. Survey, Prof. Paper 43, pp. 62-66, 1905.

<sup>3</sup> Iowa Geological Survey, vol. 8, p. 136, 1898.

<sup>4</sup> *Ibid.*, p. 159.

material were seen in some of the rocky knobs protruding through the drift near the northeast corner of section 27, Bremen township. There seems to be here a solid bed of chert, and great detached blocks, eighteen inches thick, and three or four feet in length and width, lie heaped on each other or scattered over the surrounding surface. The large blocks referred to showed no definite traces of fossils, but thousands of tons of silicified corals are embedded in the very thin drift and residual clay covering the adjacent fields. Vast numbers of these have been gathered and piled along the roadway into a rude stone wall, ten or twelve feet wide at base and several rods in length."

The writer has observed a similar relationship in an outcrop of Niagaran dolomitic limestone, ten feet in height, along a small creek, about one-half mile northeast of Hazleton, in Buchanan County, Iowa. Much chert is present in the form of nodules which are most abundant along the bedding planes, and associated with it are many fossils, especially corals. Most of these are silicified, but some of them are still calcareous.

Very similar relations were found in Niagaran limestone at the Flint Rapids of the Ekwan River, in the Patricia district of northern Ontario. At this locality, a bed of coralline limestone contains dark chert nodules, and many of the corals, even specimens situated several feet from the nodules, have been silicified.

This association is illustrated to a lesser degree in the Lower St. Louis limestone of southeastern Iowa. In a thin zone near the top of this limestone, the coral *Lithostrotion canadense* is frequently associated with chert nodules, and is then almost invariably silicified.

*Replaced fossils in chert.*—Many of the cherts which have come to the writer's attention contain silicified fossils, but the structure of these is frequently so obliterated that it is difficult to recognize them. It has been the writer's experience that many of the compact and dense cherts which appear to possess no definite structure will show traces of silicified fossils upon close inspection. These are much more distinct after the chert has been subjected to weathering. At times these included fossils still consist of calcite, or are only partially replaced by silica. In such cases, the calcareous material is soon removed by solution upon exposure, leaving only molds in



the chert. Such molds are very abundant in the Montrose chert of southeastern Iowa.

*Preservation of structure and textiles.*—In exceptional cases chert shows structures and textures almost identical with those of the associated limestones. This is illustrated by some of the cherts of the Montrose chert horizon, and the Keokuk limestone in Iowa. In these formations the texture of crinoidal layers and even the color is frequently retained by the chert. This is especially true in cases where fragments of fossils have not been wholly replaced. In more complete stages of silicification, the structures and textures are usually lost.

Ziegler<sup>5</sup> has described chert concretions in oölitic limestones of Ordovician age, near Bellefonte, Penn. These preserve the original oölitic structure and he interprets them as having been formed by replacement.

*Chert deposits not occupying definite zones.*—If we regard chert deposits as having been formed by primary deposition, we should expect these deposits to appear at the same horizon over a considerable area. This appears to be true in case of some cherty formations, but it does not hold for all. For example, Calvin has shown<sup>6</sup> that the cherts of the Niagaran dolomite of Delaware county, Iowa, occupy no definite horizon. I quote from his description:

“Chert occurs extensively as concretions in the layers of Niagara Limestone or as partings between them. Its distribution, however, both horizontally and vertically, is very erratic. In some localities, at certain horizons, it is present in enormous quantities, making up fully half, or much more than half, of the entire mass of rock exposed; in other localities at the same horizon it may be entirely absent.”

The failure of chert to follow definite horizons in the Keokuk limestone has been demonstrated in connection with the detailed work on the stratigraphy of that formation in Iowa for the State Geological Survey. At some localities certain beds in this formation are filled with chert, but only a few miles away these same horizons may show no trace of this rock, or perhaps only a few scattered nodules. The amount of chert in certain horizons of the Burlington limestone of Iowa shows a similar

<sup>5</sup> This Journal, vol. 34, p. 121 ff., 1912.

<sup>6</sup> Iowa Geol. Sur., vol. 8, p. 158.

variation. This is especially true of the chert in a bed of crinoidal limestone, 18 feet in thickness, at the very top of the formation.

*Significance of beds of silicified oölites.*—It has long been known that under favorable conditions beds of calcareous oölitic limestone may be changed over to siliceous oölitic limestone by replacement. The writer has several specimens of oölitic limestone in his collection which furnish irrefutable evidence of silicification. Nearly every stage in the process is illustrated. Attempts have been made to demonstrate that some siliceous oölites represent primary deposits. While this may be true in certain cases, it certainly cannot hold for all siliceous oölites. If, then, it is demonstrated that oölitic limestone may be silicified under favorable conditions, is it not possible that ordinary limestone may undergo the same transformation?

#### TIME AND PLACE OF REPLACEMENT.

As regards the conditions which favor replacement of limestone it is believed that in the case of most secondary cherts the silicification has proceeded on the bed of the sea, possibly contemporaneously with the deposition of the limestone. If this is true the occurrence of chert nodules within layers of compact limestone is not difficult to explain upon the basis of the replacement theory. An exception to the belief that most cherts are formed very early is furnished by the above described occurrences of chert along fissures. These have clearly been formed subsequent to the recrystallization of the limestone.

The problem of the source of the silica which has been segregated to form secondary cherts will probably always be in dispute. A number of years ago the writer gave this subject some attention while making a petrographic study of the Mississippian cherts of southeastern Iowa. In a brief paper which was published at that time<sup>7</sup> the paucity of the remains of siliceous organisms in the limestone was remarked upon, and the following conclusion was reached:

“It is probable, therefore, that much, if not all, of the silica is of inorganic origin, having been deposited in a colloidal condition upon the bed of the sea while the limestone was being formed.”

Colorado School of Mines.

<sup>7</sup>Proc. Iowa Acad. Sci., vol. 19, pp. 173-174, 1912.

## ART. XXXI.—A Large Parasuchian from the Triassic of Pennsylvania; by W. J. SINCLAIR.

Some years ago, the Geological Department of Princeton University acquired by purchase from Doctor R. S. Stahle some Parasuchian bones collected by him and Mr. R. C. Bair near York, Pennsylvania, from the red Triassic shales of the Newark group. Upon comparison, the bones prove to be referable to the form described by von Huene from the Triassic shale twenty feet below the Palisade diabase sill near Fort Lee opposite New York City, now in the American Museum of Natural History, and named by him *Rutiodon manhattanensis*. The Pennsylvania specimen, No. 11544 Princeton University Geological Museum, comprises both ilia, the left femur, the last presacral and first sacral vertebræ, an incomplete anterior caudal, the centrum of an anterior thoracic vertebra, a thoracic rib and several rib fragments, various scutes, a number of teeth and some indeterminate material. The general characters of the parts are fairly apparent from the accompanying drawings and only such as are not well shown need be described in detail.

The ilium and femur agree so closely in size and structure in the Fort Lee and York specimens that the specific identity of these two is beyond question. As pointed out by von Huene, the femur is of record size for a Parasuchian (43-44 cm. long in the Fort Lee specimen, 41½ in that from Pennsylvania), and, except for its greater curvature, resembles that of the Triassic Theropoda. The ilium is in contact with two sacral vertebræ, as shown by the articular surfaces. Of these vertebræ, only one is preserved, the anterior, seen from in front in fig. 3. The sacral ribs are completely fused with arch and centrum, although traces of suture remain. The base of the rib is expanded anteriorly and articulates with a facet on the hinder border of the centrum of the last presacral vertebra (*s*, figs. 2 and 3). At the distal end of the sacral rib, both anteriorly and posteriorly, there are facets for contact with the ribs of the last presacral and second sacral respectively. In the last presacral (fig. 2), unlike the condition in the smaller *Rutiodon carolinensis* as described by McGregor, the rib is firmly fused with arch

FIGS. 1-4.



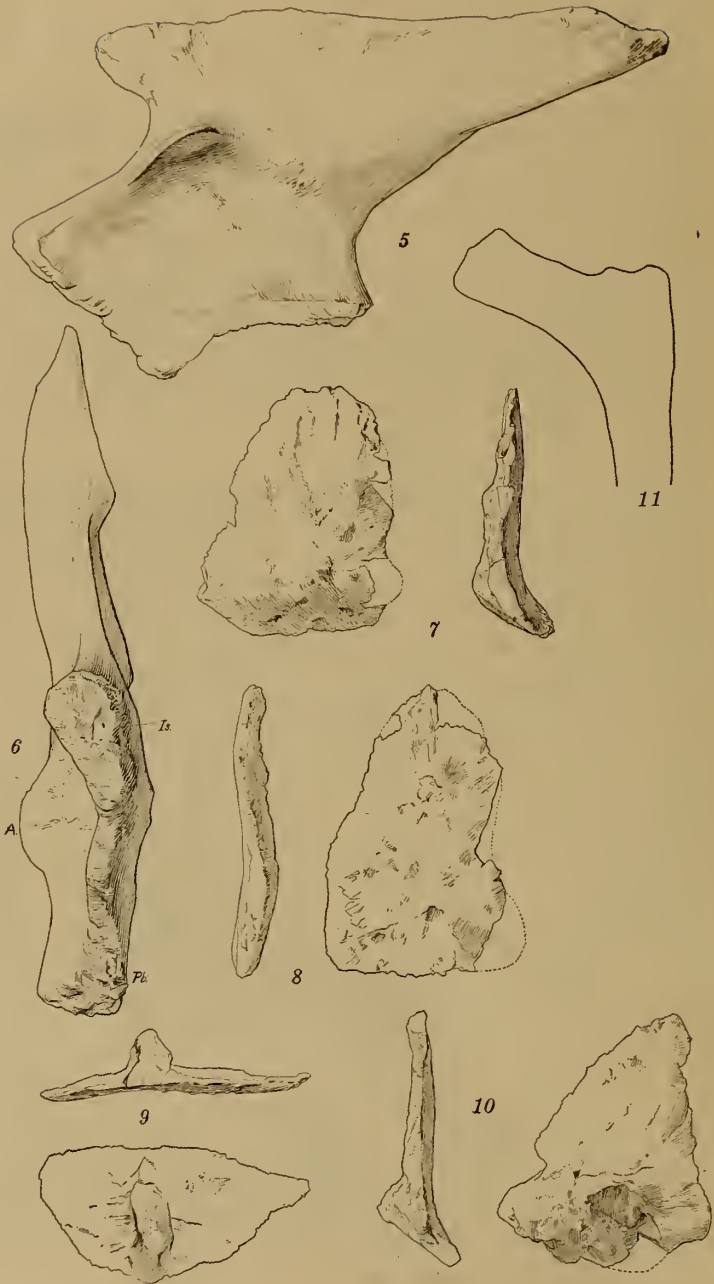
and centrum and curves backward, bearing at its distal end a slightly concave facet for articulation with the first sacral rib, but, owing to crushing, the parts cannot be brought into contact in their present position. In the anterior thoracic vertebræ (not figured), the capitular facet for the rib is placed low down on, and in conjunction with, the anterior rim of the centrum. The tubercular articulation evidently arose from the neural arch, but has been broken off. The articular surfaces of the centrum are concave anteriorly, less so posteriorly. In the last presacral and anterior caudal the centra are concave in front and almost plane behind. Both surfaces of the centrum are plane in the sacral vertebra. The rib, shown in outline in fig. 11, evidently belongs in the anterior portion of the thoracic series, as the capitular and tubercular facets are widely separated.

As no teeth are associated with the type of *Rutiodon manhattanensis*, those belonging to the specimen here described are doubly interesting. They combine characters distributed among various supposedly dinosaurian genera (*Palæoctonus*, *Clepsysaurus*) described by Cope from the Triassic of Phoenixville, Pennsylvania, and as there is every reason to believe that the teeth illustrated in fig 1 belong to a single individual, probably several of the Phoenixville dinosaurs are really Parasuchians and identical with *Rutiodon manhattanensis*. If found separately, teeth of the different shapes here described might well be referred to two or more genera. Some are conical, with the surface of the enamel showing a "silky sculpture of minute raised lines" (Cope), with the base of the crown grooved longitudinally on the outer side and with serrate cutting edges extending almost to the base of the crown, separated by unequal convex surfaces (fig. 1a). In other teeth of similar shape (fig. 1b) serrations may be wanting on the cutting edges and the latter limited to the apical portion of the crown, which is finely

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FIGS. 1-4. *Rutiodon manhattanensis*, No. 11544, Princeton University Geological Museum. 1a-j. Series of teeth showing some of the different forms. In all cross-sections, the lower edge of the outline corresponds to the surface of the tooth seen in the drawing. s indicates position of serrated cutting edges. 2. Last presacral vertebra from the left side. s indicates the facet for contact with the expanded base of the first sacral rib. 3. First sacral vertebra from in front. s indicates facet on expanded rib base for contact with the centrum of the last presacral. 4. Left femur from the outer side.

All figures one-third the natural size.



FIGS. 5-10. *Rutiodon manhattanensis*. 5. Left ilium from the outer side. 6. The same from below showing acetabulum (A) and facets for ischium and pubis (Is, Pb respectively). 7-10. Dermal scutes seen dorsally and from the side. 11. Outline of anterior thoracic rib. All figures one-third natural size.

sculptured with minute raised lines and has a few broad grooves toward the base. In others (fig. 1*d*), of a type agreeing with the description of *Clepsysaurus veatleianus*, the anterior serrate cutting edge exists only on the apical portion of the crown, the posterior edge extending to its base. The crown is rounded in front, oval in cross section at the base, with enamel almost smooth to finely sculptured with raised lines. The cutting edges may be separated by very unequal convex surfaces (figs. 1*d*, 1*f*). Finally, in teeth resembling those from Phoenixville referred to *Palæoctonus*, there are serrate cutting edges both front and rear extending to the base of the crown (figs. 1*h-j*), the outer face of the crown strongly convex, the inner less so, and with the crown showing the same fine sculpturing already noted. Some teeth have a constriction between crown and fang (figs. 1*d*, 1*h*), others do not (fig. 1*c*).

A number of well preserved dermal scutes were collected with the other bones, the series illustrated in figs. 7-10 showing some of the principal types. These are both keeled and unkeeled and have the dorsal surfaces pitted with a coarse irregular sculpture.

## MEASUREMENTS

Femur, greatest length .....	415 mm.
Ilium, length along dorsal margin .....	231
depth, dorsal margin to process between ischial and pubic articular surfaces .....	139
Sacral vertebra, greatest transverse extent across sacral ribs .....	230
middle of ventral surface of centrum to top of spine .....	212
anteroposterior diameter of spine at tip .....	46
length of centrum, anteroposteriorly ..	60
greatest width of expanded rib end, anteroposteriorly .....	69
Last presacral, middle of ventral surface of centrum to top of spine .....	214
anteroposterior diameter of spine at tip	47
length of centrum, anteroposteriorly ..	60
width of rib at tip (approx.) .....	32
Thoracic rib, capitulum to tuberculum, over all .....	86½
greatest diameter of shaft at middle ....	26

- Teeth, Fig. 1a, length of crown above base of enamel (approx.)  
31 mm.; base distorted by crushing.
- Fig. 1b, diameters of base of crown at edge of enamel  
 $10 \times 7\frac{1}{2}$  mm.
- Fig. 1c, diameters of base of crown at edge of enamel  
 $9\frac{3}{4} \times 7\frac{1}{2}$  mm.
- Fig. 1d, diameters of base of crown at edge of enamel  
 $14\frac{1}{2} \times 11\frac{1}{2}$  mm.
- Fig. 1f, diameters of base of crown at edge of enamel  
 $13 \times 11$  mm.
- Fig. 1g, diameters of base of crown at edge of enamel  
 $18 \times 13$  mm.
- Fig. 1h, diameters of base of crown at edge of enamel  
 $19\frac{1}{2} \times 11\frac{1}{2}$  mm.

Princeton University,  
Department of Geology,  
February, 1918.



ART. XXXII.—*Augite from Stromboli*; by S. KOZU and  
H. S. WASHINGTON.

INTRODUCTION.

The crystals of augite that are found loose in the ashes around the crater of Stromboli have been mentioned by several of the geologists who have visited and described the island. It would seem, however, that their optical and chemical characters have not been determined. At least no mention of them is made in the standard handbooks of Dana, Hintze, and Doelter, and we have been unable to find any mention of such data elsewhere in the literature. It was therefore thought that a somewhat detailed study of these crystals along these two lines would be of interest, especially in connection with a projected general study of the pyroxenes from Italian lavas. The optical study was undertaken by Kozu at Tohoku University, Sendai, Japan, and the chemical analyses were carried out by Washington at the Carnegie Geophysical Laboratory at Washington.

The crystals are found loosely scattered, and quite abundant, on and among the fine ashes that cover the slope encircling the active crater terrace.<sup>1</sup> Those examined by us were collected on August 12, 1914, during a visit to the island with Dr. A. L. Day. They came mostly from the ash ridge called Il Liscione, south of the crater terrace, and occur also near the gap between the Serra Vancori and the pile of ancient lava with a recently built hut, which is the head of the usual descent to San Vincenzo. This is called Porta delle Croci, probably, as Bergeat suggests, because of the abundance of the cruciform pyroxene twins. Similar crystals were also present in the masses of scoria and vesicular slag that were ejected by the explosions during our visits to the crater.

The crystals<sup>2</sup> are small, up to 12 or rarely 15 millimeters long, by about one third or one quarter of the length in thickness. In color they are black or brownish black. They show fairly sharp edges, but the faces are dull, though not pitted. Some of them have very slight

<sup>1</sup> For maps cf. H. S. Washington, *Bull. Geol. Soc. Am.*, 28, p. 249, 1917.

<sup>2</sup> Cf. A. Bergeat, *Die aeolischen Inseln*, *Abh. Bay. Ak. Wiss.*, 20, p. 46, 1899.

streaks of lava adherent to the surface, but we saw none of the olivine grains mentioned by Bergeat.

As noted by Bergeat, the forms are very simple. Only the planes  $a(100)$ ,  $b(010)$ ,<sup>3</sup>  $m(110)$ , and  $s(\bar{1}11)$  were observed. In habit they are elongated in the direction of the vertical axis and, with this modification, are represented by figs. 16, 17, 18 on page 354 of Dana's System. Twinning according to  $a(100)$  is common, and inter-penetration cruciform twins, some of them complex and made up of several individuals, are frequent. These have been studied by H. L. Barvir,<sup>4</sup> who recognizes five twinning laws besides that just mentioned. Though this was not studied by us, it would seem that some of the complex individuals are merely fortuitous intergrowths.

The regular cleavage is fairly perfect and the fracture is conchoidal, both giving bright surfaces. In thin splinters and cleavage flakes the color is a light olive-green. Pleochroism is scarcely discernible.

The specific gravity is 3.243 at 19°, as determined on selected fragments used for the analysis, with the pycnometer of Johnston and Adams,<sup>5</sup> which is capable of very accurate results.

#### OPTICAL CHARACTERS.

The three principal refractive indices were determined with Klein's total-reflectometer. The mean values of the observed critical angles for sodium light are as follows:

$$\theta_a = 70^\circ 23.5' \quad \theta_\beta = 70^\circ 58.7' \quad \theta_\gamma = 73^\circ 3.9'$$

The images produced by total reflection were not distinct, owing to hour-glass and zonal structures. However, trials made at different parts of the crystal on different dates showed that the deviations of the indices, caused by the crystal structure mentioned above, fall within the limit of the fourth decimal place. Hence the following values, obtained by computation from the angles given, were taken as the means of the principal refractive indices of the mineral.

$$a = 1.693 \quad \beta = 1.699 \quad \gamma = 1.719$$

$$\gamma - a = 0.026 \quad \gamma - \beta = 0.020 \quad \beta - a = 0.006$$

<sup>3</sup> This is usually very narrow.

<sup>4</sup> Cf. abstract in *Zs. Kryst.*, 39, p. 398, 1904.

<sup>5</sup> Johnston and Adams, *J. Am. Chem. Soc.* 34, p. 566, 1912.

The optic axial angle computed from these indices is  $2V = 57^{\circ} 58.7'$ .

If we compare these refractive indices with those<sup>6</sup> of the augite crystals from the Auvergne and Renfrew, determined by Michel-Lévy<sup>7</sup> and Lacroix<sup>8</sup> respectively, it will be seen that the values for the Stromboli augite are much lower than these. It will also be seen that the birefringences  $(\gamma - \alpha)$  and  $(\gamma - \beta)$  of the Stromboli augite are higher than those of the others, while the value of  $(\beta - \alpha)$  is practically equal to them. Hence the optic axial angle of the Stromboli augite must be smaller than those of the others.

In order to prove this, the measurement of the angle was made by the more direct method, using Wülfing's axial angle apparatus.<sup>9</sup> The mineral section was cut nearly perpendicular to the acute bisectrix and was immersed in a liquid whose refractive index for sodium light was 1.6220. The result obtained is  $2H = 61^{\circ} 24.5'$  for sodium light.  $2V$  computed from  $H$ ,  $\beta$ , and the refractive index of the liquid is  $2V = 58^{\circ} 20.5'$ . Comparing this value with that obtained by computation from the refractive indices, the difference between them is  $21.8'$ , which is so small as to be negligible in this case.<sup>10</sup>

	$\alpha$	$\beta$	$\gamma$	$\gamma - \alpha$	
Auvergne	1.706	1.712	1.728	0.022	Michel-Lévy
Auvergne	1.712	1.717	1.733	0.021	and Lacroix
Renfrew	1.6975	1.7039	1.7227	0.0252	Wülfing

<sup>7</sup> Michel-Lévy and Lacroix, *Les Minéraux des Roches*, 1888, p. 265.

<sup>8</sup> E. A. Wülfing, *Min. petr. Mitt.*, 15, p. 45, 1896.

<sup>9</sup> Thanks are offered to Prof. B. Koto for his kind permission to make use of the instrument in his laboratory at the Geological Institute, Science College, Tokyo, Imperial University.

<sup>10</sup> The effect on the calculated optic axial angle of errors in the refractive indices is given by

$$dV = \frac{\partial V}{\partial \alpha} d\alpha + \frac{\partial V}{\partial \beta} d\beta + \frac{\partial V}{\partial \gamma} d\gamma.$$

Assuming that the refractive indices are each affected by 0.001, we have

$$\frac{\partial V}{\partial \alpha} d\alpha = -2^{\circ} 2' 5'', \quad \frac{\partial V}{\partial \beta} d\beta = +2^{\circ} 57' 58'', \quad \frac{\partial V}{\partial \gamma} d\gamma = -0^{\circ} 35' 48''$$

Hence we see that any one of the three values given above is greater than the difference ( $21.8'$ ) between the optic axial angles obtained by the different methods. Supposing that  $d\gamma = 0.003$  and  $d\alpha = -0.001$  when  $d\beta$  is the only one which is zero, then  $dV = 14.7'$ , which is less than the difference above. In such a case, however, the birefringence  $(\gamma - \alpha)$  must differ to a great extent from that obtained by the total reflectometer. To test this, the compensation method was used as described below and it was proved that the value of  $(\gamma - \alpha)$  must not differ much from 0.027.

From the close agreement of the results obtained by the two different methods, it follows that the relative values of the three principal refractive indices may be accepted as almost correct, so far as these methods are concerned.

The birefringence ( $\gamma - a$ ) was tested by another method, using Babinet's compensator. In order to eliminate the difficulty of determining accurately the thickness of the mineral plate, a crystal of the Stromboli augite and one of a diopside whose indices<sup>11</sup> were carefully determined by the writer (Kozu), were affixed to a glass plate with the side pinacoids (010) parallel to it, and both crystals ground down to equal thickness and with their ground faces in the same plane.

The section thus made was used for the determination of the retardation of light passing through the crystal plates between crossed nicols. The divisions read by the compensator were  $1250 \pm 10$  for the Stromboli augite and  $1256 \pm 10$  for the Sano diopside. Hence, the retardations produced by the two mineral plates are

$$\begin{aligned} 1250 \times \kappa &= 1273.8 \text{ for Stromboli augite,} \\ 1256 \times \kappa &= 1279.9 \text{ for Sano diopside,} \end{aligned}$$

where  $\kappa$  is the constant of the compensator, 1.0190 for the wave length  $589 \mu\mu$ . If we take the value of  $(\gamma - a) = 0.0274$  for the diopside as the standard, the corresponding value for the augite is approximately 0.027. Though the result obtained by this method is not accurate enough for the discussion of the birefringence in detail, it is sufficiently so to show that the value of  $(\gamma - a)$  of the Stromboli augite is higher than those of augites which have been examined by many mineralogists.

The extinction angle ( $c \wedge c$ ) on (010) for sodium light is

<sup>11</sup> The refractive indices of two crystals of this diopside, from Sano, Province Kai, Japan, were determined. They are

$a$	$\beta$	$\gamma$	$\gamma - a$	2V (obs)	Ext. angle ( $c \wedge c$ ) on (010)
1.6732	1.6795	1.7006	0.0274		
1.6729	1.6793	1.7005	0.0276	58° 32.5'	39°

These crystals commonly occur as large, untwinned phenocrysts, reaching 3 cm. in length, in a dike rock. The mineral is quite fresh, the fractured surface showing a dark green color, and a thin section being almost colorless. In some crystals the marginal part is brown and the center green. The determinations were made on the green crystals. The mineral has been considered to be common augite by Prof. K. Jimbo and others, but without giving any optical data. In its lower refractive indices, higher birefringences, and smaller angles of the optic axes and of the extinction, it resembles much more the diopside from Ala and other localities.

43° 20' with the edge (010) $\wedge$ (100) in the acute angle made by (100) and (101).

From this description it will be seen that the Stromboli augite is somewhat different from common augite, in the lower refractive indices, in the higher birefringences ( $\gamma-a$ ) and ( $\beta-a$ ), and in the smaller angles of the optic axes and of the extinction. These characters seem to suggest that the Stromboli augite contains somewhat larger quantities of the diopside molecule than common augite.

#### CHEMICAL CHARACTERS.

The material used for chemical analysis was very carefully selected. A lot of good-sized crystals was coarsely crushed and fragments from the interior, not contaminated by adherent scoria, were picked out by hand under a lens. These were almost quite free from inclusions, very few and small grains of magnetite being seen in some of them. The amount of these was not sufficient to affect the study of the chemical composition. The specific gravity of the selected fragments was 3.243 at 19°. The analysis was carried out by the usual methods. Three precipitations with ammonia were made, to ensure a complete separation of MgO from Al<sub>2</sub>O<sub>3</sub>. TiO<sub>2</sub> and MnO were determined colorimetrically. The alkalis were determined by the Lawrence Smith method. The results are shown in Column A of Table 1.

TABLE I. ANALYSES OF AUGITES.

	A	B	C	D	E	Aa
SiO <sub>2</sub>	50.94	50.13	50.88	51.27	49.42	.849
TiO <sub>2</sub>	0.96	1.91	1.02	0.70	0.55	.012
Al <sub>2</sub> O <sub>3</sub>	3.37	7.08	5.36	3.05	4.28	.033
Fe <sub>2</sub> O <sub>3</sub>	2.05	1.10	1.21	3.08	2.86	.013
FeO	7.41	4.41	4.67	4.34	5.56	.103
MnO	0.10	0.05	trace	0.28	0.10	.001
NiO	n. d.	0.02	n. d.	0.03	n. d.	
MgO	14.59	13.73	13.78	14.21	13.58	.365
CaO	20.34	20.06	22.96	22.58	22.35	.363
SrO	0.08	n. d.	n. d.	none	n. d.	.001
Na <sub>2</sub> O	0.61	1.88	0.50	0.67	1.04	.010
K <sub>2</sub> O	0.18	0.25	...	0.06	0.38	.002
H <sub>2</sub> O+	0.08	0.11	0.34	n. d.	n. d.	
H <sub>2</sub> O—	...	...	...	none	0.09	
	100.71	100.73	100.72	100.27	100.21	

- A. Augite in basalt; Il Liscione, Stromboli (Aug. 12, 1914), H. S. Washington analyst.  
 B. Augite in analcite basalt; Seano, Monte Ferru, Sardinia, H. S. Washington analyst, *Jour. Geol.*, 22, p. 747, 1914.  
 C. Augite in andesitic tuff; Monterano, near Bracciano, Italy, F. Zambonini analyst, *Zs. Kryst.*, 40, p. 57, 1890.  
 D. Augite in syenitic lamprophyre; Two Buttes, Colorado, W. F. Hillebrand analyst. W. Cross, *Jour. Geol.*, 14, p. 168, 1906.  
 E. Augite in shonkinite; Square Butte, Montana, L. V. Pirsson analyst. Weed and Pirsson, *Bull. Geol. Soc. Am.*, 6, p. 410, 1895.  
 Aa. Molecular numbers of A.

Calculated in terms of the generally accepted pyroxenic molecules, the Stromboli augite has the following composition:

Ca(Mg,Fe)Si <sub>2</sub> O <sub>6</sub>	80.12
(Mg,Fe)SiO <sub>3</sub>	7.48
(Mg,Fe)Al <sub>2</sub> SiO <sub>6</sub>	7.03
NaFeSi <sub>2</sub> O <sub>6</sub>	5.46
	100.00

That is, it consists very largely of the diopside molecule (with MgO : FeO = 3.5:1), accompanied by small amounts of the aemite, hypersthene, and Tschermak's aluminous molecules. This composition is in accordance with the conclusions drawn from the optical data above. Whether, with this composition and with its optical characters, it should be called diopside, augitic diopside, or augite, need not be discussed here. For the present the last name has been used, as it is in accordance with Dana's System. The other pyroxenes, of very similar composition, whose analyses are given in the table, are all called augite by their describers. The name diopside may well be reserved for one of the end-members, and augite for intermediate mixtures. It is hoped to take up this question later in conjunction with Dr. H. E. Merwin.

The analyses of the other pyroxenes given, which are considered to be reliable, much resemble in their general features that of the Stromboli mineral. The only notable differences are the somewhat higher values above the others of Al<sub>2</sub>O<sub>3</sub> in B, FeO in A, and Na<sub>2</sub>O in B. As a matter of interesting comparison, though the subject cannot be discussed here, the analyses of the rocks in which they occur are given in Table II.<sup>12</sup> The differ-

<sup>12</sup> The Monterano augite (C) occurs in an andesitic tuff, of which no analysis is given.

ences in composition, as shown by their analyses and as expressed by the names applied to them, containing much the same augites, is rather striking.

TABLE II. ANALYSES OF THE ROCKS CONTAINING THE AUGITES OF TABLE I.

SiO <sub>2</sub>	50.83	51.05	44.85	50.41	46.73
Al <sub>2</sub> O <sub>3</sub>	16.66	15.09	12.55	12.27	10.05
Fe <sub>2</sub> O <sub>3</sub>	1.52	2.07	3.33	5.71	3.53
FeO	6.64	6.88	5.30	3.06	8.20
MgO	6.08	6.52	10.27	8.69	9.68
CaO	10.99	11.34	8.32	7.08	13.22
Na <sub>2</sub> O	2.66	2.53	4.77	0.97	1.81
K <sub>2</sub> O	2.05	2.02	0.72	7.53	3.76
H <sub>2</sub> O +	0.36	0.15	2.01	1.80	1.24
H <sub>2</sub> O —	...	...	0.95	0.46	...
TiO <sub>2</sub>	0.81	0.83	5.07	1.47	0.78
P <sub>2</sub> O <sub>5</sub>	1.61	1.44	1.17	0.46	1.52
MnO	0.12	0.13	0.07	0.15	0.28
NiO	n. d.	n. d.	0.23	0.04	n. d.
	100.33	*100.12	99.60	†100.42	‡100.97

\* Includes ZrO<sub>2</sub> = none, SO<sub>3</sub> = 0.06, Cr<sub>2</sub>O<sub>3</sub> = 0.05.

† Includes V<sub>2</sub>O<sub>5</sub> = 0.03, BaO = 0.23, SrO = 0.06. ‡ Includes Cl = 0.18.

A. Basalt scoria; August, 1914, Stromboli, H. S. Washington analyst. F. A. Perret, this Journal, 42, p. 451, 1916.

B. Basalt scoria; November, 1915, Stromboli, H. S. Washington analyst. F. A. Perret, *ibid.*

C. Analcite basalt; Scano, Monte Ferru, Sardinia, H. S. Washington analyst, Jour. Geol., 22, p. 748, 1914.

D. Syenitic lamprophyre; Two Buttes, Colorado, W. F. Hillebrand analyst. W. Cross, Jour. Geol., 14, p. 163, 1906.

E. Shonkinite; Square Butte, Montana, L. V. Pirsson analyst. Weed and Pirsson, Bull. Geol. Soc. Am., 6, p. 414, 1895.

Tohoku University, Sendai, Japan, and  
Carnegie Geophysical Laboratory, Washington, D. C.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *The Use of Metallic Silver as a Reducing Agent in the Volumetric Estimation of Iron.*—GRAHAM EDGAR and A. R. KEMP, of Throop College of Technology, Pasadena, Cal., have devised a new process for the volumetric determination of iron, which appears to be very convenient and rapid, and according to the numerous experimental results of the authors to be exceedingly accurate. A solution of ferric sulphate containing 0.2 g or less of iron and about 3 cc of concentrated sulphuric acid in a volume of about 75 cc is treated with from 3 to 5 g of precipitated metallic silver which has been boiled with dilute sulphuric acid and well washed. The mixture may next be boiled and then treated with a small excess of ammonium thiocyanate solution, or the latter may be added to the cold mixture at once with shaking for usually 3 to 12 minutes until the liquid is colorless. The cooled or already cold liquid is then filtered and the residue is thoroughly washed with water. To this filtrate a little ferric sulphate solution is added to serve as an indicator, an excess of silver nitrate solution is added, which discharges the color, and then, without filtering, the iron is titrated with decinormal potassium permanganate solution.

Since in this process silver is dissolved only by the ferric sulphate and not by the dilute sulphuric acid, it was found possible to modify the process with just as accurate results by employing a standard solution of ammonium thiocyanate and finally titrating back with standard silver nitrate solution. In this case it is essential to carry out the reduction in the cold. By the use of standard solutions it is possible to titrate with permanganate and then to check the result in the same sample by titrating the excess of silver nitrate with thiocyanate. When both ferrous and ferric sulphates are present in the original solution the thiocyanate titration measures the latter while the permanganate determines both. The process is not interfered with by titanium, but vanadium is reduced to the quadrivalent condition, while molybdenum, chromium and hydrochloric acid cause irregularities.—*Jour. Amer. Chem. Soc.*, 40, 777.

H. L. W.

2. *The Iodimetric Estimation of Copper and Iron.*—H. LEY has devised an interesting volumetric method for determining these two metals when they are present together. Both cupric and ferric salts liberate iodine from potassium iodide in the presence of acetic acid. When it is desired to estimate the copper the iron is precipitated as ferric phosphate by the addition of sodium phosphate solution, the liquid is then acidified with



acetic acid, potassium iodide is added, and the resulting free iodine is titrated with sodium thiosulphate solution. The ferric salt is determined by taking another portion of the original solution, making it acid with acetic acid only, adding potassium iodide and titrating as before. The difference gives the amount of iron. Aluminium and zinc do not interfere, so that the method has a wide application.—*Chem. Zeitung*, **41**, 763 (through *Jour. Chem. Soc.*). H. L. W.

3. *Chemistry in the Home*, by HENRY T. WEED. 12mo, pp. 385. New York, 1915-16 (American Book Company).—This text-book, which is intended for use in high schools, is accompanied by a loose-leaf laboratory manual containing directions for experiments with forms for reporting the results.

The course of study presented by this book is a rather extensive one for its grade, and it aims to train the pupils in scientific thinking and to give them a fund of information concerning the chemistry of everyday things related to industries and the home. Although the fundamental chemical theories are clearly presented, this side of the subject is not treated as fully as is often the case with high school text-books. On the other hand, the practical applications of chemistry that are of everyday importance are treated with unusual fullness, and it appears that these topics should be of much interest and value to the pupils. The subject of foods receives particularly extensive treatment, including elaborate tables of the compositions and calories produced by many articles of diet, tables of daily rations and diagrams of the costs of food constituents in various materials.

The book and the laboratory manual are well illustrated, and they give the impression that they present an unusually interesting and practical course of chemical study. The author states that constant effort has been made to keep the language and style simple, and in this he seems to have been generally successful, but here and there the simple explanations appear to be somewhat unsatisfactory. For example, after mentioning the luminiferous ether as an extremely rarified substance with which we believe all space to be filled, stating that it is a totally different substance from the liquid used by surgeons, and indicating that it is impossible to pump more ether into a vessel, or out of it, than it already contains, because it would leak through the sides of the vessel, he says, "If we could magnify a drop of water sufficiently, it would somewhat resemble lemon jelly, filled, not too closely, with caraway seeds. The lemon jelly would represent the ether, and the caraway seeds the particles (molecules) of water." He then goes on to show the similarity of wave-motion in the luminiferous ether to the well-known quiver of lemon jelly on the table. H. L. W.

4. *Chemistry, First Stage*; by F. P. ARMITAGE. 16mo, pp. 80. London, 1918 (Longmans, Green and Co.).—This very

small book by the Chief Science Master of St. Paul's School, England, describes a few elementary chemical demonstrations, gives simple laboratory experiments and questions connected with them, and gives a few notes describing chemical substances and processes. The course laid out is exceedingly elementary, and no chemical symbols or equations are employed. It deals with facts and omits theories. As far as it goes, however, the book is clearly written and presents interesting experiments.

H. L. W.

5. *Publications of the Yerkes Observatory, Vol. III, Parts I and II.* Chicago, 1903 and 1907 (University of Chicago Press).—Part I is entitled "The Rumford Spectroheliograph of the Yerkes Observatory," by GEORGE E. HALE and FERDINAND ELLERMAN. The spectroheliograph was invented in 1889 and it was designed for the study of the chromosphere and prominences. Since instruments of this kind do not form a part of the regular equipment of physical laboratories and as the Rumford spectroheliograph is a specially fine example of this type of apparatus, it may not be superfluous to give a brief account of the salient features and chief dimensions of this accessory of the 40 in. Yerkes refractor.

A spectroheliograph is essentially a monochromatic illuminator so arranged as to photograph the sun's image by continuous successive exposures taken after the fashion of a very narrow focal-plane shutter. With large instruments it is not feasible to follow the ideal plan of translating the spectroheliograph bodily across the solar image, hence the alternative equivalent method of simultaneously moving this image across the collimator slit and the photographic plate across the camera slit has to be followed. The diameter of the solar image formed by the 40 in. refractor is 7 in. so that the curved slits of the spectroheliograph have the uncommonly great length of 8 in. For economic reasons the collimator and camera objectives of the Rumford instrument are Voigtländer portrait lenses of linear aperture 6.25 in. and equal focal lengths. The favorable location of the declination motor on the great telescope caused it to be used, instead of the right ascension motor, to effect the simultaneous translation of the solar image and the photographic plate. Since the curve connecting the focal length of the refractor with the color is very steep in the violet and ultraviolet, the spectroheliograph is so mounted that it can be racked as a whole along the optic axis of the telescope, thus enabling sharp images of a chosen spectral line to be thrown on the collimator slit. This unilateral slit can be rotated around an axis perpendicular to the plane of its jaws until the tangent line at the center of its length becomes parallel to the refracting edges of the prism train or to the rulings of a plane grating. Since the focused heat from the sun would cause the jaws of this slit to expand and close at the center it was necessary to fix

an auxiliary screen at a short distance from the incidence side of the collimator slit. This screen, of course, is divided by a cut the edges of which are parallel to, but farther apart than, the corresponding edges of the neighboring slit. For photographing the radiations from the chromosphere and prominences at the sun's limb the direct light from the solar disk is cut out by an occulting disk having a diameter slightly less than that of the image formed by the telescope objective. This occulting screen is situated in front of the slit screen and it is moved at exactly the same rate as is imparted to the solar image by the declination motor.

After the light emerges from the collimator lens as a parallel beam it experiences one reflection at a plane mirror and then passes through a train of two prisms at minimum deviation. The total deviation is  $180^\circ$  so that the optic axes of the collimator and camera systems are parallel, and the entire spectroheliograph assumes the compact form of the letter U. On emerging from the second prism the various wave-lengths of the dispersed beam of light are brought to their respective foci in the focal surface of the camera lens. The second or camera slit is unilateral, it can be rotated around an axis normal to the plane of its jaws, and it can be translated in a plane perpendicular to the principal axis of the camera objective so as to allow one, and only one, narrow spectral line to pass through it to the photographic plate. If the first slit were straight and the second slit were given the necessary curvature (arising from oblique refraction through the prism train) the image of the sun would be greatly distorted, flattened on one side and drawn out on the other. This distortion is entirely eliminated by employing lenses of the same focal length and by making the radii of curvature of the collimator and camera slits twice as great as would be the radius of curvature of the images corresponding to a straight first slit. The direction and speed of translation are the same for both the photographic plate and the solar image on the first slit. When the dark (Fraunhofer) solar lines are used it is necessary to increase the resolving power of the dispersing system. This is accomplished by suitably adjusting a plane speculum grating between the mirror and the first prism. The grating employed has 20,000 lines to the inch on a ruled surface  $2\frac{5}{8}$  by  $3\frac{3}{4}$  inches. For studying the flocculi the *H* and *K* lines of calcium are usually found to yield the best results. Certain lines due to hydrogen, the radiations  $\lambda 4226.9$  Ca and  $\lambda 4383.7$  Fe, and a few others, are sometimes used to advantage.

In Part I, the detailed description of the Rumford spectroheliograph is appropriately followed by a preliminary account of the results obtained with this instrument. The discussion relates to the nature and minute structure of calcium flocculi,

to the form and extent of calcium floeculi at various elevations above the photosphere, to dark calcium floeculi, and to hydrogen floeculi. The text is admirably illustrated by fifteen beautiful full-page plates reproducing the original negatives of faculae, floeculi, sun-spots, etc.

Part II is entitled "The Spectrum of the High Potential Discharge between Metallic Electrodes in Liquids and in Gases at High Pressures," by GEORGE E. HALE and NORTON A. KENT. For lack of space, it is not possible to do justice to this valuable contribution to spectroscopy. Suffice it to say that, in general, the spark lines from iron electrodes in water and in solutions of sodium chloride are broadened and greatly reversed as compared with the spectrum in air at standard pressure. The lines produced under water are also much weakened and reversed by increasing the self-induction in the circuit. In air and carbon dioxide the lines are reversed and shifted toward the red by increasing the gas pressure. In general, for the same line, the shift is directly proportional to the increase in pressure. The graphs corresponding to lines of the same spectral type have equal slopes. The descriptive matter of Part II is illustrated by eight plates of the same degree of excellence as characterizes those of Part I.

*Volume IV, Part I* (1917) has the title *Stellar Parallaxes Derived from Photographs Made with the Forty-Inch Refractor*. It contains the following papers: An introductory note by the Director, EDWIN B. FROST; parallaxes of forty-two stars, by Frederick Slocum and S. Alfred Mitchell; parallaxes of seventeen stars, by Oliver J. Lee and Alfred H. Joy; parallaxes of twenty-six stars, by Lee and Georges Van Biesbroeck; index of parallaxes for 131 stars; an appendix on the investigation of a new screw measuring machine at the Yerkes Observatory, by Lee and Hannah B. Steele; and two full-page plates. H. S. U.

6. *Axial Aberrations of Lenses*.—In a recent paper by E. D. TILLYER and H. I. SHULTZ an account is given of the results of an investigation which was undertaken to determine the errors of a complex lens system that affect the definition of the image near the center of the field, and to compare the different types of lenses on the market with respect to their corrections for central definition and their applicability to the various purposes for which they might be used. The lenses studied fall under the following principal classes: Photographic lenses of relatively large aperture; projection lenses for stereopticon and motion picture work; telescope lenses of short focal length and large aperture, and telescopic systems. Hartmann's method has been extended so that it is now possible to obtain from one set of measurements the data for all the important central errors, which are—spherical aberration, zonal variation of the equivalent focal length, and axial and oblique departures from achromatism. The results of the method as applied to a complete

telescope are discussed, and are shown to be independent of the accommodation of the observer. Seventeen sets of curves for as many different lenses are given, and an illustrative discussion of one set of graphs is presented.—*Bull. No. 311, Bureau of Standards*, pp. 341-369, 1917.

H. S. U.

## II. GEOLOGY AND MINERALOGY.

1. *Publications of the United States Geological Survey*; GEORGE OTIS SMITH, Director.—Recent publications of the Survey are noted below. See earlier vol. 44, pp. 405-407, Nov., 1917:—

Thirty-eighth Annual Report of the Director. Pp. 176, 2 pls. Noticed on p. 421, May, 1918.

TOPOGRAPHIC ATLAS.—Fifty-seven sheets.

PROFESSIONAL PAPERS.—No. 93. Geology of the Navajo Country, a reconnaissance of parts of Arizona, New Mexico, and Utah; by H. E. GREGORY. Pp. 161, 34 pls., 3 figs. Noticed on p. 145, Feb., 1918.

No. 96. The Geology and Ore Deposits of Ely, Nevada; by A. C. SPENCER. Pp. 189, 15 pls., 4 figs.

No. 98. Shorter Contributions to General Geology, 1916; DAVID WHITE, Chief Geologist. Pp. 401, 102 pls., 46 figs., 2 inserts.

No. 99. Chemical Analyses of Igneous Rocks published from 1884 to 1913, with a critical discussion of the character and use of analyses (a revision and expansion of Professional Paper 14); by H. S. WASHINGTON. Pp. 1201, 1 plate, 3 figs. Noticed on p. 238, March, 1918.

No. 105. Hydraulic-Mining Debris in the Sierra Nevada; by G. K. GILBERT. Pp. 154, 34 pls., 33 figs.

No. 108. Shorter Contributions to General Geology, 1917. Chapters F, G, H, I, K.

MINERAL RESOURCES of the United States for 1917. Numerous advance chapters.

BULLETINS.—No. 597. Geology of Massachusetts and Rhode Island; by B. K. EMERSON. Pp. 289, 10 pls., 2 figs.

Nos. 651, 654. Spirit Leveling; R. B. MARSHALL, Chief Geographer.—651, Ohio, 1898-1916. Pp. 456, 2 pls.—654, Nevada, 1897-1916. Pp. 91, 1 plate.

No. 656. Anticlines in the southern part of the Big Horn Basin, Wyoming (a preliminary report on the occurrence of oil); by D. F. HEWETT and C. T. LUPTON. Pp. 192, 32 pls., 12 figs.

No. 658. Geologic Structure in the Cushing Oil and Gas Field, Oklahoma, and its relations to the oil, gas, and water; by CARL H. BEAL. Pp. 64, 11 pls., 4 figs.

No. 659. *Cannel Coal in the United States*; by G. H. ASHLEY. Pp. 128, 8 pls., 27 figs.

No. 665. *Bibliography of North American Geology for 1916*, with subject index; by JOHN M. NICKLES. Pp. 172.

Also separate chapters of Nos. 660, 661, *Economic Geology*, 1917, parts I, II. No. 690, 691, *do.*, 1918, parts I, II.

WATER SUPPLY PAPERS.—*Surface Water Supply of the United States*; NATHAN C. GROVER, Chief Hydraulic Engineer. Nos. 389, 390, 1914, Parts IX and X. Nos. 403, 404, 406, 408, 1915. Parts III, IV, VI, VIII. Also Nos. 430, 445, *Hawaii*: 430, July 1, 1913–June 30, 1915; 445, July 1, 1915–June 30, 1916. Nos. 434, 438, 1916. Parts IV, VIII.

No. 418. *Mineral Springs of Alaska*; by GERALD A. WARING. Pp. 114, 16 figs., 9 pls.

No. 424. *Surface Waters of Vermont*; by C. H. PIERCE. Pp. 218, 2 figs., 14 pls.

2. *United States Bureau of Mines*; VAN H. MANNING, Director.—The following publications have recently appeared. See earlier, p. 80, Jan., 1918.

BULLETINS.—No. 110. *Concentration experiments with the siliceous red hematite of the Birmingham District, Alabama*; by JOSEPH T. SINGEWALD, JR. Pp. 91, 1 pl., 47 figs.

No. 135. *Combustion of coal and design of furnaces*; by HENRY KREISINGER, C. E. AUGUSTINE, and F. K. OVITZ. Pp. 144, 1 pl., 45 figs.

No. 137. *The use of permissible explosives in the coal mines of Illinois*; by J. R. FLEMING and J. W. KOSTER. Pp. 110, 8 pls., 17 figs.

No. 139. *Control of hookworm infection at the deep gold mines of the Mother Lode, California*; by J. G. CUMMING and J. H. WHITE. Pp. 53, 1 pl., 5 figs.

No. 140. *Occupational hazards at blast-furnace plants and accident prevention*; by F. H. WILLCOX. Pp. 155, 16 pls.

No. 148. *Methods of increasing the recovery of oil from sands*; by J. O. LEWIS. Pp. 128, 4 pls., 32 figs.

No. 153. *The mining industry in Alaska in the calendar year 1916*; by S. S. SMITH. Pp. 91.

No. 155. *Oil-storage tanks and reservoirs*; by C. P. BOWIE. Pp. 76, 21 pls.

No. 158. *Cost accounting for oil producers*; by C. G. SMITH. Pp. 123.

No. 159. *Abstracts of current decisions on mines and mining*; by J. W. THOMPSON. Pp. 111.

Also a number of Technical Papers.

3. *The Geology and Ore Deposits of the Virgilina District of Virginia and North Carolina*; by F. B. LANEY. Pp. 176, 20 pls., 16 figs. Bulletin XIV, Virginia Geological Survey. T. L. WATSON, Director. Charlottesville, 1917.—The region covered by this report embraces some of the most important copper dis-

tricts of the Eastern United States. A detailed study is given of the ore deposits in parts of Halifax, Charlotte and Mecklenburg Counties, Va., and in Granville and Person Counties in North Carolina. The investigation covers an area of some 550 square miles.

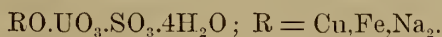
4. *Tin Deposits near Irish Creek, Virginia*; by HENRY G. FERGUSON. Pp. 19, with figs. Bulletin XV-A, Virginia Geological Survey, T. L. WATSON, Director. Charlottesville, 1918.—This bulletin is important in view of the extreme shortage of tin in the United States at the present time. The author gives an account of the Rockbridge County deposits, which are among the most promising in the country, and concludes "it may be said that the district offers some hope of reward for systematic development of the discovered veins, and a possibility that prospecting in the area of hypersthene granodiorite along the Blue Ridge in this vicinity may uncover other deposits. The best indication of a possible tin deposit appears to be the presence of the greisen-like alteration product of the granodiorite, which everywhere appears to accompany the tin-bearing veins. Where float of fragments of this muscovite-fluorite rock is found on the hillsides it should be followed up carefully. Panning of the soil of the hillside may also lead to new discoveries. Areas in which the granodiorite has suffered extensive epidotization will probably be less favorable than those in which the rock is unaltered."

5. *New Mineral Names*; by W. E. FORD (communicated—continued from vol. 44, pp. 484-486, December, 1917):—

**Collbranite.** D. F. Higgins, Econ. Geol., 13, 19, 1918. At the Suan mine, Hol Kol, Korea, in the marble walls of the ore bodies, there occurs a black acicular mineral in stellate aggregates. This has been considered as ilvaite, but from microscopic evidence, it is thought to be a highly ferriiferous pyroxene of the hedenbergite type. Named after Mr. H. Collbran and his son Mr. A. H. Collbran, who have made the Suan mine a producer.

**Gilpinit.** E. S. Larsen and G. V. Brown, Am. Min., 2, 75, 1917. Probably monoclinic. In aggregates of minute lath-shaped crystals. Probably tabular parallel to  $b$  (010) and elongated parallel to the  $c$  axis. Under the microscope shows two sets of twinning lamellæ, nearly at right angles to each other. Color pale greenish yellow to canary-yellow.  $H. = 2$ .  $G. > 3.32$ . Optical axial angle nearly  $90^\circ$ . Dispersion strong. At times optically — with  $\rho > v$ , in other cases + with  $\rho < v$ .  $c$  parallel to elongation and  $a$  normal to  $b(010)$ . Extinction angle  $c \wedge c = 5\ 1/2 - 8^\circ$ .  $a = 1.576$ ,  $\beta = 1.596$ ,  $\gamma = 1.614$ .

Comp.—A hydrous sulphate of uranium and copper.



Infusible or difficultly fusible but turns black on heating. Readily soluble in dilute acids.

From Gilpin County, Colo., coating a green copper ore or a black uraninite and associated with gypsum. In many cases had been labeled johannite or uranopilitite from which, however, it is distinguished by both chemical and optical properties. A specimen from Cornwall, England, showed similar optical characters and is probably also gilpinite.

**Mullanite.** E. V. Shannon, this Journal, 45, 66, 1918. Orthorhombic? In slender prisms, showing a number of indistinct planes. In some cases terminated by a face at right angles to prism zone. At times fibrous. Cleavage,  $c(001)$  and  $b(010)$  distinct. Color, steel-gray. Streak, brownish black.  $H. = 3.5$ .  $G. = 6.3-6.4$ .  $Comp. = 5PbS.2Sb_2S_3$ . Found at Gold Hunter mine, near town of Mullan, Coeur d'Alene district, Idaho, and from Iron Mountain mine, near Superior in western Montana. Analyzed from both localities. At Iron Mountain mine associated with epiboulangerite and sphalerite. Found in quartz at both mines. Named after Capt. John Mullan, a pioneer army engineer of the region.

**Tungstenite.** R. C. Wells and B. S. Butler, Jour. Wash. Ac. Sc., 7, 596, 1917. Earthy to foliated structure. Color and streak, dark lead-gray.  $H. = 2.5$ , marks paper easily.  $G. = 7.4$ .  $Comp. = WS_2$ . Insoluble in HCl or  $HNO_3$ . Decomposed by aqua regia or by fusion with sodium carbonate. Occurs at the Emma mine, Little Cottonwood district, Salt Lake County, Utah. Associated with quartz, galena, pyrite, tetrahedrite and argentite.

**Colerainite.** Eugene Poitevin and R. P. D. Graham; Canada Dept. Mines, Geol. Sur., Mus. Bull., 27, 66, 1918.—Hexagonal. In extremely thin and minute hexagonal plates. Often grouped in rosettes or spherical masses.  $H. = 2.5-3$ .  $G. = 2.51$ . Luster vitreous to pearly. Colorless or white. Optically +. Refractive index about 1.56.  $Comp. = 4MgO.Al_2O_3.2SiO_2.5H_2O$ . B. B. first whitens and disintegrates with a tendency to exfoliate but finally fuses quietly to a white glass. Moistened with cobalt nitrate and heated turns blue. In C. T. whitens, decrepitates and at a high temperature yields much water. Decomposed with difficulty by hydrochloric acid. Occurs in cavities as a drusy coating on white massive material which has a similar composition and properties and which is probably largely made up of the same mineral. Found on the dumps at the old Standard mine and Union pit in the asbestos and chromite district of the Black Lake area, Quebec. The name is derived from Coleraine township in which the mineral was found.

6. *The Geological Society of London.*—The Murchison Medal has recently been awarded by the Geological Society to the veteran Canadian paleontologist, DOCTOR G. F. MATTHEW, together with ten guineas, "as an acknowledgment of his valuable work on the stratigraphy and paleontology of the lower Paleozoic rocks of North America . . . His work has been



distinguished throughout by a happy combination of stratigraphical skill with paleontological knowledge."

The last annual report of this society—the oldest geological society of the world—states that it has a membership of 1231 fellows, besides 36 foreign members, and 34 foreign correspondents. The following Americans have received elections to the society: E. S. Dana (since 1894), G. K. Gilbert (1895), C. D. Walcott (1898), W. H. Dall (1898), S. W. Williston (1902), J. P. Iddings (1904), H. F. Osborn (1904), W. B. Clark (1904), F. Springer (1904), H. S. Washington (1904), J. M. Clarke (1906), F. W. Clarke (1912), W. Cross (1912), T. C. Chamberlin (1914), W. B. Scott (1914), C. R. Van Hise (1914).

7. *A Geological Handbook to Northern France*.—A geological handbook to Northern France with numerous illustrations has recently been prepared by Professor WILLIAM M. DAVIS of Cambridge. This book has been approved by the geographical committee of the National Research Council as of value to our soldiers abroad. It will be issued by the Harvard University Press and a large number of copies will be distributed free at the various cantonments; it will also be placed on sale.

### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *National Academy of Sciences*.—The annual meeting of the National Academy was held April 22-24, at the Smithsonian Institution, President Charles D. Walcott presiding. A program of unusual interest was presented, containing reports of important researches, summaries of war work connected with the National Research Council (a committee of the Academy), and the William Ellery Hale lectures on "The Beginning of Human History from the Geologic Record," by Dr. John C. Merriam, of the University of California. At the annual dinner held Tuesday evening at the Cosmos Club, the following medals and awards were presented: The *Comstock Prize* of \$1,500 for discoveries in magnetism and electricity was awarded to Samuel Jackson Barnett, Ohio State University; the *Draper Medal* for discoveries in astronomical physics, to Walter Sydney Adams of the Mount Wilson Solar Observatory; the *Daniel Giraud Elliot Medal* and Honorarium, for work in paleontology and zoology, to Frank M. Chapman, American Museum of Natural History, New York City.

The following gentlemen were elected to membership: Robert G. Aitken, Lick Observatory; George F. Atkinson, Cornell University; George D. Birkhoff, Harvard University; Percy W. Bridgman, Harvard University; Stephen A. Forbes, University of Illinois; Charles E. Mendenhall, University of Wisconsin; John C. Merriam, University of California; Henry N. Russell, Princeton University; David W. Taylor, Rear Admiral, and

Chief of the Bureau of Construction and Repair; John R. Freeman, Providence; Charles J. Herrick, University of Chicago; Ludwig Hektoen, University of Chicago; Frank B. Jewett, Western Electric Company; Walter Jones, Johns Hopkins University; Irving Langmuir, General Electric Company.

The titles of papers presented are as follows:

The effects of a prolonged reduced diet on twenty-five college men:

I. FRANCIS G. BENEDICT: On basal metabolism and nitrogen excretion.

II. WALTER R. MILES: On neuromuscular processes and mental condition.

III. H. MONMOUTH SMITH: On efficiency during muscular work and general muscular condition.

W. S. HALSTED: The partial occlusion of great arteries in man and animals.

S. J. MELTZER: The favorable effect of subcutaneous injection of magnesium sulphate in tetanus. The possible danger of intravenous injection of magnesium sulphate. The antagonistic and curative action of calcium salts in these cases.

HENRY FAIRFIELD OSBORN: The Liberty field hospital ward; adapted to American overseas summer and winter service.

SIMON FLEXNER: The war and medical research.

EDWARD KASNER: Conformal geometry.

S. J. BARNETT: Magnetism by rotation.

A. A. MICHELSON: On the correction of optical surfaces.

W. W. CAMPBELL: Some recent observations of the brighter nebulae.

R. A. MILLIKAN: Physical researches for the war.

F. W. CLARKE: Notes on isotopic lead.

LAWRENCE J. HENDERSON: The physico-chemical properties of gluten.

T. WAYLAND VAUGHAN: Correlation of the Tertiary formations of the southeastern United States, Central America and the West Indies.

W. M. DAVIS: Coast survey charts and fringing reefs of the Philippine Islands.

HENRY FAIRFIELD OSBORN and WILLIAM K. GREGORY: Recent researches on the skeletal adaptations and modes of locomotion of the Sauropod Dinosaurs.

CHARLES D. WALCOTT: Some additional data on the Cambrian Trilobites.

C. R. VAN HISE: The development of Governmental regulations during the world war.

C. HART MERRIAM: The big bears of North America.

G. H. PARKER: The growth of the Pribilof fur-seal herd between 1912 and 1917.

HENRY H. DONALDSON: A comparison of the growth changes in the nervous system of the rat with the corresponding changes in man.

ROBERT M. YERKES: Measuring the mental strength of an army.

ARTHUR G. WEBSTER: Some considerations on the exterior ballistics of a gun of 75 miles range.

C. G. ABBOT: Periodicity in the variation of the sun.

EDWIN H. HALL: Ionization in solid metals.

E. L. NICHOLS and H. L. HOWES: On the types of decay of phosphorescence.

J. P. IDDINGS: Biographical memoir of the late Arnold Hague.

JOHN M. CLARKE: Biographical memoir of the late William Bullock Clark.

2. *Carnegie Institution of Washington*; ROBERT S. WOODWARD, President. *Year Book*, No. 16. Pp. xvi, 358; illustrated.

Washington, 1918.—Even the Carnegie Institution has felt during the past year the pressure due to the conditions brought on by the war in Europe. It is gratifying to read the assurance by Dr. Woodward as to the general situation. This he expresses as follows:

“While public attention is properly engrossed in the exigencies of national and international affairs, it is well to recall that periods like the present have not been less fruitful in discoveries and advances of permanent value to our race than the periods of more peaceful activities. The course of human evolution has not run smoothly, and it does not appear to be destined to become frictionless in the near future. Neither has the general trend upward of mankind been unaccompanied by depressing reversion to the instincts of barbarism. But these sinister facts, so painfully verified in contemporary history, are mitigated by other facts which show that the essentials of progress will be the last to disappear in any possible reversion and that they may even survive and flourish amid the ruins of empires. Thus, while the ideas of Alexander and Cæsar and the long line of Greek and Roman statesmen, philosophers, and poets are still properly held to be highly worthy of critical study, it is plain that they are of a far less permanent character than the ideas, for example, of the Alexandrian school of scientists, whose contributions to knowledge relate to principles coextensive with the universe at large as well as with that small part of it wherein we happen temporarily to reside. Similarly, it is now equally plain that the ideas of the chemist Berthollet and the mathematician Fourier who, about a century ago, stood with Napoleon before the pyramids while the centuries looked down upon them, have proved incomparably more worthy of preservation and development than the ideas of that autocrat. He and his statecraft perished, but the savants of his day, conspicuously typified by Lagrange, Laplace, and Lavoisier, have won increasing and world-wide regard with the lapse of time.”

The department of the Institution which has felt the war pressure most is probably the Geophysical Laboratory, which has been called upon to exert all its energies to provide the government with an adequate amount of optical glass. Dr. Day accounts here, in detail, his vigorous efforts in this direction and in concluding remarks that: “it has proved possible, in rather less than six months, to produce optical glass from American materials in all the required varieties and at a rate sufficient to meet the current requirements. The quality is also adequate for the present emergency. Of the limitations which still confront us, none at the moment appears insurmountable, though the productions of melting-pots suitable for optical glass is a serious problem which may require considerable time for its solution. It is our present purpose, with the approval of the Trustees of the Institution, to continue the investigation

until the United States shall be entirely independent of foreign sources of supply for optical glass."

Aside from this subject, however, and in the line of the direct work of the Laboratory, Dr. Day has some statements to make which seem so important that they are quoted here at length.

"A careful appraisalment of the situation to-day, after ten years of activity, reveals the fact that the tangible grounds for anxiety about the *accessibility* of the problems which we then confronted are now for the most part dissipated. It has been adequately demonstrated that the temperature conditions which prevailed during the formative period upon the surface of the earth are well within the reach of known methods of accurate measurement; that the effects of pressure as a factor in the formation process are insignificant compared with those of temperature, except where volatile ingredients are concerned; that the established generalizations regarding solutions and the laws of physical chemistry apply broadly to silicate solutions as well as elsewhere; that the multiplicity of participating substances is not a prohibitive difficulty when these are appropriately grouped for study; and now, finally, that the fact that some of the substances which participated in the formation process were volatile and disappeared in part from the system in the process of its development is no longer an absolute bar to the competent study of such systems. All this was necessary, and with appropriate detailed development may be expected to prove sufficient for the competent study of rock formation with its allied problems and applications which was the purpose of the founders of the Geophysical Laboratory.

"The second direction in which the interests of this laboratory have advanced materially during the year is in the progress of volcano study. Perhaps for the first time in the history of volcano observation, laboratory-trained men have stood upon the brink of an active volcanic basin, fully equipped to measure the temperature distribution prevailing deep down in the boiling lava at their feet and to collect appropriate samples both of the liquid and gaseous ingredients which through their inter-reaction so largely determine the character of volcanic phenomena. The materials so collected still remain to be studied and no inference at this time can properly forecast the conclusions which will be reached as a result of these studies, but the opportunity presented this year was a rare one and the fact that trained men and appropriate facilities were on the ground to take advantage of it forms one of the bright pages in the history of this elusive science. It will be recalled that volcanoes offer the only opportunity now remaining to science to study the phenomena accompanying the formation of igneous rocks in nature, and by far the greater portion of these must remain entirely inaccessible to man because of the violence of their activity."

A second department which has been affected by the war conditions is the Mt. Wilson Solar Observatory, the director of which, Dr. Hale, has been called upon to devote his energies to the Department of Science and Research of the Council of National Defence. Fortunately the assistant director has been able to fill his place and the record of the year's work is notable, both in amount and scientific importance.

Other departments are able to record a large amount of work accomplished: as that of Botanical Research, Dr. D. T. MacDougal, director; and that of Experimental Evolution, Dr. C. B. Davenport, director.

Attention is to be called also to the Department of Terrestrial Magnetism which has now issued the third volume of its researches of the magnetic survey of the earth, carried on through the past ten years to near the end of 1916. It is interesting to add that the aggregate length of all the cruises of the Galilee and of its successor the Carnegie, to March 2, 1917, is more than 239,000 nautical miles or about eleven times the circumference of the earth. The extent and accuracy of the observations made has resulted in giving a remarkable amount of information not only in regard to the magnetic elements, but also their annual changes over the ocean. A map shows both the extensive cruises of the vessels mentioned and the land stations at which observations have been taken during the period of 1905-1917.

An important change in the Institution is the discontinuance of the Department of Economics and Sociology which, by mutual assent, was decided upon by the trustees at their meeting of December, 1916.

Recent publications of the Carnegie Institution are the following (see earlier, 44, 408, 1917):

No. 225. Contributions to Embryology. Vol. V, No. 14. The development of the cerebro-spinal spaces in pig and in man; by LEWIS H. WEED. Quarto. Pp. 116. 17 plates.

No. 249 II. The interferometry of reversed and non-reversed spectra. Part II; by CARL BARUS. Pp. 146; 97 figs.

No. 252. Papers from the Department of Marine Biology of the Carnegie Institution of Washington. ALFRED G. MAYER, director. Volume XII. Eleven papers. Pp. v, 258; with plates and text figures.

No. 254. European Treaties bearing on the history of the United States and its Dependencies to 1648; edited by FRANCES GARDINER DAVENPORT. Pp. vi, 387.

No. 255. Club types of Nuclear Polynesia; by WILLIAM CHURCHILL. Pp. 173; 3 figs., 17 pls.

3. *Carnegie Foundation for the Advancement of Teaching, Twelfth Annual Report of the President, HENRY S. PRITCHETT, and Treasurer, ROBERT A. FRANKS.* Pp. vi, 154. New York City (576 Fifth Avenue) 1917.—The Carnegie Foundation has been

carrying on its work now for some twelve years and the present time is an important one as bringing to a conclusion the results of the study and experience of this period. Briefly, as noted in the reports immediately preceding, this has been to show the inadequacy of free pensions, such as were planned at the outset, as contrasted with a contributory system. "The present report records the provision of new funds amounting to thirteen million dollars, which, together with the interest from the present endowment, will enable the Foundation to expend fifty million dollars during the next forty-five years in concluding its present system. This will gradually be replaced by a contributory system of insurance and annuities provided by *The Teachers Insurance and Annuity Association*, an insurance company incorporated under the laws of the State of New York for the provision at cost of insurance and annuities for university and college teachers all over the country."

In addition to presenting this special subject in detail, which will be at once recognized as the greatest advance which the Foundation has made, the subject of pensions in general is also discussed as they are administered elsewhere. Further there are given these results in the line of Educational Inquiry. The special studies here which the Foundation has now in hand relate to legal education, to engineering education, to the training of teachers in Missouri and of federal aid for vocational education.

On the financial side, it is stated that for the year ending June 30, 1917, the total endowment was \$15,414,000 with an accumulated surplus of \$1,361,000. The total number of allowances now in force is 336, the total number of widow's pensions 144, the general average being \$1,540. The total number of allowances granted since the beginning of the Foundation is 736, the total expenditure for this purpose having been \$5,457,000.

4. *Soil Physics and Management*; by J. G. MOSIER and A. F. GUSTAFSON. Pp. xiii, 442, with 202 illustrations. Philadelphia, 1917 (J. B. Lippincott Co.).—The authors of *Soil Physics and Management* have succeeded in the difficult task of preparing a useful text book for colleges without destroying its value for the practical agriculturist. The chapters on Water of Soils (186-221), Control of Moisture (222-277), Alkali Lands and their Reclamation (278-292), Tillage (325-354) are particularly commendable. An interesting feature of the book is the agricultural charts in the Appendix.

H. E. G.

5. *Elementary Economic Geography*; by CHARLES R. DRYER. Pp. 415, 222 illustrations. New York, 1916 (American Book Co.)—Economic geography is defined by Dryer as "a study of the different kinds of environments as they affect the different ways in which men get a living, and deals with natural resources, industries, and the distribution of useful products." In harmony with this viewpoint the world-wide relations of resources, life, and economics are presented (9-92) and followed by a carefully worked out presentation of resources and human rela-

tions within the United States (93-394). The use of this book in the eighth grade or the first year of high school would enrich the curriculum and add interest to the studies of later years.

H. E. G.

6. *A Laboratory Outline of Neurology*; by C. JUDSON HERICK and ELIZABETH C. CROSBY. Pp. xii, 120, illustrated. Philadelphia and London, 1918 (W. B. Saunders Company).—The laboratory course in neurology developed at the University of Chicago is here presented in outline. This outline is written from the same point of view as the senior author's Introduction to Neurology and, as in the latter, emphasis is laid upon the correlation of the functional with the morphological relationships of the different parts. Reference is made throughout the Outline to an extensive bibliography and it is emphasized that the student should read up each topic "as completely as possible from both the anatomical and the physiological standpoints." This is desirable, for without especial stimulus too many students are content with the letter of the textbook to the complete exclusion of all other literature on the subject.

C. H. G.

#### OBITUARY.

DR. GROVE KARL GILBERT, the geologist, one of the senior members of the staff of the U. S. Geological Survey, died at Jackson, Mich., on May 1st. He would have attained his 75th birthday on May 6th. His career as a geologist began on the Ohio State Survey in 1869; he was with the Wheeler Exploring Expedition from 1871-74 and with the survey under Powell from 1874-79. When the western surveys were united into the present national organization in 1879 he became, and has since remained, one of its geologic staff. He was one of the best known of American geologists and had received merited recognition at home and abroad. A keen observer and a patient and accurate worker he was distinguished by a comprehensive grasp of detail, united to great power of generalization, and a noted originality of mind. The great opportunities offered by the unexplored West he took full advantage of, and in several fields of geology, notably in physiography, his pioneer work was of the most fundamental kind, serving indeed as a basis upon which much of the structure of the present science has been built. Personally a man of the highest character, and of great amiability of disposition, his loss will be keenly felt by a host of friends and colleagues. It is intended to present a more extended notice of him in a later number.

DR. GEORGE JENNINGS HINDE, the well known English paleontologist, died on March 18, at the age of seventy-nine years. He lived for seven years at Toronto, and traveled widely in Canada and the United States. During his long life he remained interested in American paleontology and paleontologists, and he will be remembered for his great work on fossil sponges, and his many papers on fossil radiolarians, conodonts, annelid jaws, etc.

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Ph. Min. 4: 9 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, and a \$1.00 diamond, in improved trays ..... 3.00

Ph. Min. 5: 9 specimens, each in tray 1 x 1 inch, all in oak box..... 1.00  
Small diamond, 75 cents extra.

Ph. Min. 6: 9 specimens, each in tray  $1\frac{1}{2} \times 1\frac{1}{2}$  inches, all in oak box..... 1.25  
Small diamonds, 75 cents extra; larger diamonds \$1.50 to \$5.00 each.

#### Tenacity :

Ph. Min. 7: 5 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays.... 1.00

### II. COLLECTION ILLUSTRATING SPECIFIC GRAVITY.

Ph. Min. 8: 25 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays... \$20.00

### III. COLLECTIONS ILLUSTRATING GENERAL OPTICAL CHARACTERS OF MINERALS.

#### Diaphanelyt :

Ph. Min. 9: 5 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays.... \$ 1.50

#### Color :

Ph. Min. 10: 72 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays .. 35.00

#### Luster :

Ph. Min. 11: 16 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays... 7.50

#### Miscellaneous Characters Depending Upon Light, including Play of Colors, Change of Colors, Opalescence, Iridescence, Tarnish, Asterism, Schillerization, Fluorescence, Phosphorescence :

Ph. Min. 12: 16 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays .. \$15.00

### IV. COLLECTIONS ILLUSTRATING CHARACTERS DEPENDING UPON HEAT.

#### Fusibility :

Ph. Min. 13: 6 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays.... \$ 1.50

Ph. Min. 14: 6 specimens, each in tray  $1\frac{1}{2} \times 1\frac{1}{2}$  inches, in oak box ..... 1.25

### V. COLLECTION ILLUSTRATING CHARACTERS DEPENDING UPON ELECTRICITY AND MAGNETISM.

Ph. Min. 15: 17 specimens, averaging  $2\frac{1}{2} \times 2\frac{1}{2}$  inches, in improved trays... \$12.50

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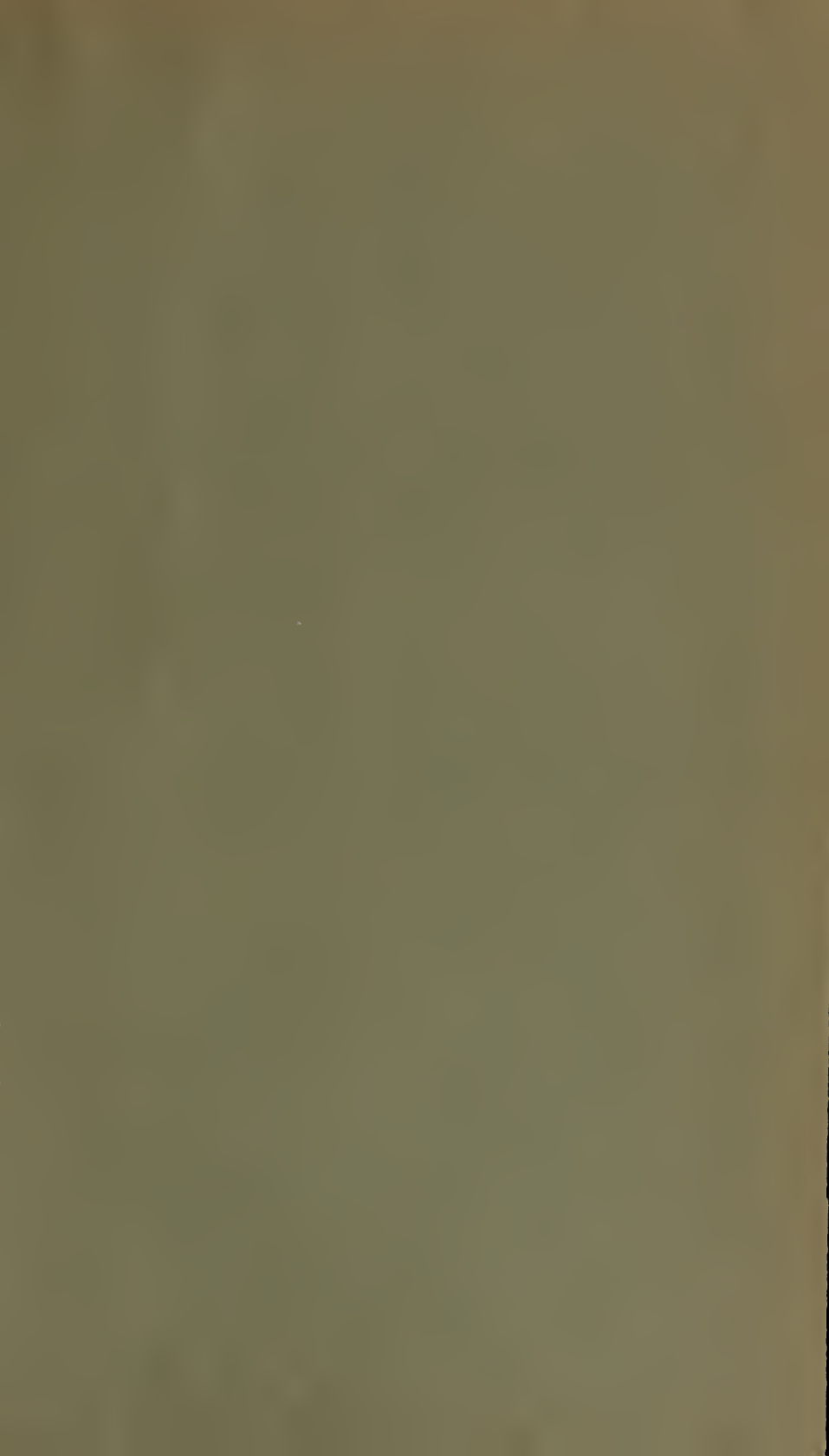
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