

### THE

# AMERICAN JOURNAL OF SCIENCE.

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## AMERICAN JOURNAL OF SCIENCE

### [FOURTH SERIES.]

### ART. I.—A Revised Geologic Time-table for North America; by CHARLES SCHUCHERT and JOSEPH BARRELL.

### Preface.

THE writers, having to teach historical geology to elementary classes in the two undergraduate schools of Yale University, have felt the need of a table of geologic chronology which shall assemble in brief space and in proper order and proportion the more significant facts of earth history. Some kind of a time-table is indeed very necessary for the elementary student in order that he may coördinate the mass of data which accumulates day by day, but not all textbooks contain such tables, and those which are given are either brief or may not express the latest views. The ideas of geologists as to what such a table should indicate grow with succeeding years. This perhaps has been especially true of the past decade.

A table of geologic ages and events is needed also as a wall chart for teaching other branches of the earth sciences, such as physical geology and organic evolution, where references must be made to the periods and eras, and it was for the purpose of such a wall chart that the table accompanying this paper was first drawn up. It is thought, however, that the results may be of use beyond this University.

The senior author is chiefly responsible for the general discussion of principles and for the portion of the chart embracing post-Proterozoic time. The junior author is responsible for the pre-Cambrian discussion and classification.

### Part I. Post-Proterozoic Time (C. S.).

The well-known and beloved Californian geologist, LeConte, in reviewing the progress of geology during the Nineteenth Century, said: Through this century a gradual movement of

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what might be called the center of gravity of geological research took place westwardly, until now, at its end, the most productive activity is here in America. This is not due to any greater ability on the part of American geologists, but to the superiority of their opportunities. Dana has well said that *America is the type continent of the world*. All geological problems are expressed here with a clearness and a simplicity not found elsewhere (1900).

North America is the type continent, because of its simplicity of geologic structure, not only throughout its vast extent but as well throughout the geologic ages. The other continent of the northern hemisphere, on the contrary, is more complex in structure, since only in the course of time, through the welding together of several land masses by orogenic (mountain-making) forces, has Eurasia been formed. A typical continent, Dana states, is "a body of land so large as to have the typical basin-like form,—that is, independent mountain chains on either side of a low interior" (1895).

A great part of the northern half of North America has the form of a depressed shield, and has been well named by Suess the Canadian Shield (see fig. 1). Here in the rocks is revealed nearly all of its pre-Cambrian history, events which took an eternity to accomplish, and the details of which will always remain far less clear than those of the southern half of the continent. Though the geological history recorded in the surface rocks of most of the United States and Mexico is far shorter and later in time, the sediments are better preserved and contain an abundance of fossils accessible to geologists. To the north, and more especially to the south and west of the shield, lie vast depression fields, or neutral and subpositive areas, which have tended through the geologic ages to lie slightly below sea-level. Because of this low level, the sea has often spread over these fields and recorded there the post-Proterozoic events.

To the east of the southern depression field occur the basal remnants of a mountain system, exposing a complex of metamorphic and igneous rocks and showing that again and again through geologic time majestic mountain ranges, studded at times with volcanoes, have been raised above the present basal structures. These mountains lay on the western side of Appalachia, the eastern shore of which has in the course of time sunk deeply into the abysses of the Atlantic ocean.

The western depression field is a very wide one, bordered on the west by another old land, Cascadia, which faced the Pacific, but of this land little is as yet known. These latter two regions were the scene of tremendous geologic activity, the struggle for dominance between the continent and the

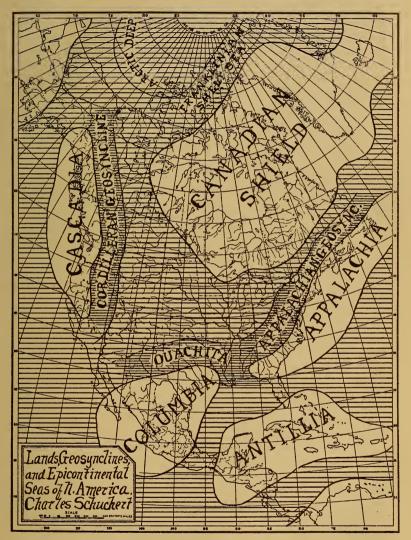


FIG. 1.

FIG. 1. The North American continent in Paleozoic time, showing in white the lands or positive elements, in darkest shading the geosynclines or subpositive elements, and in lighter shading the extensive neutral medial area. father of oceans, in which the land was victorious, but only after building and rebuilding marginal bulwarks of chain upon chain of mountains, marked by volcanoes from Alaska to Mexico City. This western region now embraces the grand Cordilleras of the continent and also all of Mexico.

Hence we see that North America has the form of an elongate basin, widely open at the north and nearly closed at the southeast; though in the latter place there stood for a long time a transverse mountain range, the Ouachitas, of which only the bases now remain, and these in part concealed by later mantles of sediments. The geology of the Arctic shelf sea is not yet well known, but the sediments in the folded United States mountains are of considerable thickness and extent. Between these elevated margins lies the great basin, much of which has always lain near sea-level, and over it, entering through the gaps between the marginal uplands, the oceanic waters have again and again flowed widely, to form interior shallow These floods have come from the four quarters, most seas. widely from the Pacific and Arctic, least from the Atlantic, and most persistently from the Mexican mediterranean. The partial deciphering of these multitudinous events in their orderly sequence, in addition to the similar unravellings in Eurasia by the geologists of that continent, has given the very imperfect geologic time-table here presented.

The basis of chronology.—The fundamental principle underlying all geologic endeavor is evolution, the oscillating but progressive changes wrought in the long ages, changes whose interpretation leads to the history of the earth—the science of Historical Geology.

The earth develops as a whole, but the record is far from being everywhere alike; even if it were so, it would not be wholly accessible for study, because sheet upon sheet of rock hides others below, and the atmospheric agencies have destroyed much through erosion. Likewise, the more complete stratigraphic record buried under the oceans is hopelessly lost. Therefore the completed geologic record will eventually be put together from the evidence of all places which are at present land, mainly, however, from the northern hemisphere, because this is preëminently the land hemisphere. Such history is largely brought about through the periodic adjustments of continental and oceanic areas settling down upon a shrinking nucleus, and in so doing crushing the crust into great folds which tend to rise, especially upon the margins of the continents. Broad movements of a vertical nature also take place at times, whereby the continents, being underlain by lighter rock matter, tend to warp up and restore the elevations destroyed by erosion, while the sea floors, loaded with sediment, tend to sink.

During the past twenty years much has been done in deciphering the historical geology of North America, and as this chronology needs to be adapted as far as possible to the older European sequence, it is well to put the scattered information into better order. The scheme here offered for North America does not as a rule go into detail beyond the "systems" of rocks or the "periods" of time, and it is also our desire to stand by the old and well-known terminology as far as possible.

We may well begin by repeating the questions asked by Suess in 1885: What constitutes a period and what determines its beginning and its end? How does it happen that these stratigraphical subdivisions extend over the whole earth? His answer then was: "If we could assemble in one brilliant tribunal the most famous masters of our science and could lay this question before them, I doubt whether the reply would be unanimous, I do not even know if it would be definite." While in this Twentieth Century we are coming much nearer to a definite answer, and see more clearly the several principles which serve as a basis for determining the earth's history, still a fixed geological chronology is not yet established.

The evidence of fossils.—Fossils furnish the first step in the process of stratigraphic correlation. Their testimony is checked by the geographic distribution of the sediments that contain them and the relation of the latter to the formations beneath and above them (superposition). These principles are easy to state but very difficult to apply accurately to so great a land mass as North America, and even though approximately a century of work has been devoted to it, the ground is only about half covered by detailed studies.

In general, sedimentation is a slow process, and by the time one foot of average rock accumulates, probably a thousand generations of marine invertebrates have appeared, passed their life on to their descendants, and vanished. Under relatively constant surroundings, it is held that but little if any recognizable change in the species is developed, but as the environment of the organisms is continually changing, even though only to a minor extent, these physical alterations cause the faunas (animal associations) at the very least to alter their combinations and to shift from place to place. They die out in one area, but gain a foothold elsewhere, and although this to-and-fro migration is slow when measured in years, yet in stratigraphy the faunal assemblages appear as if suddenly introduced. This fact has always excited the interest of the paleontologist, and he has explained the phenomena according to the view of his generation. Once he thought them due to special creations of new types or recoinages of old, but since the time of Darwin they have been looked upon as slow evolu-

### Schuchert and Barrell—Revised Geologic

tions of which glimpses only are obtained in the fragments of the geologic record; or they may be due to shiftings of faunas, or to geologically sudden migrations into the continental or interior seas from the permanent or outer oceanic reservoirs, the continuous realms of marine organic evolution. The fossil faunas from the oceans spread as fast as the sea transgressed the land, and, for practical purposes in stratigraphy, may be accepted as having appeared simultaneously in widely separated places.

In all faunas there are more or less large percentages of persistent species. These static and irregularly evolving forms cannot therefore be used as fossils determinative of limited geologic time. Although on the one hand the localized species are of the greatest value in the stratigraphy of small areas, the new forms which attain wide dispersal are, on the other hand, of most significance in correlating the time stages in separated regions, for they are the progressives, the time heralders, as distinguished from their variously conservative associates. Therefore in the chronologic correlation of the stratified rocks most dependence is put upon a few species, known as "guide fossils," together with the collateral evidence of associated forms. These guide fossils may be of any class of organisms and may be represented by many or few individuals. The more abundant they are in individuals, the greater is their geographic distribution apt to be, and the more easily do they mark a geologic formation. On the other hand, the wider the geologic distribution of a guide fossil, the less can it be depended upon for detailed chronology.

Locally successive, but distinct geologic faunas derived from the same oceanic realm usually have a more or less ancestral or direct genetic relationship with one another. In some cases they are the returning, slightly altered descendants of an older fauna, in other words, "recurrent faunas." Therefore the possibility of a "break" in sedimentation between such superposed faunas is easily overlooked and the time value of the recurrent faunas underestimated. Or, two locally superposed faunas may be totally dissimilar, not only in the species but even in the majority of the genera, and yet the time break between them be a comparatively short one, the reason for this unlikeness being that the two faunas are transgressions from different oceanic realms and have therefore had independent ancestral developments.

A geologic "period" begins as a time of quiet, following a disturbance and uplift of the land. The time of quiet is marked by the erosion of the land and the spread of shallow seas. Waterways broaden and unite across a continent, only to be drained and destroyed by the crustal unrest with conti-

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nental uplift which marks the close of periods. During the middle age of the periods, when the oceanic transgressions are greatest, the faunas throughout a continent are most alike in composition and have the greatest number of species in common; they have therefore been called by Chamberlin "cosmopolitan faunas." Again, faunas of the same age are most dissimilar in the early times of the periods, when the oceanic realms are most localized and the transgressions upon the continents are smallest. Similar restriction also takes place during the closing age of the periods, though at these times there are many more hold-over species from the earlier, widely dispersed faunas; in other words, there is no marked introduction of new organic types during the recession of the continental seas. However, when the oceans again spread over the continents, a long time has elapsed, many of the old familiar forms have disappeared under the stress of restricted habitat, and new forms have been developed, the prophets of a new period and indicative of the next trend in evolution.

The appearance of identical fossil genera of land animals, and more especially of mammals, in two continents that are now widely separated, is often taken as proof of the former connection of the two areas by land bridges that have since vanished beneath the sea, or of migration by routes in high latitudes which are no longer available because of the present frigid climates. This method of correlation is undoubtedly correct in the main, but as genera apparently alike have been developed under similar stimuli from unrelated stocks ("parallel development" and "homœomorphy"), single appearances on two con-tinents cannot be accepted as migrant individuals from a common center of evolution and dispersal until the ancestral relationship (phylogeny) has been established in each case. In the same way, single marine invertebrate genera appearing in two or more oceanic realms at the same time may be parallel developments or independent evolutions from different species of the same genus.

When the lands are least overlapped by the oceans, the fresh waters more often record themselves, and especially is this true in the areas where mountains have just been born. Unfortunately, however, these, the "continental deposits," are frequently devoid of fossils, because here the great bulk of organisms live, not in the sediments, under the protective covering of water, but on the dry land, where after death, instead of receiving natural burial, they are exposed to the atmosphere and thus either eaten by other animals or attacked by bacteria and so reduced through further oxidation into the elements from which they came. In the same way, plants fail to fossilize. As for animals living in the fresh waters, they often leave traces of themselves in the form of teeth, scales, or scattered bones, but their remains are apt to be very fragmentary, due to the streaming action of the rivers; besides, they are so unchanging in specific form through successive periods as to be of little value in chronology. The animals of the dry land, however, are the best of history markers, because they evolve far more quickly under the most changeable and trying of environments. Their remains unfortunately are rarely entombed in the sediments, and as a rule those preserved are the unfortunates that have fallen victims to accidents through drowning, or miring in soft places, especially in times of drought, or have been suffocated through protracted outpourings of volcanic ashes.

The evidence of periodic oceanic spread .- The primary principle of period value underlying geologic chronology is the recognition of the times when the surface of the earth and the oceanic level are in decided motion. This movement may be of small and narrow extent, as the result of horizontal compression (local or orogenic); or its vertical effects may be felt over areas of great magnitude (epeirogenic). Not only do the lands move up and down, the sum of this motion being in the main upward (positive movements), but it is also now clear that the ocean bottoms are periodically more or less in motion, with the sum of their movements downward (negative movements). For these reasons, the oceanic level in relation to the continents is inconstant, and therefore the marine spreadings over the lands, with their concomitant sedimentation, are not only variable in time, but as well in geographic extent. On the other hand, when the lands protrude more than usual above the strand-line, the oceans naturally overlap the continents least widely and make at such times limited marine stratigraphic records, which are restricted to the margins and their embayments and to the persistent axes of depression, the geosynclines of the continent. As the oceans and seas are all connected one with another, and are as well the receivers of most of the land wash or detritus, it follows that a displacement of the strand-line anywhere, through any cause, must be transmitted to all marine waters. Then under these waters there is continuous sedimentation, and they abound in more or less of evolving life that is most advantageously situated for burial and preservation; hence the marine stratigraphic sequence is the least broken of the several kinds of historic records accessible to geologists.

It is now known that the oceans have spread periodically and more or less widely over the North American continent, the areal extent of which is about 8,300,000 square miles. These floods occurred hardly at all during the Cenozoic, 1 per cent to 6 per cent of the continent being then covered; four times widely during the Mesozoic, the submergences reaching 3 per cent to 33 per cent; and, with the maximum spread, apparently eleven times during the Paleozoic, when 1 per cent to 47 per cent of the continent was flooded. More broadly it may be stated that the floods begin and end with shelf seas marginal to the continents and varying in extent between 1 per cent and 5 per cent of the total areas of the continental platform, the conditions being thus not unlike the present conditions of overlap; while the greatest inundations during the middle of the periods attain from 12 per cent to 47 per cent of the continent.

It is therefore apparent why the major portion of the earth's chronology depends for its determination upon the marine sediments. These formations, except in so far as they are later eroded, record the extent of the transgressions, and, in their physical characters, something of the topographic form of the adjacent lands, with a hint as well of their climates; and through their fossils they establish the chronology from place to place. However, this is by no means all, for the newer geology also teaches, as we have seen, that the strand-line is constantly and geographically irregular in motion, either very slowly transgressing more or less of this or that land, or receding as the lands emerge. Therefore in no land is there a total record, but everywhere the story is more or less incomplete, and our chronology is but a patchwork of all the local histories pieced together into one still very imperfect geologic timetable.

In the marine formations we are then everywhere dealing with oceanic overlaps whose records for the time being were more or less complete, but each series of beds is nearly everywhere separated from the adjacent ones by erosion intervals. The latter are due to the periodically recurring emergent times in the history of the continents, which may be either local or of wide extent, the marine records in the latter case being swept away by the atmospheric forces. These erosion intervals are the "breaks" and they are not only significant of absence of sedimentation, but in addition are actually records of another type, that is, erosion histories resulting in topographic forms whose carving has required the lapse of a time more or less long.

Just as the marine waters are constantly registering their existence, so also do the fresh waters, but the areas of the latter are usually of comparatively small extent. The "continental deposits" tend to be an evanescent record made at one time only to be subsequently more or less completely swept away into the sea. When we observe that this record is made in the

### Schuchert and Barrell-Revised Geologic

areas of erosion and subtraction, it is all the more astonishing to learn of the great thicknesses of some of these accumulations. Such, however, were made in regions which were undergoing pronounced subsidence. In Connecticut the coarse red Triassic formations attain to a maximum thickness of 13,000 feet, and in New Jersev to upward of 20,000 feet, while in Scotland the Old Red Sandstone of Devonian time also has a thickness of 20,000 feet. These deposits are the remains of beheaded mountains, the tops of which are deposited in their former valleys, that is, they are "intermontane continental formations." Again, other thick continental formations are intimately connected with marine deposits. Here we pass almost insensibly from the ocean or sea across the brackish water delta into the area of fresh-water deposition upon the land. A good example is the great Appalachian delta of Devonian times, the deposits of which in Pennsylvania reach a maximum thickness of upward of 10,000 feet. Because of these natural interfingering conditions, we are often able to fit the marine record into that made on the land, and so use both toward a more complete physical and organic chronology.

The evidence of erosion.—Geologic chronology has been so far almost wholly, though necessarily, interpreted on the basis of stratified rock accumulations, that is, the marine and continental strata. There is, however, still another record that has so far been almost refused recognition in our time-tables. This is the time evaluation of topographic form at any given stage of development (the physiography of the present, the paleophysiography of the past). To be sure, it is mainly a condition of removal by erosion of previously made histories, but nevertheless the topographic form of the land still remains and has a time value. We all appreciate to a certain extent the significance of unconformities as records of emergence and erosion between periods of inundation, but can any one tell what time value is to be accorded to the complete removal to sea-level of mountain ranges like the present Alps of southern Many times have similar mountain chains been Europe? washed away and then rejuvenated to some extent, only to be worn away again after each reëlevation.

The "breaks" and "lost intervals" are known to be many, but they are far greater in number, and their time durations, although admittedly very variable, are far longer than is usually believed to be the case. The geologic column will probably never be completed on the basis of the recoverable physical and organic evidence, but it will grow into greater perfection for a long time to come, and this growth will take place through the discovery of formation after formation along the lines of these breaks, and more particularly in the areas

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nearest to the continental margins. The perfection of the column will also bring about a greater harmony in the very variable estimates as to the age of the earth, as given on the one hand by the geologists and on the other by the physicists.

The major breaks in the geologic record are indicated in the time-table by "intervals," the marked erosion periods representative in the main of wide and high continents and of dominant erosion, not recorded by sediments within reach of observation; therefore in geologic chronology these are "lost times" of long duration. It was not thought desirable to give a new and independent name to each one of these intervals. but rather to use in modified form an old and familiar one. Therefore we have adopted the Greek word epi (= upon or after) as a prefix to the era terms, to indicate the subsequent time, that is, the intervals, thus naming these intervals Epi-Mesozoic, Epi-Paleozoic, Epi-Proterozoic, Epi-Neolaurentian, and Epi-Paleolaurentian. This method of naming was first proposed by Lawson for the interval following the Archean (1902, 1913). The same combination can be used, when it becomes necessary, for the intervals between the periods, as *Epi-Silurian*, etc.

Diastrophism.—As shifting of the strand-line is the most important criterion in ascertaining diastrophic action (a term to include all movements of the outer parts of the earth), it is well to state here briefly how these alternations are most readily determined. Organically they are recorded: (1) by abrupt changes in the superposed faunas, and (2) by the sudden appearance of newly evolved stocks; physically (3) by more or less obvious breaks in the sedimentation, due to sea withdrawal, (4) by changes in the character of the deposits, especially when this involves abrupt transition from organically formed strata (marl, chalk, limestone, dolomite) to mudstone and sandstone, or a change from continental to marine deposition, and (5) by marine overlaps upon rocks of earlier age, producing typical unconformities.

Correlation of formations in separated regions is made in part on a physical basis. This is done by finding similarities in disconformities (time breaks in conformably superposed or parallel strata; also called accordant unconformities), unconformities (time breaks indicated by two sets of strata inclined at varying angles to one another and easily seen by the eye=structural unconformities), and changing petrologic characters. A physical correlation is in general, however, far less reliable, and must ever remain second in importance to correlation by biotas (combined faunas and floras) for the discernment of diastrophic action. Of course, the most easily determined crustal movements are those which are compressive in character and lead to mountain-folding. Upon erosion and subsequent sea invasion, these angular or structural unconformities are the most easily found and those about which there can be the least doubt. The broad and gentle flexures known as crustal warpings, on the contrary, as a rule bring about the disconformities. The number and importance of these, on account of their difficulty of detection, are only now beginning to be appreciated.

The crustal oscillations of the earth are not due to heterogeneous and unrelated movements, but are connected, in that areas of elevation and depression remain positive or negative

### FIG. 2.

Illidealized	deformat,	n of the out	er crust or lithosphere	at the close of o geologic period
Pacific ocean basin	TheOld-land Cascadia		Continental basin emergent stage	Appalachian TheOld-Jand Atlantic ocean. geosyncline Appalachia basin
Negative	Positive	Subpositive	Neutral	Subpositive Positive Negative

FIG. 2. Diagrammatic cross section through North America in Paleozoic time at about lat. 38°, to show effects of diastrophism. Vertical scale greatly exaggerated.

throughout the eras, or during more or less long stretches of geologic time. According to Chamberlin (1910), "Deformations are inheritances, one of which follows another in due dynamical kinship. The succession is therefore homogeneous and the results co-ordinate... Under this view, ocean basins and continental elevations tended toward self-perpetuation."

The major crustal deformations are periodic in appearance, and their visible areas of movement are now in this continent, now in another; and it is this periodicity which conditions geographic history and organic evolution. All of these active and decisive movements are of long duration, and their major work is confined to the marginal areas of the continents. Farther inland, new axes or depressed folds may rise or old ones be accentuated, and so divide the continental basins into a series of smaller water-ways. Not only are the margins of the continents elevated, but apparently at the same time the oceanic basins are made either deeper or larger, or both. This simultaneous movement of the oceanic bottoms and the continental margins is proven by the fact that the major crustal deformations occur during the emergent times of the geologic periods, and this is true not only for the continent undergoing deformation, but as well for other land masses which have not moved at all, but whose strand-lines have been lowered in consequence of the oceanic enlargement.

The long-enduring middle portion of the periods is marked by relative crustal stability, as shown by more or less reduction of the continents to sea-level (peneplanation). The sediment from the eroded lands adds that much volume to the sea and causes its level to rise as a result of the partial filling. This effect, accompanying the general leveling of the land surface, produces, in the middle of the periods, maximum sea invasion. On the other hand, the earlier times of each cycle exhibit less crustal constancy and more marked erosion. The lands then warp more or less along predetermined lines, due to internal adjustments following the major movement and the reëstablishment of the balance between the sinking and rising areas (isostatic balance or isostasy), which has been altered by these deformations, by the sea invasion, and by the unloading of emergent land areas into the seas of the continents. During the closing stages of the periods, there is a renewal of crustal unrest, seen in the vanishing of the continental seas, which finally ends in another major crustal movement and in more or less complete withdrawal of the seas from the lands.

There is a certain amount of rhythm in these periodic movements and this meter permits us to group the formations into systems or periods. The more active introductory orogenic movements are of comparatively short duration. In contrast, the quieter but broader deformations within the period, of epeirogenic nature, as shown by world-wide movements of the strand-lines (eustatic movements), are of long continuance. Each submergence with the following emergence is seemingly the natural basis for the delimiting of a period. Among these periodic movements some are far more intense and of greater geographic extent than others, at times when mountain ranges in more than one continent are simultaneously or successively These are the diastrophic grand cycles, or, accordin motion. ing to Dana and LeConte, the "critical periods" or "revolutions" in the history of the earth, and they bind, as it were, the chapters into the book of geologic time.

Chamberlin (1898) has well said that "the ulterior basis of classification and nomenclature must be dependent on the existence or absence of natural divisions resulting from simultaneous phases of action of world-wide extent. . . Great earth movements affect all quarters of the globe" because "in a globe, all of whose parts owe their positions to the stress and tension of other parts, every rearrangement that rises in magnitude above the limits of local support extends its influence to the whole." The movements are not heterogeneous, but are periodic, for "the oceanic basins became progressively deeper and more capacious, while the continents became higher (degradation aside). In this assumption . . . there lies, if it be true, a basis for the natural division of geologic events, these movements being in themselves and in their immediate consequences the basis of such division.

"The major movements of the earth's surface have consisted of the sinking of the ocean bottoms and the withdrawal of additional waters into the basins whose capacities were thereby increased." Then, too, the master factor in the great crustal readjustment has been the progressively greater "radial shrinkage of the ocean bottoms" surpassing the "radial shrinkage of the continental platforms to the average amount of some 10,000 or 12,000 feet." Besides these periodic crustal readjustments resulting from internal causes, there are external readjustments of long duration, the quiescent periods, working "to precisely opposite ends, the degradation of the land and the tilling of the basins."

Terminology and definition.—The local warpings as a rule bring about the development of formations and disconformities. These are grouped together into the periods by the "minor diastrophic movements," or the "epicycles" of Willis (1913), when local mountain ranges are developed. As there are many of these movements and as they are not of the first order of magnitude, we propose to call them *disturbances*, to distinguish them from the rarer but far greater events, the "major diastrophic movements," or *revolutions* of Dana, which group the periods together into eras.

It seems probable that the periods were all separated by disturbances, events occurring now in this and now in that continent, but in each case enlarging some oceanic basin and so reacting on the strand-line the world over. On the other hand, during the revolutions, all of the oceans were enlarged by the sinking or broadening of their basins, and all the continents were more or less reëlevated. These latter are the "critical periods" in the history of the earth and are marked by the following features (somewhat modified from LeConte, 1900):

(1) By widespread deformation of the earth's crust, transmitted from place to place. This leads to the elevation of many and widely separated mountain ranges, followed by long intervals of erosion and mountain removal, and therefore by almost universal unconformities. Because of the long-enduring intervals of lost record, the subsequent faunas are not only very different, but appear as if suddenly or at least quickly evolved. Each revolution or critical period is named after one of the prominent mountain ranges formed at the time designated, for example, Laramide and Appalachian revolutions. The subsequent interval is the transition period from one era to the next.

### Time-table for North America.

(2) By widespread changes in the physical geography. That is, there are at these times a highly diversified or young topography, decided alterations in the continental outlines, the making of new or the breaking down of old land connections (the land bridges which permit intercontinental organic migrations), and marked changes in the oceanic currents, all of which also lead to marked variations of temperature and often to actual glacial periods.

(3) By marked and widespread destruction of the previously dominant, prosperous, and highly specialized organic types. This is produced partly by the physical changes and partly by the extensive migrations that are more conspicuous at these times and that therefore invite the spread of death-dealing parasitic diseases.

(4) By the marked evolution of new dominant organic types out of the small sized and less specialized stocks, and by the development of hordes of new species.

The last or Cascadian revolution is so recent that the record of it is not lost, and a study of this enables us better to comprehend the changes wrought by the earlier revolutions. LeConte regards it "as the type, as the best proof of the fact of critical periods, and as throwing abundant light on the true character of such periods, and especially on the causes of the enormous changes in organic forms during such times" (1895).

The periods usually take their names from the geographic area where the system of rocks was first considered to be of period value. Thus the Cambrian, Ordovician, Silurian, and Devonian systems were first discerned in England and Wales and take their names from ancient peoples living in these countries, or from the district itself in which the rocks are best developed. Permian is from the Province of Perm in the Urals of Russia, while Jurassic comes from the Jura mountains. Mississippian directs attention to the Mississippi valley, where these rocks are well developed; Pennsylvanian, to the greatest coal state in North America; and Comanchian (1887), to the home of the Comanche Indians in Texas. With regard to the last division, however, Shastan (1869) is an older name, having reference to the Shasta mountains of California. Triassic has reference to the tripartite development of these rocks in Germany, and is an heirloom from the days of geology when the science had not worked out the principle that formations and periods must be based upon type areas. Cretaceous is a still older inheritance from the days of mineral geology, before there was much stratigraphy, the name being based upon the chalk deposits of western Europe. Should this petrographic term be objectionable, the geographic name Platte

(1876) from the river of that name in Kansas and Wyoming could take its place in America.

The geologic time-table.-The time is not yet at hand for a complete evaluation of the minor diastrophic movements. because the recorded geologic succession in the different countries is by no means the same. For instance, the chronology of Africa south of the Sahara desert is in the main one of erosion, with a wonderful record of continental deposits and glacial formations. In other words, this continent throughout time has generally stood well above the pulsating oceans, and owing to reëlevation in recent geologic periods now stands at an average elevation of 2000 feet above sea-level. North America, on the other hand, lay near sea-level throughout the Paleozoic, was often in part submerged, and therefore has recorded in its rocks the most complete history of this era; but during the Mesozoic the greater eastern half of the continent was continually above the sea. The Mesozoic marine sedimentary record is in consequence restricted to a narrow strip along the Atlantic, to a wider area along the Gulf and Pacific margins, and to the Great Plains country, over which there flowed great inland seas from Mexico to the Arctic in Cretaceous time. To find the Mesozoic history in greater perfection we must look to the countries to the north of the Mediter-On the other hand, the Ordovician period is closed ranean. in America by the *Taconic disturbance* (named from the Taconic mountains of eastern New York), when low mountains were thrown up from Virginia to Newfoundland; whereas this movement is hardly registered in Europe outside of Great Britain. And again, the Silurian throughout western Europe is closed by the Caledonian disturbance, when mountains were raised from Ireland and Scotland through Norway into arctic Spitzbergen; while in America no marked elevation then took place. In early and middle Devonian time, however, all northeastern North America was in the throes of mountain-making and decided volcanic activity; this is the Shickshock disturbance so well seen in the mountains of the same name in southern Quebec and Gaspé.

Because of these unsatisfactory conditions in our present knowledge of the earth's history, we are not in a position to state that the periods in our table are the only ones that will eventually be recognized in North America. On the contrary, we confidently expect to see evidence developed to show that the Mississippian period embraces two diastrophic cycles or periods (Tennesseian and Waverlian); the Ordovician has certainly two and apparently four (Cincinnatian, Champlainian, Canadian and Ozarkian); while the Cambrian has three (Croixian, Acadian, and Waucobian). To keep these movements or probable diastrophic cycles of period value before geologists, we have placed their names in the fourth column of the table.

In conclusion, we may truthfully say that there is now a good deal of harmony among geologists in their use of the theory that the surface of the earth is periodically and rhythmically in motion, and that this diastrophic action is the basis of chronogenesis, developing not only cycles of sea invasion and land emergence, and cycles of erosion, but as well cycles of organic evolution. Although the eras are clearly recognizable everywhere, nevertheless, until the geologic geography of Europe is worked out in detail, we shall not be able to say that the various periods in current use are all established in nature, and it will therefore be doubtless advisable for America to continue to work out her own geologic chronology.

### Part II. Pre-Cambrian Time (J. B.).

When the International Committee in 1905 proposed a nomenclature for the pre-Cambrian rocks of the Lake Superior region, it may have seemed to some at that time that the larger relations had become fixed, and that future work, while not altering the classification, would serve to develop details. The classification then proposed represented in fact a large advance upon that apparent hopelessness of solution of the pre-Cambrian which in previous decades had been summed up in the name of the "Basement Complex," but the growth of knowledge regarding this earliest division of earth history has kept on during the past decade with equal pace, and has been perhaps as great as in any field of geology. It has revealed more clearly a distant perspective of earth history analogous on a larger scale to that vista of prehistoric human history which has been developed during this same decade in Europe. The meeting of the International Geological Congress at Toronto in 1913 was the stimulus which determined that a revision of the pre-Cambrian classification should be made, with the object of making it express more exactly the present points of view. This revision, however, like that of 1905, must be regarded as provisional only, another step toward a larger and more accurate knowledge of the long eons which preceded the fossiliferous record. At least four somewhat different classifications were proposed, but, although showing some radical differences, they nevertheless hold much in common. For the purposes of this table, that of Coleman has been most largely followed, but the views of Adams, Collins, Lawson, and M. E. Wilson have also been of use.

In arranging tables of geologic chronology, it has been customary to show the sequence of stratified formations only.

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### Schuchert and Barrell-Revised Geologic

Periods of deformation have not found recognition except as events closing periods of sedimentation. Periods of erosion have not been named, and if noted at all in the historic sequence have been represented in tables only by a line of unconformity. In the pre-Cambrian history it is necessary for any adequate representation to give to periods of deformation and periods of wide-spread erosion name and place comparable to the periods represented by known sedimentary record. The incorporation of these principles is a feature of this table. Periods of igneous invasion and crustal revolution are shown on the right, periods of sedimentary record on the The lesser erosion intervals resulting in the breaks which left. separate periods are shown by narrow spaces, the great intervals by wide spaces. Even this magnification, however, probably continues to minimize the duration of the great erosion intervals. The arrangement of the table which results serves to make prominent the most significant and distinctive features of the pre-Cambrian,—on the one hand the wide-spread crustal revolutions characterized by vast upwellings of molten rocks; on the other, the profound depth to which erosion has planed, revealing broadly at the surface, levels of the crust once subjected to regional metamorphism at depths measured in miles. In this high average attitude of the lands with respect to the sea. indicated by mountain-building and erosion, the pre-Cambrian resembles the Cenozoic more than it does the Paleozoic and Mesozoic. The completion of the present cycle of erosion will remove wide areas of sedimentary rocks of Mesozoic and Paleozoic age now lying above sea-level, and greatly broaden the exposures of pre-Cambrian rocks. The continental record of the present, like that of the pre-Cambrian, will become one dominantly of diastrophism and erosion, with sedimentation in geosynclines, but all on a lesser scale of magnitude.

To note in descending order certain of the problems presented in the present table: the attention may be turned first to the use of the names Proterozoic and Archeozoic, with their popular rendition as the Age of Primitive Marine Invertebrates and the Age of Unicellular Life. The reason for this usage is the desire for conformity with the system of classification used for the later geologic ages. The Proterozoic, however, is broken here into an early and a late division, separated by a period of profound diastrophism, following a use made by Coleman in the Dana Memorial Lectures on the Silliman Foundation, given at Yale University in December, 1913, and to be published during 1914 by the Yale University Press. The limitations of these divisions are thus structural rather than biologic, but this is true in a measure also of the later eras, as argued by

Chamberlin.\* As the names of successive great divisions of earth history, to be applied in widely separated regions, these terms Archeozoic and Proterozoic imply a less definite correlation than the more localized terms of Paleolaurentian. Neolaurentian, and Algonkian, used here for the Canadian Shield. For this reason these "zoic" names appear to have real value, as well as for the fact that by their use harmony is maintained through the whole scheme of geologic chronology. The nature of the faunas of the Proterozoic and Archeozoic is unknown, as is also the time in earth history when the Metazoa first rose to dominance over the Protozoa. The dividing line therefore cannot be drawn from biologic evidence; but even if a fair knowledge of the life of these times was possessed, it is probable that it would be found gradational to a considerable degree, and these broad names as here used could still apply without doing violence to the biotas of the Paleo- and Neolaurentian.

In this table the name Huronian has been restricted to the series originally studied by Logan. The Animikie, often called the Upper Huronian, is separated by a wide-spread unconformity and in its wider regional extent is distinct from the original Huronian. On the other hand, many of the areas formerly called Lower Huronian are composed of rocks which are separated by a crustal revolution and a following great erosion interval from the true Huronian. Three distinct series have thus become linked in past decades under one name, but the tendency of modern classification is in just the opposite direction. That which is here still called Huronian is no doubt susceptible of division, but there would be questionable value in introducing such subdivisions in this table and it would involve correlations which only those personally familiar with the fields should undertake.

The first great advance in the understanding of the Laurentian, the basal Archean, lay in the recognition that the gneisses were largely of igneous origin and were younger than certain lavas and sediments which rested upon them. It became apparent that vast domes and irregular bodies of molten rock had welled up from the unknown depths, had displaced and engulfed the older foundations of the crust, and had permeated and altered the surficial rock cover which still remained. These great masses of igneous rock are known as batholiths. In the invasion and injection of the older rocks they have absorbed material into themselves and added their emanations to the enveloping rocks. Mountain-making pressures also came into play and combined their action with that of igneous

\* Van Hise and Leith, Pre-Cambrian Geology of North America, Bull. 360, U. S. Geol. Surv., 1909, p. 21. invasion. Batholithic mountains and regional metamorphism were the result.

The greatest additional advance in recent years regarding the pre-Cambrian classification is doubtless the differentiation of the Laurentian igneous invasion and crustal disruption into two distinct crustal revolutions separated by a long era of erosion and sedimentation. Such a difference in age in the Laurentian base is discussed by Van Hise and Leith (op. cit., p. 28), part of the fundamental granites being regarded as intrusive in the Algonkian. The term Laurentian they recommend to be restricted to the older granites intrusive into the Keewatin, but not into younger rocks, and they point out the confusion which results when the determination of the age of the granite is neglected.

When in 1889 it was proposed by the United States Geological Survey to classify the pre-Cambrian rocks into two great divisions, the Archean and Algonkian, it was not known that the granitic base held any important masses of sediments; and the Archean, represented mostly by Keewatin basaltic lavas and Laurentian intrusive granites, both in altered forms, that is, greenstones and gneisses, was looked upon as a primal igneous eon. The Algonkian in contrast was thought to consist dominantly of sediments, though including much igneous material. Later work has largely broken down this distinction. The enormously thick Grenville series and the Sudburian were once widely spread, but have been mostly swallowed in the rising granites. Important intrusions cut also the Huronian and Animikian. In view of this intermeshing of what were once thought to be two kinds of dominant terrestrial activity, distinctly separated in time, the term Algonkian has largely lost its usefulness. If used at all, it should apparently be restricted to the rocks laid down after the second of the wide-spread granitic invasions which disrupted the foundations of the Canadian Shield.

The first of the granites, Lawson in his recent paper continues to call the Laurentian, the second great invasion he has named the Algoman, and he places it after the Huronian. Other writers, however, place the second before the Huronian; Coleman, moreover, considers it probable that the Laurentian of Logan's original area belongs to the later invasion, not the earlier, and the name refers more properly therefore to the later of the two. Such a conclusion leaves the earlier granite and gneiss nameless. In order to avoid confusion until more definite knowledge is attained, the writer proposes to call the older the *Paleolaurentian*, the later the *Neolaurentian*. Probably much of the fundamental granite gneiss for a long time, if ever, cannot be classified positively into either the one or the other division. For such areas the general name of Laurentian will continue to apply, and may include rocks of two widely different ages. Thus the field geologist is not faced by the difficulty of indicating the age and relations of the basement rock of the Canadian Shield before such are known in his locality.

The presence of vast batholithic invasions is not now regarded as so distinctively a process related to earth origin as it was formerly, though in the Laurentian it does seem to have occurred on a grander scale than in any later era and in that respect is doubtless related to the earlier stages of the earth. The metamorphic province of the Appalachians, for example, has been intruded by granite gneisses in the Paleozoic, the extent of their exposure being shown by the blotches of red on the geologic map of North America published by the U.S. Geological Survey in 1911. The areas of concealed granites and gneisses are without doubt of far wider extension, connecting in depth what are now seen as isolated areas. If erosion were to plane as deeply in the metamorphic regions of the Appalachians, it would doubtless reveal there a basement complex of Paleozoic and older rocks comparable in character to the Laurentian. The Cordilleran Province is also widely underlain by igneous rocks, but these are mostly of post-Paleo-In the Sierras and Coast ranges they have become zoic date. broadly exposed by erosion, and a deeper planation would there also widen and unify the exposures of igneous rock.

The recognition of at least two great periods of batholithic invasion in the pre-Cambrian raises the question whether there may not be more, and whether the basal fundamental gneiss in different parts of the world, as Van Hise has previously noted, may not have varying ages. With increase of knowledge this seems more strongly a possibility and should serve as a caution against hasty correlations of widely different regions. Lawson puts the great Algoman igneous irruption and the following Eparchean interval between the Huronian and Animikian. Others regard the greater break as below the Huronian. If, however, batholithic invasion should be found to occur widely at this horizon, it might result in a division of the pre-Cambrian of the Canadian Shield into four, in place of the present three divisions, as these in turn now tend to supplant the older usage of a two-fold division into Archean and Algonkian.

Molten rock accumulates in reservoirs deep in the crust and the higher intrusions and extrusions are given off from these. But while standing quiescent, the fluid acts like an unstable emulsion. On the one hand, the lime, iron, and magnesia tend to segregate more or less together, retaining less than the average per cent of silica. This dominance of metallic oxides gives basic

magmas, fluid at lower temperatures and more thinly fluid than those which are richer in silica. The common solidified forms are the basaltic surface rocks and, at greater depths, the diabases and gabbros; rocks rich in hornblende, pyroxene, and olivine. On the other hand, the alkaline oxides, soda and potash, tend to separate from the heavier metallic oxides and keep with them most of the silica, the acid radicle of the common rock minerals. They thus give rise to the acidic magmas, solidifying into rocks dominated by alkaline feldspar and quartz. Such rocks are, however, difficult to melt and become pasty rather than fluid, when heated in the furnace. But in the laboratory of nature the fusion takes place at great depths in the crust and the magmas are surcharged with gases which, because of the pressure of the overlying rock, cannot escape. Their presence in various degrees of concentration gives all degrees of fluidity and consequent capacity for intrusion. As a whole, however, the basic magmas are probably more fluid even at depth, and are markedly more fluid on approach to the The acid magmas at the surface betray their viscous surface. nature in pumice, obsidian, and rhyolite; at depth, on the contrary, they give rise to granites and to the slightly more basic forms known as granodiorites. In thin injection sheets and in the vein-like nature of pegmatite dikes they there betray a high local fluidity, but in the greater masses the structural phenomena not uncommonly suggest a higher viscosity and therefore a lessened capacity to rise through overlying rocks.

The maintained fluidity of basic magmas makes easy their extrusion in enormous volume, in spite of their high density. In some regions the great lava fields of Cenozoic date show no evidence as to whether more acidic phases of the regional magmas are concealed beneath, but where erosion in the Cordillera has exposed the granite sand granodiorites to view, the latter are commonly seen to have been preceded in the same regions by great extrusions of lavas and breccias, mostly of intermediate or basic nature. A period of great batholithic invasion may therefore be connected genetically with a preceding period of lava and breccia outpourings. The Neolaurentian batholithic invasion was preceded by very basic lava flows and tuffs, as is seen in the upper parts of the Sudbury series. The Paleolaurentian invasion was preceded by the vast basaltic flows of the Keewatin.

These facts concerning the recurrence here and there through geologic time of regional igneous activity, volcanic phenomena culminating in subcrustal foundering and the cradling of the surface rocks upon newer foundations, when taken in conjunction with the widely separated ages of the Paleo- and Neolaurentian invasions, show that it is no longer safe to regard the Keewatin and Laurentian as parts of a primal igneous eon. They are distinctive in their wide-spread extent and seem to have developed on a scale and with an intensity that are characteristic of those early ages, but are not unique in time.

This point of view suggests the possibility of a still more distant vista of geologic history. The Coutchiching of Lawson, long doubted but determined recently to have in part a real existence, lies conformably beneath the Keewatin lavas. The Grenville, perhaps the thickest of known sedimentary series, is torn and injected by granite and is generally agreed to have preceded the Paleolaurentian revolution. There is no certainty as yet, however, regarding its relation to the Keewatin. Miller and Knight in the Madoc area have found a series of rocks resembling the Grenville and overlying a series of greenstone schists correlated with the Keewatin greenstones. As the Canadian investigators have pointed out, however, the Grenville is so generally separated from the Keewatin of the Lake Superior succession by a belt of batholiths that no convincing general correlation between the two regions is yet possible. In either case, whether older or younger than the Keewatin, the vast thickness and sedimentary character of the Grenville series would seem to mark out those rocks as the records of a period or era which should ultimately be separated from the Keewatin. The Grenville shows how very far removed in time is the following Laurentian crustal disruption from the origin of the earth. Before that recurrence of the reign of fire, the orderly processes of air and water had been in operation for ages, making and depositing sediments whose thickness is measured by many tens of thousands of feet. The limestone in the Grenville, estimated at more than nine miles in thickness, and by far the greatest in amount of any known pre-Cambrian formation, testifies further to the efficiency of chemical weathering, a process frequently inefficient in later pre-Cambrian ages.

The Grenville everywhere floats upon and is torn to pieces by younger igneous rocks. Its original floor may be everywhere destroyed. Deep erosion has now removed all but the more downsunken troughs or included masses. The interior forces generated in the depths of the earth and the external forces born of the ancient sun thus limit, as if to a glimpse between two curtains, our vision of this oldest known period of the earth. But the history which the Grenville records shows that even this is not the primal eon. That is hidden, perhaps forever, from vision and from hammer.

# GEOLOGIC CHRONOLOGY FOR NORTH AMERICA.

(1) Classification based on Superposition of Strata, and Erosion Intervals.

Eras	Major Divisions	Periods	Epochs		Advances in Life	Dominant Life	
PSY- CHO- ZOIC			Recent (Alluvial or Post-Glacial)	Cascadian Revolution	Rise of world civili- zation The era of mental life	AGE OF MAN	
	QUATER- NARY	Glacial	Pleistocene	adian Re	Periodic glaciation Extinction of great mammals		
OIC JIFE)		Late Tertiary	Pliocene	Casca	Transformation of man-ape into man	AGE OF MAMMALS	
CENOZOIC (Modern Life)	Tertiary	(Neogene)	Miocene		Culmination of mammals	AND	
CE (Moi		Early Tertiary	Oligocene		Rise of higher mammals	MODERN FLORAS	
		(Påleogene)	Eocene		Vanishing of archaic mammals		
	Late Mesozoic	Epi-Mesozoic Interval		olution	Rise of archaic mammals		
()		LATE Cretaceous	Lance	Laramide Revolution	Extinction of great reptiles		
MESOZOIC (Medieval, Life)		cronaccous	Montanian Coloradian		Extreme specializa- tion of reptiles	AGE OF REPTILES	
		Comanchian			Rise of flowering plants	REFILES	
	EARLY	Jurassic			Rise of birds and flying reptiles		
	Mesozoic	Triassic			Rise of dinosaurs		

CORRELATION BY MEANS OF FOSSILS.

[Continued on the next page.]

# GEOLOGIC CHRONOLOGY FOR NORTH AMERICA.

(1) Classification based on Superposition of Strata, and Erosion Intervals.

Eras	Major Divisions	Periods	New Periods		Advances in Life	Dominant Life	
·		Epi-Paleoz	oic Interval	Revolution	Extinction of ancient life		
	Late Paleozoic	Permian		Appalachian Revo	Rise of land verte- brates Rise of modern insects and ammonites Periodic glaciation	AGE OF AMPHIB- IANS	
	or Carbon-	Pennsylvanian		Appal	Rise of primitive reptiles and insects	AND	
ZOIC Lufe)	IFEROUS	Mississippian	Tennesseiar	L	Rise of ancient sharks	LYCOPODS	
			Waverlian		Rise of Echinoderma		
	Middle	Devonian			Rise of amphibians First known land floras	AGE OF	
PALEOZOIC (Ancient Life)	PALEOZOIC	Silurian			Rise of lung-fishes and scorpions	FISHES	
P P			Cincinnatian		Rise of land plants and corals		
		Ordovician	Champlainian		Rise of armored fishes	AGE OF	
	Early		Canadian Ozarkian		Rise of nautilids	HIGHER	
	PALEOZOIC		Croixian		Rise of shelled animals	(SHELLED)	
		Cambrian	Acadian		Dominance of trilobites	BRATES	
			Waucobian		First known marine faunas		

CORRELATION BY MEANS OF FOSSILS.

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Archean of earlier authors.

Order of events according to Coleman. Classification based on sequence rocks, crustal movements, and cycles of erosion. CORRELATION WITHOUT THE AID OF FOSSILS. (5)

Dominanr Liff (Inferred)	AGE OF	PRIMITIVE MARINE INVERTEBRATES	(Fossils almost unknown. Delimitation of base of this age indefinite)		
	ka ity	tends to	Neolauren		evolution
Physical Characters	Great Epi-Proterozoic Interval. Over much of the earth the unconformity	Continental sediments and basic volcanics. Metalliferous de- posits in older rocks	Sediments dominant Great Iron Series	The Eparchean Interval of Lawson	Aqueous and glacial deposits Oldest known fossils (Archæo- cyathinæ)
PERIODSRecorded dominantlyby surface depositsby internal structures(Sedimentary and igneous)phism)	coic Interval. Over muc				
PE Recorded dominantly by surface deposits (Sedimentary and igneous)	Great Epi-Proteroz	Keweenawan	Animikian (Upper Huronian)		Huronian (Lower)
Major Divisions			Algonkian		
Eras	LATE PROTEROZOIC				

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Schuchert and Barrell-Revised Geologic

				AGE OF UNICELLULAR LIFE Protozoa	AND PROTOFHYTA (Fossils wholly unknown)	
Epi-Neolaurentian Interval. Peneplanation of mountains and continents	Batholithic mountain-building Metamorphism and igneous invasion of Sudburian and older rocks	Basic lava flows in upper part Conglomerates and quartzites domi- nant (Temiscaming, Pontiao, etc.)	Epi-Paleolaurentian Interval. Profound erosion of mountains and continents	Batholithic mountain-building Igneous invasion of Keewatin Crustal disruption	Basic volcanics and iron formations Coutchiching schists and gneisses Grenville calcareous sediments	NING OF EARTH HISTORY
nterval. Peneplanati	Neolaurentian Revolution		nterval. Profound er	Paleolaurentian Revolution		UNRECOVERABLE BEGINNING OF
Epi-Neolaurentian I		Sudburian	Epi-Paleolaurentian I	-	Keewatin Coutchiching Gren- Ville?	THE UNRECO
	NEO- LAURENTIAN			PALEO- LAURENTIAN		-
ی) SIOZO	PROTER IMITIVE LIFI BR	VJAAJ (Pr aT) OHTUA JATAA		никь Цика СНЕОZOI	<b>ЯА</b> Ч)	

Time-table for North America.

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COSMIC HISTORY

# ART. II.—The Relations of the Alexandrian Series in Illinois and Missouri to the Silurian Section of Iowa; by T. E. SAVAGE.

AMONG the criteria employed in determining the geological position of strata, their fossil content and stratigraphic relations are conceded by almost all geologists to be of the highest value, and to rank first in importance. A notable example of the error likely to result from disregarding these reliable criteria in making correlations, and reversing the usual order of procedure by "directly applying the broader paleogeographic principles to the solution of local problems in stratigraphy," is shown in a recent paper by Charles Keyes entitled "Paleogeographical Affinities of the Alexandrian Series."\*

In this paper Keyes discusses the strata of the Edgewood formation as developed in the vicinity of Louisiana, Missouri, recently described by the writer, † and asserts (1) that there is a marked plane of unconformity present at the base of the Bowling Green limestone member; (2) that the Bowling Green limestone member represents an overlap of a northern Silurian formation upon an earlier southern deposition represented by the underlying portion of the Edgewood formation; and (3) that the stratigraphic affinities of the Bowling Green limestone member are with the Gower limestone in the upper part of the Silurian section of Iowa, with which he thinks it should be associated. It is unfortunate that no facts are presented in support of these assertions, as geologists are left without means of properly judging with regard to the source and merits of the data upon which the statements are based.

In my paper on the Alexandrian series<sup>‡</sup> the Bowling Green limestone member was shown to be closely allied to the underlying strata of the Edgewood formation, and it was clearly shown that this limestone was unconformably overlain by the Sexton Creek limestone, which corresponds in general age to that of the Brassfield of Indiana, Ohio, and Kentucky. Considerable additional information on the strata of the Alexandrian series of the Upper Mississippi valley has been obtained by the writer during the summer of 1913, all of which completely corroborates the views of the Bowling Green limestone member presented in my paper above mentioned. They show conclusively that the affinities of this limestone are with the Edgewood formation, and that, stratigraphically, this upper member

<sup>\*</sup> This Journal, vol. xxxvii, pp. 254-256, 1914.

<sup>†</sup>Bull. Geol. Soc. America, vol. xxiv, pp. 359-376, 1913.

<sup>1</sup> Ibid., pp. 359-361, 1913.

of the Edgewood is older than any part of the Silurian section of Iowa previously recognized.

The section given by Keyes\* of the Silurian "rocks and their immediate associations as displayed in the deep valley of Noix Creek and elsewhere in the vicinity of Louisiana, in Pike County, Missouri," is misleading in two particulars, (1) because at no place in the valley of Noix Creek or elsewhere within at least eight miles of Louisiana, Missouri, is the member No. 2 of his section a brown limestone ten feet thick, but it is there a light gray oölite, having a maximum thickness of seven or eight feet, the thickness decreasing towards the east and west from Louisiana; and (2) because an unconformity at the base of the Bowling Green limestone member is apparent only where the oölite phase of the underlying portion of the Edgewood is developed.

### The unconformity below the Bowling Green limestone member.

The change from the oölite below to the brown magnesian limestone of the Bowling Green member above is abrupt in the vicinity of Louisiana, and farther east across the river in Pike and Calhoun Counties, Illinois; but about seven miles west of Louisiana, Missouri, near the west border of the oölite along Noix Creek, the oölite passes upward with a gradual transition through two feet of mixed oölite and brown limestone into the brown Bowling Green limestone member without any indication of a sedimentary break. Along the valley of Noix Creek between Watson Station and Bowling Green, west of the extension of the oölite, the Silurian strata consist entirely of brown limestone, having a thickness of 20 to 25 feet, within which no plane of unconformity can be distinguished. In the vicinity of Edgewood and Cyrene, where the oölite phase is not developed, there is also no apparent unconformity at the base of the Bowling Green limestone member, as shown in the writer's section of the Alexandrian strata near Edgewood. The unconformity at the base of the Bowling Green limestone member thus appears to be limited to the east side of the area of distribution of the Edgewood formation in this region, where it is underlain by the oölite phase of the Edgewood.

The oölite is thickest, about seven feet, on the west side of the river in the vicinity of Louisiana and Clarksville, Missouri. It is less than half that thickness farther east, on the Illinois side of the river, where it is succeeded by 9 to 15 feet of the brown Bowling Green limestone. Moreover, in the exposures in Illinois the upper part of the oölite, present in the vicinity of Louisiana and Clarksville, Missouri, is absent. These relations

+ Bull. Geol. Soc. America, vol. xxiv, p. 363, 1913.

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<sup>\*</sup> This Journal, vol. xxxvii, p. 254, 1914.

# 30 T. E. Savage—Relations of the Alexandrian Series.

of the Bowling Green limestone member to the underlying portion of the Edgewood formation in this region indicate the following sequence of events: During early Edgewood time the part of the basin in which the Edgewood strata in Pike County, Missouri, were laid down was deepest towards the west side of the area of distribution of these rocks, and was progressively shallower towards the east margin, along the east side of Pike County, Missouri, and in Pike and Calhoun Counties, Illinois, where conditions were favorable for the formation of oolite. During the progress of early Edgewood sedimentation the sea was gradually contracting towards the west side of the basin, until just previous to the beginning of deposition of the Bowling Green limestone, when the east margin of the sea had receded to a few miles west of Louisiana, Missouri. Bowling Green limestone deposition was initiated by a slight uplift of the region bordering the west side of the Edgewood basin in Pike and Lincoln Counties, Missouri, accompanied by a subsidence of the area east of the line of uplift. Sedimentation was thus uninterrupted in the west part of the basin, but the warping resulted in the overlap of the Bowling Green limestone upon the surface of the oölite farther east where there is an abrupt change in lithology and a short sedimentary hiatus at the base of the Bowling Green member.

That the unconformity between the oölite and the brown Bowling Green limestone is not of much time significance is also shown by the fact that the fossils that have been found in the Bowling Green limestone member are all typical Edgewood species.

### Faunal affinities of the Bowling Green limestone member.

Near Watson station, about eight miles southwest of Louisiana, the fossils Atrypa præmarginalis, A. putilla, Camarotæchia? concinna, and Dalmanella edgewoodensis were collected from the lower part of the Bowling Green limestone, above which no trace of unconformity could be detected.

In the exposure along the Chicago and Alton railroad, about  $2\frac{1}{2}$  miles northeast of Bowling Green, the writer collected a number of shells of *Atrypa putilla* from the ledge of brown Bowling Green limestone, within which no evidence of unconformity was found.

In the east bank of Daggett's branch and along the river bluff at the west end of Grafton, and along a stream  $2\frac{1}{2}$  miles farther west, in Jersey County, Illinois, good exposures of the Edgewood and associated strata are presented. The Edgewood formation here rests upon Maquoketa shale, and consists of a

### T. E. Savage-Relations of the Alexandrian Series. 31

thickness of three feet of oölite (Noix oölite member), succeeded by 9 to 14 feet of brown limestone (Bowling Green limestone member) which is followed unconformably by about 25 feet of gray to brown (Sexton Creek) limestone containing *Pentamerella? manniensis* in the lower part, and *Rhinopora* near verrucosa, Strophonella filistriata, Stricklandinia triplesiana, Triplecia ortoni, and other common Brassfield fossils near the top. The brown (Bowling Green) limestone member in this region furnished a few good shells of Atrypa præmarginalis.

An important addition to our knowledge of the Channahon limestone member, and its relation to the Edgewood formation in southwest Illinois and Pike County, Missouri, and to the Essex limestone in Kankakee County, Illinois, was made during the summer of 1913. This information proves the correctness of the previous correlation of the Channahon limestone, and indicates that sedimentation was continuous in that region from the bottom of the Channahon limestone member of the Edgewood to the top of the brown limestone corresponding to the Bowling Green member.

In the south bank of Des Plaines river, two miles south of Channahon and one mile below the exposure of the Channahon limestone previously described,\* strata corresponding to No. 2 of the old section of the Channahon limestone are exposed above 8 feet of bluish (Maquoketa) shale. In making an excavation near this place the rocks from a zone 5 to 7 feet higher than number 2 of the old section were taken out and piled near by. From the stone taken from this excavation the following fossils were collected :—Lyellia thebesensis, Atrypa præmarginalis, Atrypa putilla, Camarotæchia? concinna, Dalmanella edgewoodensis, Rhynchotreta thebesensis, Schuchertella curvistriata, Whitfieldella ovoides, Cyclonema daytonensis, Dalmanites sp.

One and one-half miles farther down the river a small quarry has been opened in the south bank, exposing a thickness of about 14 feet of brown limestone, the lower part of which was at about the same level, and represented about the same horizon, as the rocks taken out of the excavation. The limestone in the lower part of this quarry contained Lyellia thebesensis, Atrypa putilla, Dalmanella edgewoodensis, and Whitfieldella ovoides, while that in the middle and upper parts was almost barren, furnishing only a very few shells of Atrypa putilla and Whitfieldella ovoides. A few rods south of this quarry a ledge of gray limestone 9 feet thick, containing characteristic Sexton Creek fossils, is exposed at a level about 6 feet above the top of the upper brown limestone in the quarry.

\* Bull. Geol. Soc. America, vol. xxiv, p. 367, 1913.

### 32 T. E. Savage-Relations of the Alexandrian Series.

These exposures indicate that the Channahon limestone member described in former papers represents only the lower part of the Edgewood formation at this place, and the fossils in the limestone taken from the excavation show clearly that this horizon is the equivalent of the Cyrene member of the Edgewood limestone as developed near Edgewood and Cyrene in Pike County, Missouri, and near Thebes in Alexander County, Illinois. The succeeding brown, almost barren limestone that appears in the middle and upper parts of the quarry exposure corresponds to the Bowling Green member of the Edgewood formation. In the quarry no trace of a sedimentary break appears between the upper more barren brown limestone corresponding to the Bowling Green member and the underlying more fossiliferous portion of the Edgewood formation.

While the Bowling Green limestone member of the Edgewood formation in Illinois and Missouri is almost barren of fossils, careful search in the several good exposures has yielded a few shells of the following species :—Atrypa præmarginalis, Atrypa putilla, Camarotæchia? concinna, Dalmanella edgewoodensis; Whitfieldella ovoides.

These are all characteristic Edgewood fossils, not one of which have been found in the Gower or Anamosa limestone or in any other horizon hitherto recognized in the Silurian rocks of Iowa. They clearly link the Bowling Green limestone with the Edgewood formation, as was indicated in my paper on the Alexandrian series.

#### Stratigraphic relations of the Bowling Green limestone member.

The close relation of the Bowling Green limestone member with the underlying lower portion of the Edgewood formation has been already described. It was shown in my paper on the Alexandrian series that the Bowling Green limestone member of the Edgewood is in many places unconformably overlain by the Sexton Creek limestone of about Brassfield age. The lower layers of the Sexton Creek limestone almost everywhere contain the fossils *Pentamerella ? manniensis* and *Pentamerus* cf. ovalis, which mark a narrow zone near the base of the formation. In a horizon 18 to 25 feet above the *Pentamerella ? manniensis* zone the following species are abundant:— *Rhinopora* near verrucosa, Strophonella filistriata, Stricklandinia triplesiana, Stricklandinia sp., Triplecia ortoni, and other fossils characteristic of the Brassfield limestone of Indiana, Ohio, and Kentucky.

In the river bluff between Clarkesville and Kisenger, in Pike County, Missouri, the Bowling Green limestone member is followed unconformably by 9 to 12 feet of gray non-

### T. E. Savage—Relations of the Alexandrian Series.

magnesian limestone (Sexton Creek), the lower part of which furnished Pentamerella? manniensis, and Pentamerus cf. ovalis. In the opposite bluff, on the Illinois side of the river, the Sexton Creek limestone containing Pentamerella? manniensis and Pentamerus cf. ovalis in the basal portion, and Rhinopora near verrucosa, Stricklandinia triplesiana, Triplecia ortoni and their associates in a zone 25 feet higher, may be seen overlying the Bowling Green limestone member in several exposures from a place  $2\frac{1}{2}$  miles north of Pleasant Hill in Pike County southward to 15 miles below Hamburg, in Calhoun County. A typical section of the Edgewood and Sexton Creek strata in this region is given on page 371 of my paper on the Alexandrian series. The same relations of the Bowling Green limestone member to the underlying oölite phase of the Edgewood below and the overlying Sexton Creek limestone are exposed at a number of places in Jersey County, west and northwest of Grafton.

In northeast Illinois the *Pentamerella? manniensis* zone of the Sexton Creek limestone occurs above the upper brown Bowling Green limestone member of the Edgewood formation in the exposures along Kankakee river below Custer Park, in Kankakee County; along the Des Plaines river southeast and south of Channahon; and near Essex, in Will County, Illinois.

It is now known that the Essex limestone exposed in the bank of Horse Creek, near the town of Essex in Will County, Illinois, corresponds to the limestone removed in the excavation two miles below Channahon, and to that exposed in the lower part of the quarry along the Des Plaines river  $1\frac{1}{2}$  miles farther south. The chert masses bearing Pentameralla? manniensis, in number three of the published section of the Essex limestone, have been found to have come from a horizon some feet higher, from which they slumped down to the place where they now rest upon the lower part of the brown limestone equivalent to the Bowling Green member of the Edgewood at that place. With these discoveries, the Essex limestone is seen to represent a horizon of the Edgewood a little higher than the old Channahon limestone previously known, and it is overlain by the brown, almost barren magnesian limestone corresponding to the Bowling Green member of the Edgewood, which, in this vicinity, as along the Kankakee river below Custer Park, and along the Des Plaines river south of Channahon, and in the river bluff below Clarksville, in Pike County, Missouri, and in Pike, Calhoun and Jersey Counties, Illinois, is unconformably overlain by the Sexton Creek (Brassfield) limestone containing the fossils already mentioned.

AM. JOUR. Sci.—Fourth Series, Vol. XXXVIII, No. 223.—July, 1914.

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# 34 T. E. Savage-Relations of the Alexandrian Series.

There is no doubt that the place of the Bowling Green limestone member of the Edgewood formation in the geologic column is below the Sexton Creek limestone, which from its fossils is known to be of about Brassfield age.

# Alexandrian strata in Iowa and northwest Illinois.

The Winston limestone.—Strata nearly equivalent in time to the Edgewood and Sexton Creek limestones, respectively, of northeastern and southern Illinois and eastern Missouri, have been found in Jo Daviess and Carroll Counties, Illinois, and in northeastern Iowa. However, the early Silurian strata in northwest Illinois and in Iowa present such different aspects and show such differences in their faunas compared with the normal Edgewood and Sexton Creek limestones, as to make it probable that they were deposited in a sea that advanced upon the region from the north, as were the overlying Niagaran dolomites in the same region.

Early Silurian strata representing the Edgewood period of deposition were first recognized in Jo Daviess County in an exposure about six miles southeast of Galena Junction, in the cut at the station of Winston at the south end of the tunnel made by the Chicago Great Western railroad, where the following section was made:

# Section at Winston, at south end of Chicago Great Western tunnel.

Alexandrian limestone	Feet
3. Dolomite, yellow, earthy, fine-grained, in rather thin, even layers	22
2. Sandstone, bluish, calcareous, and shaly; con- spicuously laminated	$\frac{1}{2}$
A break in sedimentation.	
Maquoketa shale	

In the above section members 2 and 3 furnished the fossils Lingula sp., Orbiculoidea sp., Plectambonites sp., Schuchertella sp., Dalmanella edgewoodensis, Atrypa putilla, Atrypa præmarginalis, Camarotæchia? cf. concinna, Calymene sp., Encrinurus sp., and Prætus determinatus.

Of the above species, Dalmanella edgewoodensis, Atrypa putilla, Atrypa præmarginalis, Camarotæchia? concinna, and Prætus determinatus denote the Edgewood age of the strata, but the absence of such fossils as Lyellia thebesensis, Rhynchotreta thebesensis, Whitfieldella ovoides, Cyphaspis intermedia, and other characteristic Edgewood species which

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are always associated with the above in the normal Edgewood strata makes it improbable that the sea in which the strata at Winston were laid down was connected with the southern Edgewood basin. For the early Silurian rocks exposed at the south end of the Chicago Great Western tunnel and equivalent strata in northwestern Illinois and northeastern Iowa representing about the same period of deposition as the Edgewood formation farther south and east, but which are thought to belong to a northern province, the name *Winston limestone* is proposed, from the locality where this limestone was first recognized.

Strata corresponding to the Winston limestone as exposed at the tunnel, outcrop in several places along the bluffs of Mississippi river in Carroll County, Illinois, and Jackson County, Iowa, where they are unconformably overlain by the very cherty horizon of the Hopkinton dolomite. In the northwest part of Belleview, Iowa, a thickness of about 40 feet of this limestone is exposed. The thickness decreases southward so that less than 18 feet are present at Savanna, Illinois, and these strata are seen to feather out in the river bluff between Sabula and Elk River, Iowa.

The Winston limestone as here defined includes only the lower part, below the cherty dolomite, of the division designated by Wilson\* as the basal member of the Niagara limestone in northeastern Iowa.

The Waucoma limestone.—Strata representing the time interval of the Sexton Creek limestone of northeastern and southern Illinois appear to be absent in the Mississippi river bluffs, but they are present in Jo Daviess County, Illinois, and occur farther northwest in Iowa. The best exposures known are along Little Turkey river in Fayette County, Iowa, where a ledge of light gray, non-magnesian limestone 10 to 20 feet thick outcrops in several places between the villages of Waucoma and Auburn. This limestone rests unconformably upon the Maquoketa shale, the Winston limestone being absent in this region. It is succeeded by normal Hopkinton dolomite of Niagaran age. An outcrop of this limestone in the banks of the river three miles southeast of Waucoma furnished the following fossils: Clathrodictyon vesiculosum Diphyphyllum cf. cæspitosum, Pachydictya sp., Atrypa cf. marginalis, Dinobolus sp. (The same species is found in the Sexton Creek limestone, having the shell less circular in outline, and the interior platform narrower in proportion to the length than in D. conradi.) Leptana rhomboidalis, Platystrophia daytonensis, Plectambonites transversalis var. elegantula, Schuchertella tenuis, Strophonella

\* Am. Geologist, vol. xvi, pp. 277 and 278, 1895.

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filistriata, S. hanoverenis, Whitfieldella sp., Cyclonema daytonensis, Illænus daytonensis, Illænus cf. madisonianus.

The above species indicate for this limestone an age nearly equivalent to the Sexton Creek limestone of southern and northeastern Illinois and the Brassfield of Ohio and Kentucky, but such characteristic Sexton Creek fossils as *Rhinopora* near verrucosa, *Pentamerella*? manniensis, *Stricklandinia tri*plesiana, *Stricklandinia* sp., and *Triplecia ortoni* were not found in this region. Since a northern sea invasion is known to have occurred during the Sexton Creek (Brassfield) period of deposition, it is thought that this limestone may represent deposition in a northern province during Sexton Creek time. Hence it may be known as the *Waucoma limestone*, from the village of that name in Fayette County, Iowa, near which it is well exposed.

The relations of the Alexandrian strata of eastern Missouri and southern and northeastern Illinois to the Silurian limestone of Iowa are shown in tabular form below.

Table showing the	e relations	of the	Alexandrian series	of 1	Illinois
			Silurian of Iowa.		

	Eastern Mo., and southern and northeastern Ill.	Iowa
Niagaran		Gower limestone
Series		Hopkinton dolomite
	Sexton Creek limestone	Waucoma limestone
Alexandrian Series	Edgewood Bowling Green formation Cyrene limestone member	Winston limestone
	Girardeau limestone	

#### Summary.

It has been shown that the unconformity below the Bowling Green limestone member is not general, but is limited to the area in which the oolite phase of the underlying portion of the Edgewood formation is developed.

The statigraphic relations and the fossil content of the Bowling Green limestone member proves that this limestone is closely allied to the underlying portion of the Edgewood formation and that it is older than the Sexton Creek (Brassfield) limestone; and, further, that it has no provincial, stratigraphic or faunal affinities with the Gower limestone of the Iowa Silurian section.

The Channahon limestone member, as described in earlier papers, represents only the lower part of the Edgewood formation; the higher portions of the typical Cyrene member and the Bowling Green limestone member are now known to be developed along the Des Plaines river south of Channahon in Will County, Illinois.

The Essex limestone is known to correspond to the Edgewood formation as developed along the Des Plaines river, below Channahon, Illinois.

Alexandrian strata representing respectively the Edgewood and Sexton Creek periods of deposition are present in Jo Daviess and Carroll Counties, Illinois, and in northeastern Iowa, where they present such differences in lithology and fossils from those formations in eastern Missouri and southern and northeastern Illinois, that they are thought to represent deposits in a northern province during Alexandrian time.

University of Illinois, Urbana, Ill.

# ART. III.—On a New Mode of Occurrence of Scapolite; by J. STANSFIELD.

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THE writer has recently met with the mineral scapolite under circumstances which appear to be exceptional, but which nevertheless admit of a rational explanation. The explanation set forth below is such that similar occurrences may be expected in other localities. The scapolite occurs in a vein of pegmatite, part of the pegmatite being composed of scapolite and quartz.

The occurrence in question is situated at Lot 20, Range 8, of the Township of Buckingham, Quebec, at the locality known as the Walker mine. There is an old excavation from which graphite was formerly taken, at a point 500 ft. north of the main pit. All the rocks here exposed are of pre-Cambrian age. The country-rock is composed of well-banded gneisses with a small amount of Grenville limestone on the east face of the pit. The gneissic banding at the south end of the pit dips

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approximately vertically, and strikes along the length of the pit, i. e. N. 20° E. The northern end of the pit is occupied by a rounded nose covered by a pegmatite vein. The pegmatite has been broken through during mining operations, exposing the gneiss below it. From the exposures now to be seen it appears probable that the gneiss has been folded into a sharp anticline. The pegmatite which was intruded at a later date has taken on the form of an anticline, pitching to the south at an angle of 35°, assuming a form which is comparable with those of the saddle-reefs of Bendigo and of the "barrels" of Nova Scotia. The pegmatite vein has a thickness of about one foot and its upper surface is peculiarly smoothed. This surface was in close contact with the graphite ore-body, the ore being about one foot in thickness and being composed of almost solid graphite at the contact with the pegmatite, becoming poorer in graphite away from the pegmatite. With the removal of the ore this smoothed surface has been laid bare, showing an appearance very similar to the smoothed and polished surfaces connected with glaciation.

A thin section of the ore from the east face shows it to be an altered Grenville limestone impregnated with graphite, and shows the development of lime-bearing silicates as at the main pit.\*

At the point where the pegmatite and altered limestone are in contact the pegmatite is seen to be composed of quartz and a greenish-yellow mineral, at first supposed to be a variety of feldspar, but found on examination to be scapolite. This scapolite-pegmatite is an integral part of the pegmatite vein, and as such, is distinct from the altered limestone carrying the graphite, and also carrying scapolite. The area of the scapolite-pegmatite is but small, amounting to a few square feet only.

Microscopic characters.—The rock is composed essentially of quartz and scapolite. The relations of the two minerals to each other are usually like those of a eutectic, and simulate the olivine-anorthite type† rather than the orthoclase-quartz type of eutectic relations. Occasionally, however, the scapolite shows a tendency to the development of crystalline form. The scapolite, then, crystallized in part before the quartz, in part simultaneously with the quartz. The quartz shows strain shadows and has inclusions of small particles of graphite. Strings of gas bubbles are present and many very fine elongated needles of an opaque mineral are numerous in the quartz, being similar to those usually referred to rutile, though the characteristic twinning of that mineral is not seen.

The scapolite shows the uniaxial and negative character of that mineral, and in basal sections the development of two cleav-

\*12th International Geological Congress, Guide Book No. 3, p. 103.

<sup>†</sup>Geol. of Small Islands of Inverness-shire, Harker, 1908, p. 86.

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ages at right angles. The development of the prism faces of the first and second order, m(110) and a(100), is well shown in basal sections of those individuals which crystallized before the quartz. It has a high birefringence, indicating it to be nearer meionite than marialite. The analysis confirms this. Some sections show abundant inclusions of the type characteristic of scapolite. Some of them are negative crystals and occur with definite linear arrangement with their elongation

FIG. 1.



FIG. 1. Smoothed upper surface of pegmatite dike with banded gneiss below it. Walker mine, Quebec.

parallel to one of the cleavage directions, while others show roughly circular cross-section and have no definite arrangement. The latter type may be unpropitious sections of negative crystals. The nature of these inclusions has not been more closely investigated.

There is a small amount of a chloritic mineral present. It has been formed at the expense of the scapolite and is associated with graphite. A part of the chloritic mineral shows radial arrangement. Calcite occurs in very small amount within the scapolite and with the chlorite and is probably a decomposition product of the scapolite.

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Interpretation.—The explanation of the occurrence is simple. The pegmatite, before consolidation, assimilated a small amount oi the limestone into which it intruded, and the assimilated lime gave rise to the formation of the lime-bearing silicate scapolite, instead of orthoclase, as in the rest of the vein. The chlorine required for the formation of the scapolite was an original constituent of the pegmatite, and is seen to have been capable of transmission, at least to a small distance, into the country rock, as shown by the presence of scapolite in the altered limestone of the ore mass.

A partial analysis of the scapolite of the pegmatite vein, which has a specific gravity of 2.690 [pycnometer], shows it to contain 16.24 per cent of CaO. This, taken in conjunction with the fact that the feldspar of the vein is orthoclase, clearly indicates that its formation is a result of the assimilation of lime from the country rock.

This occurrence, in addition to the novel features described above, throws an important light on the problem of assimilation by igneous magmas. It shows that in the case of even a small vein of pegmatite, such as is usually regarded as being intruded at low temperatures, speaking relatively of magmatic temperatures, the absorption of lime from a limestone country rock can take place, and that also, which is the important point, the absorbed lime may go toward the formation of limesilicates and not merely be re-deposited as calcite. If assimilation may take place on the small scale represented in this occurrence (involving only a few cubic feet of magma), it is probable that on the larger batholithic scale it may play an important part in the change of the average composition of a large magma-reservoir, and so become an important factor in the differentiation of rock types. Limestone is a rock which lends itself to assimilation perhaps more readily than any other. Some of the possibilities arising from the assimilation of limestone have been discussed recently by Daly.\* The present paper can be regarded as a proof of the possibility of assimilation and as showing that assimilation of limestone is a comparatively easy process requiring temperatures that are easily within experimental reach. So that the experimental proof that new rock types of the more restricted kinds can be formed from an average magma by the assimilation of limestone should now be undertaken in the laboratory.

McGill University, Montreal.

\* Bull. G. S. A., xxi, pp. 87-118, 1910.

# ART. IV.—An Improvement of the Barium Sulphate Determination of Sulphur in Soluble Sulphates when Sodium Salts are Present; by W. A. TURNER.

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

WHEN barium sulphate is precipitated by the reaction between a soluble barium salt and a soluble alkali sulphate, or in presence of large quantities of alkali salts, there is likely to be, as is well known, considerable contamination of the precipitate. Alkali sulphates and barium chloride may be found in the ignited sulphate, while hydrochloric and sulphuric acids may be volatilized in the ignition.\* If the precipitation is made with the object of determining barium, the ignited precipitate may be dissolved in hot concentrated sulphuric acid, recovered in crystalline form by evaporation of the sulphuric acid, filtered, washed free from impurities, ignited and weighed in a satisfactory condition of purity.<sup>+</sup> The precipitate formed by an excess of barium chloride, for the purpose of determining the sulphate ion, and contaminated by that reagent, cannot, however, be purified by recrystallization from sulphuric acid since, in this action, the included barium chloride is converted to barium sulphate and added to the amount which represents the sulphate ion to be determined. The magnitude of the error encountered is largely dependent upon the conditions under which the determination While the method may be modified so as to reduce is made. one source of error to a minimum, the same modification may increase another source of error so that the final result is not satisfactory. In an exhaustive study of the sources of error and the influence of various factors on them, Allen and Johnston and Johnston and Adams (loc. cit.) find no method of eliminating the observed phenomena, but by making a series of corrections are able to derive results which are accurate, or nearly accurate.

The investigation of which this paper is an account was directed to the elimination of error, due to the incomplete formation of the insoluble barium sulphate, by removing the alkali salts in a preliminary treatment with hydrochloric acid.

It appeared in preliminary experimentation that the determination of the sulphate ion of pure copper sulphate by precipitating with barium chloride, added (as is usual) in dilute solution and gradually to the hot solution of the copper salt, yields results very near the theory—the tendency of the barium

\*Hulett and Duschak, Zs. anorg. Chem., xl, 196, 1904; Allen and Johnston, Jour. Am. Chem. Soc., xxxii, 588, 1910; Johnston and Adams, ibid., xxxiii, 829, 1911.

<sup>†</sup> Mar, this Journal (3), xli, 288, 1891; Gooch and Hill, ibid. (4), xxxv, 311, 1913.

sulphate to carry with it another sulphate, by inclusion or combination, being much less marked in the case of copper sulphate than in the case of the alkali sulphates.\* For the experiments to be described, the copper sulphate was prepared by twice crystallizing the presumably pure (C. P.) salt from the hot water solution while stirring vigorously to promote the separation of the substance in finely divided form. These crystals dried in air for two days gave, on analysis, the following results:

#### TABLE I.

#### Analysis of Pure Copper Sulphate.

			Theory	Error in		
No.	$CuSO_45H_2O$	BaSO <sub>4</sub>	for	terms of	Error in	terms
of	found	found	$BaSO_4$	$BaSO_4$	of -5	5O <sub>4</sub>
exp.	$\operatorname{grm}$ .	grm.	$\operatorname{grm}$ .	$\operatorname{grm}$ .	grm.	$\operatorname{per}\operatorname{cent}$
1.	1.1668	1.0904	1.0911	-0.0002	-0.0003	-0.03
2.	1.5373	1.4383	1.4375	+0.0008	+0.0003	+0.05
3.	0.9042	0.8453	0.8455	-0.0005	-0.0001	-0.01
4.	1.3812	1.2906	1.2915	-0.0009	-0.0004	-0.03

These results are obviously very close to theory, but it is not improbable that in them some slight tendency toward the carrying down of copper sulphate with the barium sulphate may have been counteracted by the inevitable inclusion of traces of barium chloride.

Upon making the precipitation under exactly similar conditions, excepting the presence of alkali salts, the error due to the carrying down of unconverted alkali sulphate is at once made evident by the error of deficiency. This is shown in the results of Table II.

			Theory	Error in	Erro	r in	Alkali
No.	$CuSO_45H_2O$	$BaSO_4$	for	terms of	terms	s of	salt
of	taken	found	$BaSO_4$	$BaSO_4$	-S0	$\mathcal{D}_4$	added
exp.	$\operatorname{grm}$ .	$\operatorname{grm}$ .	grm.	grm.	grm.	$\operatorname{per}\operatorname{cent}$	grm.
1.	1.0879	1.0049	1.0173	-0.0124	-0.0021	-0.20	$\tilde{a}^*$
2.	1.4373	1.3154	1.3450	-0.0596	-0.0152	-0.91	5†

## \* NaCl + KCl

The next step was the attempt to eliminate the error, due to incomplete conversion of the alkali sulphate, by the preliminary precipitation and removal of the alkali chloride. An accurately weighed portion of copper sulphate with an approximately known weight of alkali chloride was dissolved in a small

\* Allen and Johnston (loc. cit.) find this to be true also of the sulphate of another bivalent element, viz., magnesium. + Richards and Parker, Proc. Am. Acad., xxxi, 67, 1896, Zs. anorg. Chem.,

viii, 413, 1895.

amount (25<sup>cm\*</sup>) of water, the solution saturated with gaseous hydrogen chloride, the precipitated alkali chloride filtered off on asbestos in the perforated crucible and washed with concentrated hydrochloric acid. The filtrate was evaporated on the steam-bath (after dilution with an equal volume of water to prevent mechanical loss during the evaporation), the residue diluted, filtered (to remove possible traces of silica derived from the glass container), acidified with 1<sup>cm\*</sup> of four per cent hydrochloric acid, and treated, as before, at a volume of 350<sup>cm\*</sup>, with barium chloride. The results follow:

#### TABLE III.

No. of	$\begin{array}{c} { m CuSO_45H_2O} \\ { m taken} \end{array}$	BaSO₄ found	Theo <b>ry</b> for BaSO4	Error in terms of BaSO4	Error terms —S	s of c	Sodium hloride added
exp.	grm.	grm.	grm.	grm.	grm.	per cent	grm.
1.	0.9774	0.9196	0.9139	+0.0057	+0.0024	+0.26	3
2.	1.0976	1.0325	1.0263	+0.0062	+0.0025	+0.25	3
3.	1.3255	1.2444	1.2395	+0.0049	+0.0020	+0.16	3
4.	1.2855	1.2057	1.2021	+0.0036	+0.0012	+0.12	3

In this process the negative error of the former process, due to incomplete conversion of the soluble sulphate to barium sulphate, is eliminated and replaced by a positive error which can only be due to the inclusion of foreign matter, either barium chloride, or, possibly, a trace of silica, derived from the glass during the long evaporation of the hydrochloric acid solution and not completely removed by one dehydration and filtration.

In the following set of experiments aqueous hydrochloric acid was substituted for the gaseous acid and the precipitation of the sodium chloride was made by adding to the concentrated solution of the weighed copper sulphate and sodium chloride, (about 10<sup>cc</sup>), approximately five times its volume of the concentrated acid; the precipitated chloride was filtered off and the solution further treated as described above. The results of this treatment are given in Table IV.

TABLE IV.

No. of	${cuSO_45H_2O} {taken}$	BaSO4 found	Theory for BaSO <sub>4</sub>	Error in terms of BaSO4	Error in terms of $-SO_4$		Sodium chloride added
exp.	grm.	grm.	grm.	grm.	grm.	per cent	grm.
1.	0.8444	0.7912	0.7896	+0.0016	+0.0006	+0.08	3
2.	0.9775	0.9145	0.9141	+0.0001	+0.0005	+0.02	3
3.	0.9801	0.9158	0.9165	-0.0002	-0.0003	-0.03	3
4.	1.3620	1.2742	1.2736	+0.0006	+0.0005	+0.01	3

#### W. A. Turner-Sulphur in Soluble Sulphates.

It is to be seen that very fair results—very probably due, however, to a balance between the now largely reduced error due to incomplete conversion of the soluble alkali sulphate into barium sulphate and a small error due to inclusion of foreign matter—are obtained by the use of concentrated aqueous hydrochloric acid to remove the sodium salt. Experiments in which the removal of potassium chloride was similarly attempted were not equally successful, no doubt on account of the greater solubility of potassium chloride in hydrochloric acid and the greater tendency of the barium sulphate to carry down the unconverted potassium sulphate.

This method of eliminating the effect of sodium salts in the precipitation of barium sulphate would seem to have some application in the analysis of sulphides and insoluble substances where fusion with sodium carbonate is necessary. Where sodium carbonate and potassium nitrate are ordinarily used, sodium carbonate and sodium peroxide may be substituted so that only sodium salts need be removed by the treatment with hydrochloric acid.

Whenever the sulphate ion is to be determined by precipitation as barium sulphate from a solution containing sodium salts the results of the analysis may be very much improved by the removal of the sodium before precipitating the barium sulphate. The method suggested may be summarized as follows:

The substance, representing about one gram of barium sulphate, is dissolved (after fusion, if necessary, with sodium carbonate and sodium peroxide) in the least convenient quantity of water. It is then treated with five volumes of concentrated hydrochloric acid and the resulting precipitate of alkali chloride is filtered off on asbestos in a perforated crucible, by the aid of suction, into a beaker under a bell-jar. After the precipitate of alkali chloride has been completely washed by concentrated hydrochloric acid contained in a gravity wash-bottle, the filtrate and washings, diluted with an equal volume of water, are evaporated to dryness on the steam-bath, the residue taken up with a little water and 1<sup>cm<sup>3</sup></sup> of four per cent hydrochloric acid and then filtered through a small filter. The solution is then diluted to 350<sup>cms<sup>3</sup></sup>, heated to boiling and a slight excess  $(1-2^{cms^3})$  10 per cent barium chloride solution added drop by drop from a burette. The precipitate is allowed to digest on the steam-bath for some hours, over night if convenient, and then filtered on the perforated crucible, ignited at low red heat and weighed.

To Professor F. A. Gooch my thanks are due for kindly assistance and counsel in carrying out this work.

# ART. V.—An Unconformity in the Narragansett Basin of Rhode Island and Massachusetts; by G. F. LOUGHLIN and L. A. HECHINGER.\*

# Introduction and Statement of Conclusions.

As the presence of Permian beds associated with the earlier Carboniferous strata of eastern Massachusetts and Rhode Island has been suggested at various times, it may be of interest to present the evidence of a strong, though obscure unconformity within this sedimentary series which accords in position with the approximate division between what have been tentatively regarded as Permian and Pennsylvanian rocks. The investigation of this unconformity is far from complete, but, as its existence has been demonstrated and as neither of the writers is likely to have any further opportunity to visit the region, it seems proper to place on record the results thus far obtained, with the hope that other investigators may continue the work. The existence of this unconformity was suggested by the results of previous work by the senior author,<sup>†</sup> who found that the Sterling granite gneiss was intrusive into the "Coal Measures" along the southwestern border of the Narragansett Basin (fig. 1), whereas the sedimentary rocks of the Norfolk County and Boston Basins were younger than all different types of granite in the areas surrounding them. These contrasting results gave rise to the alternative hypotheses: (1) that there are present in the region two or more granite batholiths, one or more older, and one younger than all the sedimentary rocks; or (2) that the granites are not necessarily of widely different ages, but that there is within the sedimentary series a pronounced unconformity, representing a period of upheaval and granite intrusion and a succeeding period of erosion long enough to expose the newly intruded granite.

As a satisfactory study of the granite problem would have required extensive areal mapping, whereas the existence of the unconformity could be investigated within a limited area and in the limited time at the writers' disposal, the latter problem was undertaken. Lithologic proof of the unconformity's existence has been found, but field evidence as a whole is so obscure that it is not yet, and may never be, possible to give more than a rough approximation to the location of this important structural feature.

\*Published by permission of the Director of the United States Geological Survey.

†Loughlin, G. F., this Journal, 4th ser., vol. xxix, pp. 447-457, 1910. Loughlin, G. F., this Journal, 4th ser., vol. xxxii, pp. 17-32, 1911.

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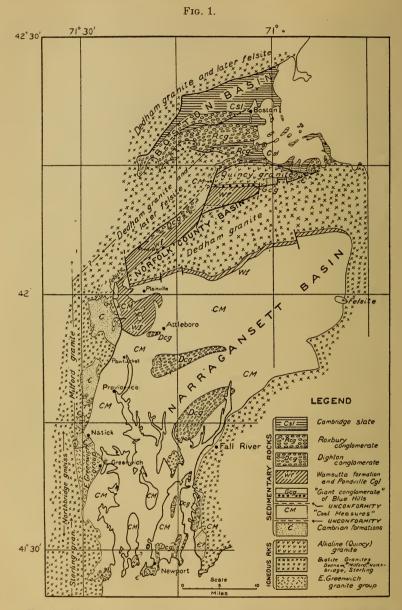


FIG. 1. Map showing distribution of formations in and around the Narragansett, Norfolk County and Boston Basins. Narragansett Basin after Woodworth and Foerste, western border of Narragansett Basin (except southern part) after Emerson and Perry, Norfolk County Basin generalized from the writers' reconnaissance work, Boston Basin largely after Crosby and Mansfield.

The unconformity separates the "Coal Measures" below from the Dighton conglomerate above, and the latter is assigned by the authors to the Permian. There is some indication that the Wamsutta formation and Pondville conglomerate are also Permian, but present evidence on this point is very meager, and the tentative assignment of these rocks to the Permian should be regarded as a working hypothesis rather than a final conclusion. In the light of the new data here presented a tentative correlation table is given, correlating the upper conglomerate of the Norfolk County Basin and the upper part of the Roxbury conglomerate with the Dighton conglomerate. The discussion of the stratigraphic problem necessarily involves some discussion of the present state of the granite problem, and it is suggested that the different biotite granites in the region may be parts of one extensive and complex batholith, rather than representatives of two or more batholiths of widely separated geologic ages, as has been supposed by several who have worked in the region. The evidence, however, on this point is also so meager that no final conclusion, only a suggestion, can be offered.

#### Summary of Areal Geology.

The positions of the three sedimentary basins are shown in fig. 1. The rocks in them are practically all conglomerates, sandstones (or arkoses), and slates, showing varying degrees of dynamic metamorphism. As these rocks have all been derived from rocks in the immediately surrounding areas, their difference in composition can best be noted after the surrounding rocks have been described. The surrounding rocks are largely granites and closely related rocks. Cambrian quartzites, slates, schists, and limestones are also present and have furnished material to the strata in all of the three basins; but only the granites are of sufficiently critical importance to need description here.

#### Grunites.

*East Greenwich granite group.*\*—The East Greenwich granite group occupies a comparatively small area, along the west border of the Narragansett Basin at East Greenwich. It comprises four principal varieties: granite and granite porphyry, a basic phase of the granite porphyry, a blue quartz-microcline porphyry, and a microgranite. A micrographic texture is a character common to all these varieties, and is especially well developed in a large part of the microgranite. Microcline is

\* The data given here are abstracted from Emerson and Perry's description. See U. S. Geol. Survey, Bull. 311, pp. 58-65, 1907. the principal feldspar, and in the one illustration given\* is characterized by prominent albite, but inconspicuous pericline, twinning.

Sterling granite-gneiss.—The Sterling granite-gneiss forms the southwestern border of the Narragansett Basin and extends westward into Connecticut. It includes two principal varieties: a normal phase, of pink to gray color, of strongly gneissoid to eugranitic texture, and composed of basic oligoclase, strongly twinned microcline, quartz, and biotite, with little or no muscovite; a contact phase of light gray color, eugranitic to gneissic texture, and composed of basic oligoclase, strongly twinned microcline, quartz, muscovite with biotite subordinate or inconspicuous, and, in some places, garnet. Local porphyritic variations of the eugranitic parts, and "augen gneiss" variations of the gneissoid parts, are present in the normal phase. The contact phase is accompanied by a large amount of pegmatite of similar composition, and pegmatitic apophyses from it are intrusive into the "Coal Measures" of the southwestern part of the Narragansett Basin. The microcline in both phases has the typical "gitter" structure, and may show some, but in no case much, perthitic structure. Chemical alteration in both phases is, as a rule, not conspicuous, but small amounts of epidote, sericite, and chlorite may be seen in thin section.

Northbridge gneiss and Milford granite.-Northward the Sterling granite gneiss area overlaps that of the Northbridge gneiss, and the two appear to be parts of the same batholith.+ Emerson and Perry, thowever, have mapped the Northbridge gneiss as pre-Cambrian. North of Natick, R. I., the Milford granite, intrusive through Cambrian strata, is the most extensive granite immediately west of the Narragansett Basin. This granite is generally similar to the Northbridge gneiss and Sterling granite gneiss. According to Emerson and Perry, § its most gneissoid parts can not be sharply distinguished in the field from the Northbridge gneiss, but in thin section its alkalic feldspar is a microcline microperthite, whereas that of the Northbridge gneiss is strongly twinned microcline without conspicuous perthitic intergrowth. The plagioclase member of the microperthite is dusted with epidote, and in thin sections studied by the present writers, plagioclase grains show a conspicuous microscopic alteration to epidote and sericite, and the biotite grains to chlorite. The authors above cited regard the Milford granite as older than the "Coal Measures" of the Narragansett Basin, but their descriptions, cited on a later page, suggest that this interpretation is open to question.

<sup>\*</sup> Idem fig. 6.

<sup>Loughlin, G. F., this Journal, (4)., vol. xxix, pp. 450, 451, and 454, 1910.
‡ U. S. Geol. Survey Bull. 311, p. 10, 1907.
§ Op. cit., p. 10. || Op. cit., pp. 39-40.</sup> 

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Dedham granite.—The Dedham granite with associated basic plutonic rocks covers a large area, including the northwestern corner of the Narragansett Basin and almost the entire northwest side of the Norfolk County Basin. At several places it is cut and in part covered by bodies of felsite. Rocks of the same general descriptions surround the Boston and Norfolk County basins, and probably occupy much of the area east of the Narragansett Basin, but the writers' acquaintance with the latter field is too limited to warrant a more positive statement. Granite similar in all respects to the porphyritic phase of the Dedham granite is exposed on Newport Neck and Conanicut Island at the southern end of the Narragansett Basin. The complete series of rocks probably includes all types and gradations from alaskite and aplite, through common biotite granite, granodiorite, diorite, and gabbro, but only the first two types need con-sideration here. The biotite granite is greenish gray to pink or even red, medium- to coarse-grained and in places coarsely porphyritic. Gneissic structure is almost everywhere absent. Its principal minerals are basic oligoclase (to andesine), strongly twinned microcline-microperthite (potassic member dominant), quartz, biotite, and in some cases hornblende. Epidote and chlorite are everywhere conspicuous, either in short irregular veins, or replacing plagioclase and the black silicates. Microscopic sericite is also abundant, and secondary quartz and calcite may be present, especially in the veins. The aplitic phase is of generally pink color and varies in texture from an evengrained aplite to granite-porphyry. The mineral composition and character is much the same as in the type just described, save that the plagioclase is more sodic and the green alteration minerals are less conspicuous. The Dedham granite is clearly younger than Cambrian rocks, and older than Permian, but its relations to "Coal Measures" and Milford granite have not been definitely determined.

Quincy granite.\*—The Quincy granite occupies a limited area at the northeast end of the Norfolk County Basin, separating it from the Boston Basin. The main body is bluish gray, or pink where locally oxidized, and medium-grained. Its feldspar is a microcline microperthite in which the two members are in about equal amount, the microcline member showing only albite twinning and the albite member frequently forming a continuous rim around the main intergrown portion. Plagioclase is scarce or absent. The black minerals are riebeckitic amphibole and ægerite, both in distinct grains and in minute crystals impregnating the feldspar and quartz. Gran-

\*An exhaustive study of the Quincy granite and associated alkaline rocks has been made by C. H. Warren. Petrology of the alkali-granites and porphyries of Quincy and the Blue Hills, Mass., Am. Acad. Arts & Sci., vol. xlix, No. 5, pp. 203-330, Sept. 1913.

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ite-porphyry and quartz felsite-porphyry with the same characteristic minerals border the main mass. Besides the principal occurrence, Emerson and Perry\* have mapped granitic rocks of similar character along the west border of the Narragansett Basin at Cumberland, R. I., and Woodworth<sup>+</sup> mentions limited occurrences near Hanover Four Corners, Easton, and Mans-field, Mass. Recent field studies by C. H. Warren and Sidney Powers in Cumberland, R. I., and by F. H. Lahee in Sharon, Mass., have discovered new areas of the same alkaline type of granite and have produced undoubted proof that it is intrusive into the Milford and Dedham granites, the alkaline type having chilled contacts against the others.<sup>‡</sup> The main area of Quincy granite is older than rocks which will be shown to be of probable Permian age.

Comparison of granites .- Comparison of the foregoing descriptions shows that the East Greenwich granite group has textural features very distinct from those of all the other granites. The Quincy granite also is distinctly different from the others in mineral and chemical composition as well as in certain textural details, and is clearly intrusive into the Milford and Dedham granites. The other granites are similar to one another in mineral composition save for local variations, such as the contact phase of the Sterling granite gneiss and the alaskitic phases of the Dedham granite. They present certain textural variations, but these are not reliable criteria for their distinction, as the Sterling alone varies from engranitic to highly gneissoid, and variations in the texture of the Milford granite render a sharp distinction between it and the Northbridge gneiss impossible. The Dedham granite, owing to its general lack of gneissoid structure and its more pronounced degree of chemical alteration, may appear distinct from the other granites, but the results of field work thus far have not proved any sharp structural or textural differences between it and the Milford granite, § and its greater degree of alteration, as will be shown later, appears to coincide in areal extent with the area most severely affected by the upheaval of Permian rocks. No published results of a systematic study of all these granite areas is avail-

\*Op. cit., p. 51 et seq. † Woodworth, J. B., U. S. Geol. Survey, Mon. 33, p. 116. ‡ Personal communication by C. H. Warren. Warren and Powers are publishing their results in Geol. Soc. America Bull., vol. xxv. 1914.

\$ The writers, during their limited observations in the granite areas, were unable to find any reliable textural criteria for distinguishing the Dedham, Milford, and Sterling granites from one another. C. H. Warren, in a personal communication, states that the results of field and laboratory studies by Mr. Sidney Powers and himself in various parts of the region, and espe-cially in the vicinity of Diamond Hill, R. I., lead him to believe that different medium- to coarse-grained biotite granites are in reality parts of one extensive batholith.

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able at present, and reliable structural data pointing to their separation or correlation is lacking. Certain distinctions in age have been made, but the structural evidence for these distinctions, some of which is cited in this paper, does not appear convincing, and it remains for future work to determine the structural and age relations of these granites to one another. Until this is done, some of the statements here presented must be regarded as tentative. Further attention will be called to the granite problem on later pages.

#### SEDIMENTARY ROCKS.

#### Narragansett Basin.

The sedimentary rocks of the Narragansett Basin are grouped by Woodworth as follows:\*

- 4. Dighton conglomerate group
- 3. Rhode Island Coal Measures
- 2. Wamsutta group
- 1. Pondville group (conglomerates with basal arkose)

As the Pondville and Wamsutta formations are limited to the northern part of the Narragansett and to the adjoining Norfolk County Basins, and as the evidence at hand regarding them is scant, they will not be considered until after the "Coal Measures" and the Dighton conglomerate.

The "Coal Measures."-The "Coal Measures" are the most extensive formation of the Narragansett Basin, and in their southern part include what Foerste has called the Kingstown series (fig. 1), which is cut by apophyses of the Sterling granite gneiss. The part of Foerste's Kingstown series studied by the senior author? is limited to the southwest part of the Basin nearby the granite contact. It consists of an alternating series of light to dark gray arkose, conglomerate, and phyllite, and one or more graphitic beds. The conglomerate pebbles, besides Cambrian quartzite, and schists, include white-weathering quartz felsite-porphyry and granite of the East Greenwich type. The arkose and the conglomerate matrix consist of quartz, plagioclase, some microcline of the East Greenwich granite type, biotite, and muscovite. There is a total absence of pebbles or mineral grains characteristic of any of the other granites involved in the problem-notably the Milford and Dedham types.

At Natick, R. I., north of the area visited by the writer, Foerste<sup>+</sup> describes the basal conglomerate beds of the "Coal

\* U. S. Geol. Survey Mon. 33, p. 134.

† This Journal (4), vol. xxix, p. 455, 1910.

‡Op. cit., p. 254.

Measures" as resting unconformably on Cambrian quartzite and granite, and as containing large pebbles of the granite. These structural features are, in the main, confirmed by Emerson and Perry," who describe the Carboniferous conglomerate resting on the Milford granite, but their microscopic study of the granite pebbles proves them all to belong to the East Greenwich type and none to the Milford. At one place near Natick they describe "a contact of the Milford granite and the conglomerate which might be interpreted as an intrusive contact, since it . . . cuts across the laminæ of the sericite schist (metamorphosed Carboniferous). The alteration of the rock here is probably due to crushing. The extreme metamorphism of the conglomerate, combined with the small amount of mashing and jointing, is very characteristic." Farther north, in Cranston, R. I., they describe a few places where the Carboniferous conglomerate and Milford granite become intimately blended along the contact. These descriptions, both of structural relations and of total absence of Milford granite pebbles in the conglomerate, convey to one who has only studied the contact along the undoubtedly intrusive Sterling granite gneiss the impression that the Milford granite also is intrusive into the "Coal Measures" conglomerate; Emerson and Perry, however, regard the conglomerate as resting unconformably on the granite. There is, nevertheless, no question that there is a total absence in the "Coal Measures" conglomerate of any pebbles of the Sterling, Northbridge, Milford, and Dedham types of gneiss and granite. The writers were able to study outcrops remote from the contact only in the area between Providence and the northern boundary of the Basin, and here also no trace of any of the granites in question was found. Pebbles of a quartz-felsite porphyry with white weathered surfaces are numerous in the conglomerate exposures of this area, but their microscopic characters are so obscured by alteration that the writers can not determine their source.

Fossil plants and insects have been found in the "Coal Measures" at a number of localities, + and have been determined by Lesquereux as equivalent to the Upper Carboniferous or Pennsylvanian. One species, Sigillaria volzii, found west of Plainville, Mass., is stated by him to be rare in the "Coal Measures" of America, one specimen being seen by him from the Plymouth F vein in Pennsylvania, a horizon near the top of the anthracite field.<sup>‡</sup> Haynes,<sup>§</sup> in 1912, found impressions

\* U. S. Geol. Survey, Bull. 311, pp. 39-40, 1907.

+ Lists of these fossils are given by Woodworth, op. cit., pp. 202-205, after Lesquereux and Scudder.

<sup>‡</sup>Cited by Woodworth, op. cit., p. 181. § Haynes, W. P., Discovery of bivalve crustacea in the Coal Measures near Pawtucket, R. I., Science, new ser., vol. xxxvii, pp. 191-192, 1913.

of bivalve crustacea of the genera *Leaia* and *Estheria* in the "Coal Measures" near Pawtucket, R. I. These are said to correspond closely to specimens found in the "Coal Measures" of Illinois and Indiana. and in the Conemaugh formation of the Carboniferous of Pennsylvania. Haynes remarks that fossils of the two genera occur at several horizons in the "Coal Measures" and that neither genus therefore is a good horizon marker. He also remarks that by correlation with the Conemaugh formation, this horizon in the Narragansett Basin would be the equivalent of the middle of the "Lower Barren Measures" of middle Pennsylvanian age. There seems, therefore, from combined fossil evidence, no occasion for doubt that the "Coal Measures" of the Narragansett Basin are of Pennsylvanian age.

The Dighton conglomerate.—The Dighton conglomerate, with which is correlated and mapped the Purgatory conglomerate of the southeast part of the Basin,\* is prevailingly of very coarse texture in marked contrast to the typical "Coal Measures," but includes beds of finer conglomerate and sandstone. It forms isolated areas of considerable size along synclinal axes (fig. 1) and its beds in some places have very steep dips. The writers have been able to study only the areas in the northern part of the Basin, but find in these a uniform and distinctive composition. The pebbles include, besides an abundance of quartzite, vein quartz, felsite and slate, a large amount of Sterling granite gneiss, and a considerable proportion of the metamorphosed "Coal Measures" arkose, of the type identical with that in Foerste's Kingstown series. The Sterling granite pebbles are largely of the muscovitic and pegmatitic contact phase, and also represent the normal gneissoid type. Some of the granite pebbles are free from marked gneissoid structure, and it cannot safely be said whether they represent a eugranitic variation of the Sterling, or a medium grained type of the Milford or Dedham granites. Some of the pebbles are distinctly epidotized, but such an alteration is not a safe criterion for distinction, since the Sterling and Milford granites, as well as the Dedham, are altered locally, and it is very possible that the alteration so characteristic of the Dedham granite was developed during the period of upheaval which followed deposition of the Dighton conglomerate.

The identity of the metamorphosed arkose pebbles is proved both by their megascopic and microscopic characters, which agree in all essential details with those of the type rock. One pebble was collected showing an igneous contact between the arkose and the contact phase of Sterling granite gneiss.

\* Mon. U. S. Geol. Survey, No. 33, p. 134.

*Proof of unconformity.*—The presence in the Dighton conglomerate of pebbles of Sterling granite gneiss and of the arkose is absolute proof that an unconformity exists between the Dighton and the "Coal Measures." The unconformity represents a time interval long enough to account for the intrusion of an extensive granite batholith, an essentially contemporaneous period of intense folding and dynamic metamorphism,\* and a subsequent period sufficient for erosion to uncover a portion of the newly intruded granite.

The writers were unable to find any structural indication of an angular unconformity in the exposures examined by them, but this is not surprising, as outcrops are separated by extensive drift-covered areas, and it is possible that all traces of the unconformable contacts are covered. Furthermore, the fact that both the older and newer formations have been severely compressed and folded may obscure or obliterate any unconformable contacts. Only a beginning, however, of the attempt to locate the contact has been made, and it is hoped that some of those within reach of the field may have the time to make a thorough search, and by correlation of beds through their pebble compositions may at least succeed in mapping the approximate position of the contact.

Age of Dighton conglomerate.-- No fossils + have been found in the Dighton conglomerate, but it is now possible to assign to it a definite age on structural grounds. It is separated by an unconformity from the "Coal Measures," and in the writers' opinion must be post-Pennsylvanian; on the other hand, it is itself intensely folded and compressed, in marked contrast to the red Triassic beds to the west in Connecticut and Massachusetts, which have suffered no conspicuous amount of folding or compression. It therefore appears to be pre-Triassic, although an absolute correlation on structural grounds between two such isolated areas is of course impossible. The only age between Pennsylvanian and Triassic is the Permian, and to this age, in the writers' opinion, the Dighton conglomerate should therefore be assigned. It is interesting to note that Woodworth<sup>‡</sup> suspected the existence of the unconformity because of the contrasting climatic and physiographic conditions which must have prevailed during the deposition of the relatively fine-textured "Coal Measures" with their coal beds,

\*Loughlin, G. F., this Journal (4), vol. xxix. pp. 454-455, May, 1910. Lahee, F. H., Relations of the degree of metamorphism to geological structure and to acid igneous intrusion in the Narragansett Basin, R. I., ibid., xxxiii, pp. 466-467, 1912.

<sup>†</sup>Since the writing of this paragraph, David White has orally informed the writer that he has found obscure fossil plant fragments in the Dighton conglomerate which are suggestive of Permian age.

‡ Op. cit., pp. 186-187.

and the coarse Dighton conglomerate. He accordingly suggested the possibility that a part or all of the Dighton conglomerate might be of Permian age.

Discussion of the granite problem.—The fact that the Sterling granite-gneiss and its equivalents have been traced as far west as the Triassic trough of Connecticut<sup>\*</sup> and that a northward continuation of them cuts fossiliferous Carboniferous phyllites at Worcester, Mass., + which are regarded by some, including the writers, as of probable Pennsylvanian age, and is believed to extend as far northward as Andover, Mass., if not into New Hampshire, gives some idea of the extent of this granite batholith, and of the area affected during the period of upheaval which took place between the deposition of the "Coal Measures" and the Dighton conglomerate.

So extensive an area was doubtless marked by different intensities of compression in different parts, in consequence of which the granite, which was being intruded at the time, developed a highly gnessoid structure in some places and only moderate or inconspicuous foliation in others. Again, some portions of the granite may not have consolidated until after intense compression had ceased. It is reasonable to assume that in such places conditions were especially favorable for differentiation into different granitic as well as dioritic types, giving rise to the Dedham type of granite with its varia-tions and associated basic rocks. The structural relations of the Quincy alkali-granite type of the biotite granites is proof that it represents a distinctly later eruption; but, as it will be shown later that the Quincy granite is older than conglomerate of probable Permian age, the alkaline granite is to be considered the last product of the complex batholithic period, erupted after regional compression had ceased and the upper portions of the biotite granite and older sedimentary rocks had cooled sufficiently to give rise to the chilled margins which characterize the Quincy granite.

It will doubtless be contended that the time interval between late Pennsylvanian and early Permian was insufficient to account for so extensive and complicated a period of upheaval and batholithic intrusion; that the Dedham and Milford granites are of much earlier date, that the Quincy type was intruded at some time between this early date and the Carboniferous, and that the Sterling granite represents the latest of 3 distinct batholithic intrusions. In reply it may be said that even if the other granites can be proved to be of distinctly

\*Loughlin, G. F., The gabbros and associated rocks at Preston, Conn., U. S. Geol. Survey, Bull. 492, pp. 133-135, 1912. †Emerson, B. K., and Perry, J. H., The geology of Worcester, Mass.

earlier age than the Sterling and its equivalents, the area affected by the upheaval accompanying the intrusion of latter granites will not be diminished, and the earlier granites must be regarded as remnants of older batholiths which escaped obliteration within the area affected by the latest batholith.\* Such relations, of course, are possible, but have not been proved. The hypothesis of a single complex batholith is entitled to quite as much consideration, and, if proved by more extended and detailed work, will go far towards clearing away several of the stratigraphic and structural complications which have persisted under the multiple batholith hypothesis.

That the single batholith hypothesis is far from impossible may be shown by comparison with igneous rock areas in the West. Igneous rocks, both intrusive and effusive, extend over much of the Cordillera and represent a great variety of types, from very acidic to very basic, and from subalkaline to alkaline. These were mostly erupted within an interval between late Cretaceous and early to middle Tertiary time, and, in some restricted areas, within narrower limits. As they accompanied, or closely followed, the Laramide revolution, there was in the West a period of extensive upheaval and complicated igneous activity within a short interval of geologic time-late Cretaceous to early or middle Tertiary. In the Sierra Nevada, the plutonic rocks, consisting largely of granodiorite but ranging from granite to gabbro, are intrusive into steeply dipping Jurassic slates, but are distinctly older than lower Cretaceous beds. Both upheaval of the Jurassic slates and the extensive intrusion of the igneous complex took place within the interval between late Jurassic and early Cretaceous. It is, therefore, demanding no excessive speed of geologic processes to hold the view that all the granites within the small portion of New England under consideration were erupted during the interval between late Pennsylvanian and early Permian. Attention may also be called to the extensive igneous activity which existed throughout a large part of Europe during late Carboniferous and early Permian time. In fact the deformation and igneous activity which took place between the deposition of the "Coal Measures" of Rhode Island and the Dighton conglomerate give to the area under consideration a European rather than American character.

\* In this case, the earlier biotite granites may prove to be the equivalents of the granite along the northeast half of the Maine coast, which has been determined to be of Devonian (?) age. U. S. Geol. Survey Geol. Atlas, Penobscot Bay folio (No. 149), 1907; or they may be correlated with the Taconic revolution, as stated by C. H. Clapp. (The igneous rocks of Essex Co., Mass.: abstract of thesis presented in part fulfillment of degree of Ph.D., Mass. Inst. Tech., Boston, Mass., 1910.) Dr. Clapp's detailed discussion of the granite problem is awaiting publication.

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Evidence of two orographic periods.-Another point of interest is the evidence that two periods of orographic upheaval have taken place in the area: The first, at the close of, or during, Pennsylvanian time, was accompanied by the invasion of an extensive granite batholith; the second was sufficient to develop steeply dipping folds and intense compression effects, but there is no evidence that it was accompanied by granitic intrusion. It seems, from the writers' acquaintance with the surrounding region, that the first upheaval acted generally in an east-west direction, accounting for the present prevailing north-south strikes of strata and of schistosity, whereas the second acted for the most part in a nearly north-south direction, developing the folds with nearly east-west axes. Further study of the folds in the southeast part of the Narragansett Basin may require a modification of the last part of this statement. The earlier upheaval was probably very widespread, whereas the second one, based on correlations which follow, extended over a relatively limited area of the present land surface, which embraces the present Narragansett, Norfolk County, and Boston basins, but whose outer limits are not known. The characteristic alteration and abundance of slickensided fractures in the Dedham granite are most marked in the areas adjacent to these basins, and are the same in composition and character as those which characterize the more highly sheared and compressed exposures of the conglomerates in the basins. As these conglomerates contain Dedham granite pebbles, the alteration, both of the granite and of the conglomerates, is believed to have been developed during the second orographic period.

#### Pondville Conglomerate.

The Pondville conglomerate,\* or Pondville group as Woodworth<sup>+</sup> called it, consists of gray to whitish basal arkose and suprabasal conglomerate beds. It is limited to the northern border of the Narragansett Basin and to the southeastern border of the Norfolk County Basin. It grades upward into the Wamsutta formation and rests unconformably upon biotite granite, separating the latter from the overlying Wamsutta formation, save at a few places where Wamsutta beds rests directly upon the granite. The type section at Pondville in the Norfolk Basin shows granite passing by almost insensible gradations into arkose, which is directly overlain by alternating beds of arkose and grits with vein-quartz pebbles and occasional nodules of biotite granite. Above these is an alternating succession of quartz-pebble conglomerates and red

> \* This name has been adopted by the U. S. Geol. Survey. † Op. cit., pp. 134-141.

and green slates. Woodworth states\* that "the prevailing whitish and grayish hues of the basal arkose, and of the conglomerates immediately above them, are in strong contrast to the often vivid reds of the overlying and occasionally intercalated Wamsutta series," and advances the supposition "that the superficial products of weathering previous to their transportation in Carboniferous time were leached of their iron salts, which penetrated downward. The first transportation of detritus affected the superficial leached layer, and thus the basal beds became white. . . When erosion had stripped away the bleached materials at the surface, it reached the highly discolored rock beneath, as yet very imperfectly disintegrated, from which were produced the red beds of the Wamsutta series."

The granite pebbles from the Pondville conglomerate, as well as from the Wamsutta formation, are of the same type, both in megascopic and microscopic characters, as the underlying granite mass. The granite mass, though in an area which is prevailingly of the Dedham type, has characters strongly resembling variations of the Sterling granite-gneiss in which gneissoid structure is absent or inconspicuous.

The Wamsutta formation.—The name Wamsutta group was given by Woodworth<sup>+</sup> to designate the series of red conglomerates, sandstones, and shales which occupy the northern part of the Narragansett Basin and are continuous with the strata of the Norfolk County Basin. It passes downward into the Pondville conglomerate, and in places is exposed resting directly on granite. The writers studied this formation in the northwest part, and along part of the northern border of the Narragansett Basin, but in the limited time at their disposal found no exposures where the relations of the Wamsutta to the other sedimentary formations were clearly indicated. They will, therefore, confine themselves to consideration of the composition of the Wamsutta formation, before attempting to discuss structural relations.

The principal pebbles in the conglomerate beds are quartzite, granite representing different variations of the Dedham (and Milford?) types and locally felsite of the type which cuts the Dedham granite in nearby areas, not the white-weathered type so abundant in the "Coal measures." The presence of Dedham granite pebbles points to a more intimate relation of the Wamsutta formation to the Dighton conglomerate, containing Sterling (and Dedham?) granite pebbles, than to the "Coal Measures" which contain neither. This relation can only be suggested at present, as the relations between the Dedham, Milford and Sterling granites must be proved before the

\* Op. cit., p. 138.

† Op. cit., p. 141.

significance of granite pebbles in the conglomerate can be finally known. No pebbles strongly resembling the muscovitic contact phase of the Sterling granite-gneiss were noted.

The Wamsutta exposures are so isolated, both with respect to themselves and to the other formations, that structural features of critical value are largely, if not wholly, concealed. The main Wamsutta area is separated from the granite area on the west and southwest by a narrow band of "Coal Measures," but all contacts in the area studied are concealed. The strikes and dips of the two formations where studied are discordant, and suggest a concealed unconformity or a fault. Study of composition at this place was inconclusive. The Wamsutta (and Pondville) beds are chiefly fine highly quartzose conglomerates and sandstones, with all their pebbles badly stained with iron oxide. Weathered red feldspar from the nearby granite was found, but if any "Coal Measures" material was present, its identity was destroyed by red staining. Woodworth, who interpreted the Wamsutta as underlying the northmost part of the "Coal Measures" and grading southward into their lower portion, assumed a fault at this place (fig. 1), the Wamsutta beds rising with respect to the "Coal Measures." He suggests faults at other places to account for discrepancies in the stratigraphy, but the data shown in his illustrations are very meager.\* He states elsewheret that steep dips, faulting and isolation of outcrops renders it impossible to work out the stratigraphy with certainty.

The only fossils found in the Wamsutta formation are a few specimens of *Calamites sp.* and *Cordaites sp.*, both of which genera range through the Pennsylvania and into the Permian.

The writers regret their inability to arrive at a more satisfactory conclusion regarding the stratigraphic relations of the Wamsutta formation in this basin. They can only express the opinion that, in view of the extreme obscurity of structural features, the composition of the beds suggests that the Wamsutta may be more closely related to the Dighton conglomerate, which is regarded by the authors as of Permian age, than to the "Coal Measures." If more thorough study succeeds in the discovery of undoubted pebbles of the "Coal Measures" strata and of the contact phase of the Sterling granite-gneiss, the Permian age of the Pondville conglomerate and of the Wamsutta formation may be considered proved; on the other hand, if future discoveries of fossils prove these formations to be of Pennsylvanian age, the unconformity indicated in the second and third columns of the correlation table must be placed above the Wamsutta formation. In the

> \* Op. cit., p. 157, fig. 16; and p. 184. † Op. cit., pp. 143-146.

latter case there will also be absolute proof that the Dedham and Milford granites are pre-Pennsylvanian and quite distinct from the late or post-Pennsylvanian Sterling granitegneiss; and both of the tentative hypotheses suggested in this paper will become untenable.\* A little additional evidence, which, though scant, is more conclusive, will be given in the following section.

# The Norfolk County Basin.

The structure of the Norfolk County Basin is obscure and complicated, and the Basin as a whole has never received adequate study. The statigraphy of the Basin, in consequence, is only known in a general and probably imperfect way. The part of the Basin west of Canton Junction, or the transverse fault shown in fig. 1, appears, so far as could be learned from reconnaissance work, to be of monoclinal structure, with northwesterly dip. The southeast border is marked by an unconformable contact with granite of the Dedham type, and the northwest border by a fault, along which the sedimentary strata dip down against an area of Dedham granite. The strata include the Pondville conglomerate, overlain by a thick series of red and occasional green beds which are continuous with the Wamsutta formation of the Narragansett Basin. The red beds pass upward into medium to coarse conglomerates in which are intercalated occasional red and green slate beds. The main series of red beds and the overlying conglomerate are identical in essential composition, and the chief difference between them appears to be a difference in the amount of fine red matrix which determines the degree of redness. Where the fine red matrix is inconspicuous in either formation, the beds have a green or greenish-gray color. Dedham granite pebbles are numerous in both formations, and in the

\*As a third possible set of conditions, it may be supposed that although no fossils of critical stratigraphic value may be discovered in the Pondville and Wamsutta formations, some structural evidence may be found which will prove the Dedham and Milford granites to be pre-Pennsylvanian and therefore distinctly older than the Sterling granite-gneiss. In this case, the presence of Dedham and Milford granite pebbles in the Pondville and Wamsutta formations will afford no definite clue to the age of these strata; for the fact remains that the "Coal Measures" contain no pebbles of the granites in question, but do contain pebbles and grains derived from formations which are certainly older than the granites and which, according to this view, are supposed to have once formed a cover over the granites. If the Pondville and Wamsutta formations are older than the "Coal Measures," it is necessary to explain why the younger formation was derived only from rocks of pre-granite age, whereas the two older formations were derived largely from the granites which could have been exposed only after a large part of the pre-granite rocks covering them had been removed. The cause can hardly be attributed to difference in chemical conditions of weathering, as the "Coal Measures" contain an abundance of feldspathic material.

# in the Narragansett Basin.

upper conglomerate a few pebbles resembling the gneissoid Sterling type were found. None resembling the muscovitic contact phase of the Sterling type were noted. Occasional small arkose pebbles identical in composition with typical beds in the "Coal Measures" were also found, but only in a few outcrops. This evidence indicates that the red (Wamsutta) strata and the overlying conglomerate were derived from one general source and in one continuous period of deposition, the earlier part of which was marked by an abundance, and the latter part by a scarcity, of the fine red matrix. The presence of "Coal Measures" arkose and Sterling granite pebbles in the coarse conglomerates favors its correlation with the Dighton conglomerate, which is regarded by the writers as of Permian age.

The part of the Norfolk Basin east of Canton Junction has been described\* as consisting essentially of the north limb of a syncline, bounded by a profound fault on the south side and by an unconformable contact along the Quincy granite of the Blue Hills on the north side. This eastern part of the Basin thus lies in an opposite attitude to the western part. The strata present are a local basal conglomerate of extreme coarseness overlain by the series of red beds. The upper conglomerate is not represented. The basal conglomerate contains pebbles of both Quincy and Dedham granite, and the red strata pebbles of the Dedham granite. An occasional small arkose pebble of the "Coal Measures" type was also found. The presence of these occasional arkose pebbles in the red strata further suggests their correlation with the Permian, and this tentative correlation is indicated in the table on page 63; but owing to the scarcity of the arkose pebbles and to the absence of fossils of critical value, the writers refrain from committing themselves to more than a tentative correlation.

It is interesting in this connection to note the presence west of the Blue Hills<sup>+</sup> (fig. 1) of an isolated outcrop of altered sandstone with black carbonaceous partings, of the same general character as beds in the "Coal Measures" (fig. 1). Its complete isolation prevents more than this mere suggestion of correlation based on lithologic appearance.

#### The Boston Basin.

The Boston Basin strata consists chiefly of the Roxbury conglomerate and the overlying Cambridge slate. The conglomerate has generally been regarded as equivalent to the

<sup>\*</sup>W. O. Crosby has given a detailed description of this area; (Geology of the Boston Basin, vol. 1, Part 3, The Blue Hills Complex. Boston Soc. Nat. Hist.).

A summarized description has been given by G. F. Loughlin; this Journal (4), vol. xxxii, pp. 17-35, 1911. † See also this Journal (4), xxxii, p. 26, fig. 2.

strata of the Norfolk County Basin, and evidence both lithologic and structural supporting this correlation has been presented in a paper previously cited.\* The evidence presented in the present paper thus correlates the Roxbury conglomerate as Permian, and in this respect accords with conclusions of others who have produced evidence pointing to the glacial origin of a part of the conglomerate, and therefore assign it to the Permian, an age of wide-spread glaciation. Crosby<sup>+</sup> for a number of years has suggested that the coarse conglomerates in the Boston Basin were of possible glacial or aqueo-glacial origin. The late N. S. Shaler expressed similar views.

Mansfield,<sup>‡</sup> in his study of the Roxbury conglomerate, concluded that aqueo-glacial conditions probably existed during its deposition. Later, in 1910, Sayles and La Forges described localities in Hyde Park and Squantum, Mass., where an upper horizon of the Roxbury conglomerate presented characteristics typical of tillite. Regarding the age of the conglomerate, they say: "In view of the accumulating evidence of glaciation in many parts of the world in Permian time, it seems a reasonable assumption that if glacial conditions prevailed in eastern New England at some time late in the Carboniferous period, they were contemporaneous with similar conditions elsewhere, and hence that glacial deposits found in the Carboniferous rocks of the Boston region were formed in Permian time." The coarse textures of the conglomerate above the red strata in the Norfolk County Basin and of the Dighton conglomerate in the Narragansett Basin accord with that of the Roxbury conglomerate so far as indications of Permian climate are concerned, though no identification of tillite has been made in them. The unconformity between fossiliferous "Coal Measures" and Dighton conglomerate demonstrated in the present paper thus furnishes definite structural proof in support of the Permian age of the conglomerates as suggested by Sayles and La Forge.

### Tentative Correlation of Strata in the Three Basins.

The accompanying table summarizes the tentative revision of the stratigraphy of the three basins. The position of the Pondville conglomerate and Wamsutta formation is obviously

\* Loughlin, G. F., this Journal, (4), vol. xxxii, pp. 25-31, 1911. † Crosby, W. O., Oral communications. Prof. Crosby has alluded to this point at different places in his "Geology of the Boston Basin." ‡ Mansfield, G. R., The origin and structure of the Roxbury conglomerate. Harvard Coll. Mus. Comp. Zool., Bull., vol. xlix (Geol. Ser. vol. viii, No. 4), 2000 1000 p. 260, 1906.

S Sayles, R. W., and La Forge, L.: The glacial origin of the Roxbury Conglomerate, Science, n. s., vol. xxxii, pp. 723-724, 1910.

	Rocton Racin	TTOROT TIONOOT	Cambridge slate	Bovburw aonolomometa	oublouterate	: ;		Braintree slate	Weymouth formation <sup>3</sup>	Base destroyed by intrusion	
ABLE	Norfolk County Basin		Erosion surface	Upper conglomerate = Dighton conglomerate	Wamsutta formation	Pondville conglomerate (including basal arkose) and locally the "giant conglomerate"; exact re- lations to each other undetermined			•	Base destroyed by intrusion	
TENTATIVE CORRELATION TABLE		Northern part		1		H	ประกูษฐาย เป็นชื่อมีชื่อ เป็นชื่อมีชื่อ เป็นการเป็น เรื่อมีชื่อ เรื่อมีชื่อ เรื่อมีชื่อ เรื่อมีชื่อ เรื่อมีชื่อ เรื่อมีชื่อ เรี เรื่อ เรื่อ เรื่อ เรื่อ เรื่อ เรื่อ เรื่อ เรื่อ เรี เรื่อ เรี เรี เรื่อ เรี เรื่อ เรี เรี เรี เรี เรี เรื่อ เรี เรี เรี เรี เรี เรี เรี เรี เรี เรี	Unconformity Unconformity?- Braintree slate?	Cambrian (and pre-Cambrian?) quartzite.		Base destroyed by intrusion
CORRE	t Basin	Northe		-Erosion surface	Wamsutta formation	Pondville conglomerate (including basal arkose	-urta svis stitoic i s i s i s i s i		etite stite setim	id Brg	<u></u>
NTATIVE	Narragansett Basin	Central and Southern parts	Erosion surface	Dighton conglomerate		Unconformity (igneous ac- tivity and erosion)	sures"	Unconformity	Cambrian (and pre- Cambrian?) quartz- ite, schists, etc., <sup>1</sup>	cut by East Green- wich granite group	Base destroyed by intrusion
TH		Central	Erosion	Dighton		Unconf tivitv	sə. 91	tiasry 91 iasry 9a (	itoid 9vi ilsălts vo ? 9tial91	zurtal d tuo bas)	
	Age classification Tentative age clas-	sincation proposed in this paper	-	Permian		Permian ?	Pennsylvanian	Middle Cambrian	Lower Cambrian		Pre-Cambrian ?
	Age classification	of U. S. Geolog- ical Survey			Carboniferous		Pennsylvanian	Middle Cambrian	Lower Cambrian		Pre-Cambrian ?

For description of these rocks see Emerson and Perry; U. S. Geol. Survey, Bull. 311.
 For description of these rocks see Crosby, W. O., "Geol. of Boston Basin, Part'III (The Blue Hills Complex)": Occ. Papers, Boston Soc. Nat. Hist., 1900.
 Name proposed by La Forge in Science, n. s., vol. xxix, p. 945, 1909, for the fossiliferous beds of Lower Cambrian age in the Boston Basin. For description of rocks see Crosby, W. O., "Geol. of Boston Basin, Part III (The Blue Hills Complex)": Occ. Papers, Boston Soc. Nat. Hist., 1900.
 As the presence of effusive felsite resting on an erosion surface of granite indicates an unconformity older than that marked by complexate

resting on felsite and granite, the unconformity at the base of the Permian is in reality a double one.

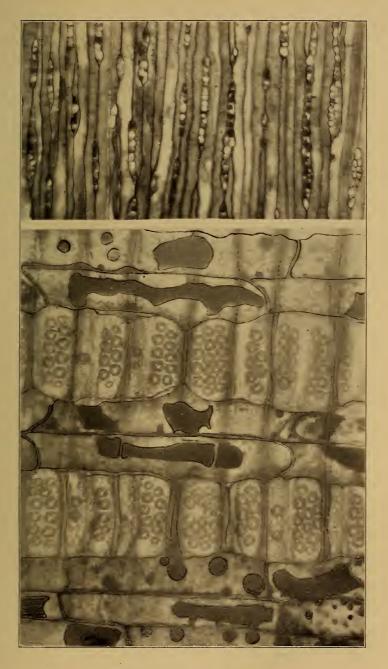
## 64 Loughlin and Hechinger—Narragansett Basin.

the weakest point in the argument, owing to the scarcity in them of "Coal Measures" pebbles, and to the present indefinite state of correlation of the Dedham, Milford and Sterling granites, and it is hoped that others will have an opportunity to gather more evidence which will afford a more convincing determination of the question. So far as the writers' experiences go, it seems that the answer to this question may best be found through a correlation of the different biotite-granite areas (save the East Greenwich). There is at present in the writers' opinion no convincing evidence of more than one general age for these extensive granite masses; in other words, no proof that they are not parts of one immense complex batholith. If future discoveries of fossils in the Pondville and Wamsutta strata shall prove them to be of Pennsylvanian age, they will also prove the Dedham and Milford granites to be distinctly older than the Sterling. If, on the other hand, further work proves that the biotite granites are all parts of one batholith, which varies from place to place in textural features, or in the relative prominence of micas and hornblende, the Permian age of the Pondville conglomerate and Wamsutta formation will be a necessary corollary to the proof. In this case the granites, both the biotite and the later alkaline types, which have heretofore necessarily been designated merely as post-Cambrian, may be classed within the narrow limits, late Pennsylvanian and early Permian. This involves a very profound period of intrusion, upheaval, and erosion between these two ages which in general have been regarded as closely associated; but proof of such a great time break has already been presented in this paper.

In conclusion, the writers wish to remind their readers that while the unconformity between the "Coal Measures" and the Dighton conglomerate and the Permian age of the latter are offered as final conclusions, the tentative assignment of the Pondville conglomerate and Wamsutta formation to the Permian and the correlation of the biotite granites as parts of one extensive complex batholith must be regarded as working hypotheses. No matter whether these hypotheses are finally proved or disapproved, in either case a valuable contribution to the local geology will have been made.

The writers wish here to express their sincere thanks to David White, Arthur Keith, and Laurence La Forge of the U. S. Geological Survey, and to Profs. W. O. Crosby, C. H. Warren, and H. W. Shimer of the Massachusetts Institute of Technology, for their helpful comments and suggestions, and to Miss M. G. Wilmarth of the U. S. Geological Survey for invaluable clerical assistance during the preparation of this paper.

Callixylon (Cordaites) Oweni, sp. nov.



Callixylon (Cordaites) Oweni, sp. nov.

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ART. VI.—Cordaitean Wood from the Indiana Black Shale; by MARION G. ELKINS and G. R. WIELAND. With Plates I and II.

## I. ILLUSTRATION AND DESCRIPTION (by Miss Elkins).

Early in the year 1911, Dr. G. R. Wieland handed me for description three sections of Cordaitean wood, which he had prepared from Yale Museum material, and in addition, certain of his notes concerning these sections and four photomicrographs, which accompany this paper. In regard to this material, Dr. Wieland says:

"I noticed among some unstudied examples of silicified wood in the Yale collections a medium sized hand specimen from Lexington, Scott County, Indiana, which had evidently been acquired many years ago from Mr. J. H. Thompson of Hanover. Later, on inquiry, Dr. Edward M. Kindle, who is thoroughly familiar with the Indiana localities and stratigraphy, assured me that the specimen must certainly be from the Black Shales of the Upper Indiana Devonian, which are approximately of the same age as the Genesee Shales of New York. He also stated that sections of trunks, a foot or more in diameter, had at various times been noted in the Black Shales."

A further description of this locality is found in the Sixth Annual Report of the Geological Survey of Indiana, 1874:

"Resting on the black shale are found large fossil trees. Some of these specimens are of great size; all are silicified. The fossil tree exhumed from the black shale by J. Richardson and myself (W. W. Borden) on the land of E. B. Gurnsey near Henryville, Clarke County, and exhibited at the Indianapolis Exposition of 1873, measured over sixteen feet in length and two feet in diameter, and had a jointed structure which is a characteristic feature of all these fossil trees. Another large specimen of tree, measuring nineteen feet in length and three feet in the broadest part, being somewhat flattened, was taken from the black shale a short distance north of Vienna by James Powers of Lexington and exhibited at the Indianapolis Exposition of 1874. This fossil wood is very closely associated with the black shale, and large specimens are found in almost every outcrop on the headwaters of Silver Creek in Clarke County. I have never yet met with a specimen above the summit of the black shale. A stump of one of these fossil trees is to be seen in Finley Township."

The material sectioned by Dr. Wieland without doubt came from this locality, but it is not known whether the Yale hand specimen is a section of one of the trunks mentioned in the Indiana Report or not.

AM. JOUR. Sci.—Fourth Series, Vol. XXXVIII, No. 223.—July, 1914.

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Preparation of Material.—Concerning the preparation of this material, Dr. Wieland says:

"The initial trial section was a transverse one cut from the entire specimen,  $6 \times 4$  centimeters in area, and showed that the tissues had not been subjected to decay, although with the exception of a central area of about  $2 \times 1.2$  centimeters, the cell walls had been crushed together into a nearly dense mass. Carefully oriented sections were next cut from the well-preserved central portions of the specimen, as thus indicated. As completed these are of exquisite beauty, and yield all the essential structural details."

The dimensions of the sections from the area of perfect conservation described here are: transverse,  $25 \times 15^{\text{mm}}$ ; radial,  $20 \times 13^{\text{mm}}$ ; tangential,  $12 \times 11^{\text{mm}}$ . These sections must have been cut with the very finest skill since they easily permit study under a 1/12 oil immersion focussed through the entire thickness, structure details being sharp over the entire section and from surface to surface.

Description of Material.—Before describing the material in hand, it may be of convenience to the reader to briefly recall the generic characters of Cordaitean wood.\* The wood is made up entirely of tracheids. In the protoxylem they are spiral and scalariform; transition stages occur leading to the characteristic pitted tracheids of the secondary wood. The tracheids are conspicuously rectangular in cross section and occur in regular, radial rows. Hexagonal bordered pits appear only on the radial walls of the tracheid in from one to five vertical rows. This primitive multiseriate arrangement of pits is however likewise an Araucarineous feature. Penhallow in North American Gymnosperms speaks of the hexagonal form and compact arrangement of pits as being two constant Cordaitean characteristics. Growth rings, when present, are for the greater part obscure. Medullary rays are rather numerous, usually uniseriate, though often partly biseriate. The ray cells are mostly of one kind, long and thin walled; the terminal walls are oblique or curved; the lateral walls are alone provided with bordered pits. Specialized resin canals are wanting in the wood, though in one species, Cordaites materiarum, resinous plates occur in the tracheids near the rays. Wood parenchyma is unknown.<sup>+</sup> The secondary wood<sup>±</sup> of

\*Penhallow, D. P.; Notes on the North American Species of Dadoxylon. Trans. Roy. Soc. Canada, vol. vi, sec. iv, p. 61, 1900-1901.

Penhallow, D. P., North American Gymnosperms, p. 57, 1907.
‡ Coulter, J. M., and Chamberlain, C. J., Morphology of Gymnosperms, p. 165, 1910. [Seward and Scott.]
Thomson, R. B., On the Comparative Anatomy and Affinities of the Araucarineae. Phil. Trans. Roy. Soc. of London, ser. B, vol. cciv, pp. 1-50, pl's 1-7. May, 1913.

*Cordaites* so closely resembles that of *Araucaria* that it is "really indistinguishable."\*

Penhallow, in his classification of North American species of *Dadoxylon*, places the species in two groups: in one group the growth rings are distinct, in the other group the growth rings are obscure or obsolete. In the first group the demarcation between the fall and spring wood is quite abrupt and well defined; in the second group, the annular appearance is mainly due to a line of tracheids with radially shortened diameters, the transition into the elements of the surrounding tissue taking place similarly and gradually on either side of the ring, so that it would be impossible to determine either the inner or the outer face if it were not for careful orientation. These two groups strongly suggest Araucarian affinities and ancient parallels to the *Dammara* and *Araucaria* types of modern Araucariæ.

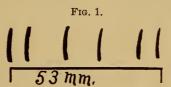


Fig. 1. Showing the proportional distance of six growth rings from each other.  $\times$  3.

The species under consideration, which, for convenience, will be referred to as the Indiana species, falls into the group with somewhat obscure growth rings and is, therefore, an Araucarioid type.

In a transverse section of the Indiana species, the growth rings, though not conspicuous, are quite apparent when viewed either macroscopically or microscopically. To the unaided eye they appear as fine parallel lines traversing a homogeneous field. In the section studied, the dimensions of which have already been given, there occur six growth rings; these vary in distance from each other in the proportion indicated in fig. 1. With the microscope the rings can be identified only

\*Wood now referred to Cordaites was formerly called Araucarioxylon. and Dadoxylon. According to some authors, Dadoxylon is a general name for Paleozoic wood of Cordaitean type. Penhallow properly considers it a noncommittal term harboring forms of doubtful affinity. Araucarioxylon is of necessity often applied somewhat generally to post-carboniferous wood resembling Araucaria, but which may actually include woods of diverse families. Cordaites was first applied to woods known to accompany Cordaitean leaves and fruits. Now it is a group name including Dadoxylon and Araucarioxylon. Other terms applied to Cordaitean wood of infrequent use have here been avoided. Penhallow uses Dadoxylon as synonymous with Cordaites. For further discussion of Cordaitean nomenclature see the introduction to Penhallow's Notes on the North American Species of Dadoxylon; also see Coulter and Chamberlain's Morphology of Gymnosperms, Chapter IV, and especially Knowlton in Proc. U. S. National Mus., Vol. XII, 1889.

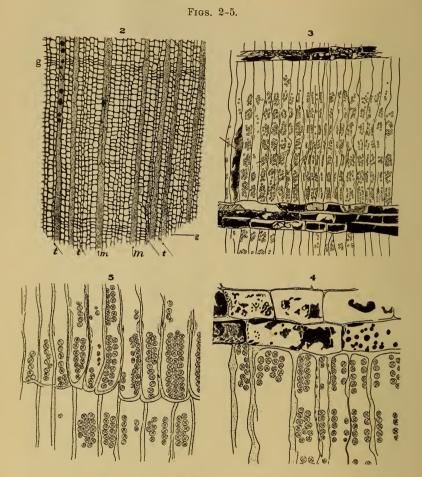


FIG. 2. Transverse section of wood showing two growth rings, g.m, medullary rays. The cellular structure of the medullary rays is not shown, as the cell walls are seen only with difficulty. Resinous tracheids occasional. The rows of tracheids marked t are probably near their terminations, hence of smaller diameter than the neighboring cells. (See similar cells in photomicrograph 1.) Note the isolated cells with shortened radial diameters.  $\times 30$ .

FIG. 3. Radial section of wood showing rays and tracheids. Note the contents of the tracheid to the left. The pitless appearance of parts of tracheids is due to extreme thinness of section, both radial walls being cut away. A growth ring five cells broad traverses the middle of the figure.  $\times 50 \pm$ .

FIG. 4. Radial section of wood more highly magnified than fig. 3. The presence of a growth ring tracheid is indicated by single rows of pits in tracheid in midfield. The pits in the lower part of tracheids were cut away. The medullary ray is six cells in height, but only two rows of ray cells are shown.  $\times 140$ .

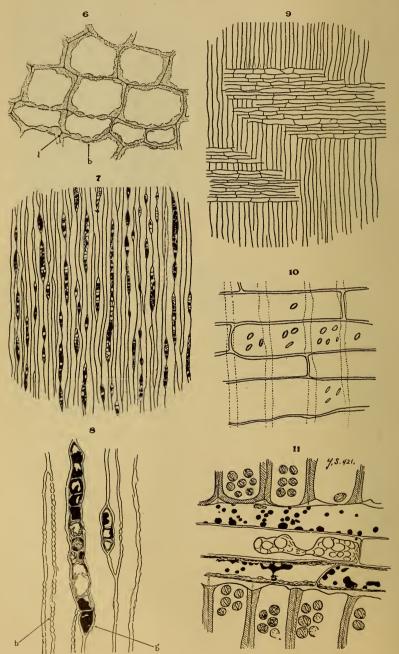
shown.  $\times 140$ . FIG. 5. The same as fig. 4. Showing series of tracheids cut near termination and including a growth ring to the left.  $\times 140$ .

# Elkins and Wieland-On Devonian Wood.

as narrow bands, one to three tracheids in thickness; these tracheids are distinguished by their radially shortened diameters, fig. 2, photomicrograph 1. On either side of the ring the tracheids quickly though not abruptly attain the normal tracheid dimensions. The slight curvature of the rings affords the only means of judging which may be the outer ones, and indicates a trunk of large size. This type of ring is practically identical with that of modern Araucariæ. The significance of this structure in *Cordaites* is not fully known, though in the judgment of both the present writers it obviously indicates some kind of seasonal or other climatic variation, such rings not so far being known to have any relation to fructification. Whatever the cause, it often failed to affect cells in the growth ring area; for bridges of full sized tracheids are frequently observed crossing the growth rings. Scattered cells with strikingly short radial diameters also occur between the rings.

The *tracheids* in cross section are usually rectangular; some, however, are circular, evidently at the points of constriction, which as one may plainly see in longitudinal sections both radial and tangential occur quite regularly near the tracheid There is, however, so much variation in size that it ends. scarcely seems feasible to use tracheid dimensions as a specific character, except as the upper and lower limits of size variation may corroborate the diagnosis of a species already determined from more fixed characters. This size variation does not include rows of seemingly small tracheids extending radially, which are in reality normal tracheids appearing in this section near their termination, where the diameters, particularly the tangential diameters, are shortened (figs. 2 ( $\hat{t}$ ), 5 and 7). The thickness of the walls, also, can hardly be determined accurately since they either vary or may, as silicified, appear somewhat irregular and ragged; although Penhallow in his description of *Dadoxylon* species gives the thickness of cell walls and cell diameters as specific characters.

By far the most interesting and finely preserved structure is the bordered pit. These pits are strikingly arranged in radial bands not varying markedly either in width or distance apart (fig. 3, photomicrograph 1). The number of vertical rows of pits varies generally with the size of the tracheid from one to four. The position of the growth ring can readily be discerned in a radial section by the occurrence of one or more tracheids of comparatively short radial diameter, containing a single vertical row of pits sometimes slightly smaller than the others, figs. 3 and 4. But the single row usually conforms to the radial band arrangement of pit grouping in each of these lesser tracheids. The number of pits to a group may be as few as three in the growth ring tracheid up to as many as forty on FIGS. 6-11.



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the normal wood tracheid where, presumably owing to termination of a ray cell, two of the largest single groups coalesce; they may be crowded or lie well apart. Several examples like the following have been noted: two distinct radial bands gradually approach each other, coalesce for the distance of several tracheids, then part, resuming their separate identities. Along the line of coalescence occur the large or double groups of pits. In the main, however, the radial grouping of the pits is the most striking feature of the wood, appearing with great regularity over large areas of the radial section. The pit groups are normally separated by about the width of a ray cell, and the radial surface of the tracheids between the groups is finely but characteristically rugose. Furthermore, the dominance of the group system of pits is conditioned by induration and thickening of the appressed tracheid walls between the groups, with presence of intercellular spaces. This feature is quite apparent under even low powers, and so definite that it may be studied to advantage with a 1/12 oil immersion and ocular 5. In the tangential section a spindle-shaped interspace may mark the point of tracheid wall thickening between the pit groups.

The bordered pits are circular or elliptical in outline, occasionally irregularly flattened. The hexagonal form, which is reputed to be a constant feature of Cordaitean bordered pits, appears to be wanting here. Even when the pits are very close together they maintain their circular outline (figure 4 and 5, photomicrograph 4). Occasionally pits occur which might be considered hexagonal, though such are not a striking feature (photomicrograph 4). The oblique slit-like opening extends nearly the full diameter of the pit and lies at right angles to the corresponding orifice in the wall of the adjacent tracheid, thus presenting a cross-like arrangement to the eye. And in the sections where the slits cross there is formed a rhombic perforation of the paired pits across which one looks through

FIG. 6. Detail of transverse section. Note the bordered pits, b, and the middle lamella,  $l_{\cdot} \times 240$ .

FIG. 7. Tangential section of wood.  $\times 30 \pm$ . [Another area is shown  $\times 105$  by Wieland as fig. 43 of his American Fossil Cycads.]

Fig. 8. Detail of tangential section showing two medullary rays and portions of tracheids with the actual distribution of the bordered and semibordered pits. b, bordered pits; b', semi-bordered pits connecting tracheid and ray cell. The middle lamella is not distinct in this section.  $\times$  120.

FIG. 9. Outlines of ray cells and tracheids showing their arrangement.  $\times$  30.

FIG. 10. Radial section of wood. Detail of ray cells showing the semibordered pits, also indicated in fig. 8. The vertical dotted lines indicate tracheid walls.  $\times$  240.

tracheid walls.  $\times$  240. FIG. 11. Radial section detail showing ray three cells in height crossing pitted tracheids. Lower ray cells thicker walled with considerable intercellular space next the tracheids; middle ray cells squarish, and containing tyloses. Other ray cells with much vacuolated resin attached to cell walls. Resin vacuoles of upper ray cell all on cell wall, not in interior. nearly clear silica, the pit walls being distinctly dense. Similarly arranged cross-like orifices are present in Pityoxylon Chasense as described by Thomson and Allin,\* who claim that this latter species is of Cordaitean affinity and not related to the Abietineæ. The X-like aspect of the apertures in the pits also characterizes Araucaria brasiliana, as long since figured by Winkler; while Goeppert noted this feature in fossil forms.

The presence of pits in the walls of the tracheids may be seen, though with less distinctness, in transverse or tangential sections. The walls, when viewed with a high power of the microscope, exhibit series of broken, bulging outlines, which plainly indicate the presence of the pits (figures 6 and 8). The position of the middle lamella is also absolutely distinct with oil immersion  $\frac{1}{12}$  oc. 2 in all the sections (figure 6). Whether or not a torus is present I cannot now say.

The *medullary ray*, because of the large amount of dark colored material in many of the cells, is a conspicuous feature. The rays, viewed in a transverse section, are very similar, being usually one cell in breadth, though sometimes two cells The biseriate ray of this species is, however, always wide. partly uniseriate (figure 7, photomicrograph 3). A radial section shows that the rays, though narrow, are of considerable depth as appears in figure 9. In a tangential section the ray is seen to vary from a single cell in depth and breadth to a ray forty cells in depth and from one to two cells in breadth. Between the two extremes all gradations may be found (cf. figure 7). Dadoxylon Pedroi, of Zeiller, however, exceeds the Indiana species in the remarkable height of its rays, which sometimes consist of even fifty superposed cells.§

The ray cells are parenchymatous, long and thin walled. Using the tracheid width as a unit of measurement the ray cells range from two to eight tracheids in length; the terminal wall is vertical, curved or oblique. A tangential view of the wood shows the ray cells to be rectangular, oval or circular in cross-section and of exceedingly variable size. The horizontal walls of the outermost cells are irregular, seeming to extend in pointed projections between the tracheids (cf. photomicrograph 3); this often gives the appearance of an abrupt narrowing at the ends of the ray cells, which is really a return to the normal diameter. Through the lateral walls, the ray cells communicate with the tracheids by means of pits, which are simple in the ray cell wall and bordered in the tracheid wall;

\* Thomson, R. B., and Allin, A. E., Do the Abietineæ Extend to the Carboniferous? Botanical Gazette, vol. liii, No. 4, April, 1912.

†Winkler, C. Zur Anatomie von Araucaria braziliensis, Botanische Zeitung 1872, p. 583, (Tafel VII).
‡ Goeppert, H. R., Monographie der Fossilen Coniferen, Leiden, 1850.
§ Zeiller, M. R., Note sur la Flore Fossile des Gisements Houillers de Rio Grande do Sul., Bull. Soc. Géol. de France, Série 3, Tome 24, p. 624, 1896.

this is inferred from the appearance of a single oblique slit in each pit of the ray cell. In examining the pits on the walls of the ray cells it is occasionally possible to detect the border of the pit in the adjoining tracheid wall; or depending on the plane of the section the border is indistinct and only a slit or broader aperture is visible. However the relation of the slit semi-bordered pits to ray cell and tracheid can always be clearly discerned, the slit appearing first when seen from the interior of the ray cell, the semi-border when the view is from the tracheid side. The shallowness of these pits and narrowness of slit combined with greater distance apart renders them virtually invisible in the transverse and tangential section, even when highly magnified; though some evidence of them may be observed as illustrated in figure 8.

I, of course, have some hesitation in describing the ray pit features, as so thorough and careful a student of gymnosperm structure as Thomson (loc. cit.) says :

"The medullary ray cells are characteristically thin walled in the Araucarians, and are comparable to those in the Cordaitean forms. They are also unpitted in the Araucarineæ as in the latter. Often these cells have been wrongly spoken of as having pits on the lateral walls where they come into contact with the tracheids, some anatomists even going so far as to distinguish the pitting as of the bordered type. Gothan has noted this especially in the case of Penhallow when discussing the latter's statement that there are ray tracheids in *Cordaites Clarkii*. He says that all Penhallow's ray cells are tracheids on account of their pitting. With this as a basis and the fact that the ray tracheids have not been figured he goes so far as to question this unique example of their occurrence in the Cordaitean forms. I have carefully examined the type set of sections and have found no evidence to contradict Gothan's conclusion."

However this may be, and the point is indeed of far-reaching import in determining the relationships amongst ancient gymnosperms and the modern lines of descent, I can only figure the structures as shown in fig. 8, which appears correct. That the ray parenchyma cells vary greatly in length and development is of course true, as fig. 9 well shows.

The contents of the ray cells occur as dark opaque masses (tyloses) almost entirely filling the cell or scattered like little droplets. These masses have been described as resinous or starchy matter, and their appearance does strongly suggest a resinous vacuolation. Penhallow states that the ray cells of *C. Newberryi* are of one kind only, resinous and starch bearing.\* E. C. Jeffrey, in describing an Araucarian genus, says that the rays are not clear in transverse section; certain dark spots occur, which are not resiniferous parenchyma, but car-

\* North American Species of Dadoxylon, p. 64.

bonized aggregations not infrequent in petrified wood.\* Of course the exigencies of silicification must be fully taken into account, but doubtless the resinous character of the bodies here described can be definitely established after various well conserved fossil species have been fully and thoroughly studied.

Certain of the tracheids also contain dark silicified bodies, which appear to be of resinous origin (cf. r in figures 2 and 3).

In 1900 Professor Penhallow of McGill University published an interesting and suggestive account of the Dadoxylon species of North America. In this paper he describes a species,-Cordaites Newberryi-which was discovered in the Middle Devonian of Ohio by Dr. Newberry and in the Carboniferous of Ohio by Claypole. The species from the Indiana Black Shale, as described above, bears a striking resemblance to Cordaites Newberryi. However there are several clear variations. Before quoting from Penhallow's account, which is the most complete, I may refer to several brief earlier accounts of this species.

Dawson merely describes Dadoxylon Newberryi as having areoles (pits) in two or three rows with large oblique pores and numerous rays made up of eighteen rows of narrow cells in two series.<sup>+</sup> Later he describes carbonized or silicified trunks from the Hamilton of New York having hexagonal areoles with oval pores.<sup>‡</sup> Newberry gives a much more definite description; he states that the wood cells are quadrangular; the largest diameter noted, 04-05<sup>mm</sup>; the thickness of the wall,  $01^{\text{mm}}$ ; the length of the ray cell, 4-5 times the diameter; the terminal walls are oblique; the areoles are in groups of one to three rows; the pores are elliptical and obliquely inclined; the areole diameter is 01<sup>mm</sup>. The rays are single or double in width and consist of from one to twenty superposed cells. Nearly all the ray cells contain globules of resinous matter.§ Penhallow's description agrees in general with that of Newberry, but Penhallow emphasizes a character which is the important and distinguishing feature of this species, namely the arrangement of the pits in radial bands and hence in definite groups of pits, 6 to 13 in number, in each tracheid. Newberry mentions the pit groups without emphasis and fails to note the radial band. Penhallow in reference to the growth rings says: "In a radial extent of 17 millimeters, this species shows no evidence of growth rings."

\*Jeffrey, E. C., A New Araucarian Genus from the Triassic "Wood-worthia Arizonica." Proc. Boston Soc. Nat. Hist., vol. 34, No. 9, July, 1910. † Dawson, J. W., Fossil Land Plants of the Devonian and Upper Silurian.

Geol. Surv. of Canada, 1871.

<sup>‡</sup>Dawson, J. W., Fossil Plants of Erian (Devonian) and Upper Silurian

Formations of Canada. Geol. Surv. of Canada, Pt. II, 1882. S Newberry, J. S., Devonian Plants from Ohio. Jour. Cincinnati Soc. Nat. Hist., vol. xii, pp. 48-56, 1889.

#### Elkins and Wieland-On Devonian Wood.

# II. SPECIFIC CHARACTERS (by Dr. Wieland).

Of the generic identity of *Cordaites Newberryi* and the Indiana form before us we rest assured since the larger characters are the same, and in the specialized feature of tracheidal pit groups both closely agree. Both then are clearly of the same genus, but must represent distinct species, since in the material studied by Penhallow growth rings are not present in a radial extent of  $17^{mm}$ , while in the Indiana specimen there occur in the same distance six growth rings which could not be overlooked even in a cursory examination. Taking the growth rings as a basis of classification and relying upon the accuracy of Penhallow's description, the main features of these species may therefore be tabulated thus:

#### Comparison of Cordaites Newberryi and the Indiana Species.

Callixylon (Cordaites) Newberryi

Callixylon Oweni

Tracheids  $45-60 \times 45-60$  mic.

Walls about  $5 \pm \text{mic.}$  thick.

#### Transverse

rings.

Tracheids  $44 \times 55$  mic.

- Walls about 12.5 mic. thick.
- In a radial extent of  $17^{mm}$  no evidence of growth rings (obscure or obsolete).
- Tracheids conspicuously squarish, sometimes unequal in the two diameters.
- Tracheids squarish, sometimes round.

In a radial extent of 15<sup>mm</sup> 6 growth

Ray cells distinct because of contents.

#### Radial

- Ray cells resinous and starch-bearing, long and narrow, about equal to 3-7 tracheids, ends conspicuously narrower, the pits on the lateral walls 3-6, chiefly 4 per tracheid, the slit-like orifice nearly the full diameter of the pit.
- Bordered pits numerous, round, about 9.3 mic. broad, distributed in radially disposed groups of about 6-13, the orifice diagonal, nearly extending the diameter of pit.
- Ray cells often with opaque material, long and narrow, about equal to 2-S tracheids, ends not conspicuously narrower, the pits on the lateral walls usually 6-S per tracheid, the slit-like orifice nearly the full diameter of the pit, pits simple in the ray cell wall, bordered in the tracheid wall.
- Bordered pits numerous, round or elliptical, distributed in radially disposed groups of 3-40, groups of 40 probably double groups, in 1-4 vertical rows per tracheid, orifice diagonal, which with the corresponding orifice of adjacent tracheid gives the appearance of a cross. Tracheids resinous (?)

#### Tangential

- Rays of medium height, 1-2 rarely 3-seriate in part, 24-55 mic. broad the oval or round cells all thin walled.
- Rays from 1-40 cells in height, 1-2 seriate, never 8-seriate, 30-45 mic. broad, all cells thin walled, oval or round in section, vary in size, most of them contain more or less resinous (?) material with frequent tyloses.

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In defining new species it is sometimes desirable to state certain facts of negation as succinctly as may be. Accordingly in the present case it is well to repeat that the exact nature of the growth ring especially in forms so ancient as those in question is not fully understood. And since the growth rings described above occur at irregular intervals it is possible that a longer period of growth may have ensued at times between two successive appearances of the stimulus necessary to cause the formation of growth rings. It is also possible that the specimen studied by Penhallow may have been taken from an area between two such successive rings of unusual width. This is merely a conjecture. The far greater chance is that both specimens are average trunk wood, and do differ by presence and absence of the growth rings.

Furthermore Penhallow describes the ends of the ray cells as being conspicuously narrowed. It is true that the ends of the ray cells in the Indiana specimen are often narrower than the rest of the cell, but it is not a constant feature and is never conspicuously true. The reader may recall that in the description of the ray cells it was stated that the horizontal walls of the outer rows of cells were frequently irregular and appeared to narrow at the ends when only returning to the normal cell diameter, a condition which might be misleading. There are other minor differences between C. Newberryi and the Indiana form in regard to the number of pits in a group, the height of a ray, etc., which could be accounted for in a species with very wide limits of variation, as seen from the preceding table. But one may only conclude that in the absence of evidence that the differences apparently present are simply variations within the species, the logical course is to erect a new species based on good material.

In dealing with the present fine fossil tree from Indiana it has been preferable so far to use the old names applied to wood of Cordaitean affinity; but in naming the new species quite clearly indicated to be present it appears necessary to include it together with the *Cordaites Newberryi* in the new genus, *Callixylon*, recently established by Zalessky\* with apparent correctness for Cordaitalean woods with grouped bordered pits. A new Russian form he describes, *Callixylon Trifilievi*, from the Upper Devonian of Bolchaia-Karakouba, district of Marioupol in the province of Ekaterinoslaw, has this character. Only the preliminary description of this Russian species with three photomicrographs has so far come to hand. But Zalessky shows that while the Araucarian type of pitting is present, and the grouping is distinct as in our two American forms, the

\* Etude sur l'Anatomie du Dadoxylon Tchihatcheffi Goeppert sp., par M. D. Zalessky. Mémoires du Comité Géologique de Russie, Nouvelle Série, Liv. 68, St. Petersbourg, 1911, pp. 29 with 4 plates.

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species, *Callixylon Trifilievi*, plainly differs, having smaller medullary rays with less biseriation and, so far as the figures show, fewer bordered pits in the groups.<sup>\*</sup> As to whether or not the American species have, like *C. Trifilievi*, a fine development of primary xylem is of course more or less conjectural, so that in accepting classification under *Callixylon* a sharp doubt remains. However, no other course appears consistent, and our species is therefore named in honor of the early Indiana geologist, David Dale Owen, and the illustrious family to which he belonged,—

# Callixylon Oweni sp. nov.

Inasmuch as the characters of this new form have been clearly brought out in the preceding descriptions, while Callixylon (Cordaites) Newberryi is not very well known (efforts to locate the types having so far failed), and C. Trifilievi awaits further description, it is not necessary to here append a searching recapitulation of the specific characters separating the three members of Calligylon, C. Newberryi, C. Oweni and C. Trifilievi. It is sufficient to state in résumé that all three plainly differ in various minor features and that while the small medullary rays and low number of bordered pits to the group clearly separate Callixylon (Cordaites) Newberryi Dawson from C. Trifilievi Zalessky, both are further isolated from Callixylon Oweni by obscurity or absence of the growth rings, which, while not a strongly fixed character, are in the latter species distinct. Moreover it could at most only produce confusion to assign this perfectly conserved material to so imperfectly known a species as C. Newberryi in reality is.

I have in other connections urged the necessity for basing types on the best known material.

In conclusion it may be added that the main value of this contribution must consist in Miss Elkins' excellently drawn

\* The lateral tracheidal bordered pits of the Callixylon species are small of diameter, not large as in many modern conifers and cycads, the actual dimensions having some interest as follows :—In Callixylon Newberryi the pits have a diameter of 9 microns, in C. Oweni 10 to 11 microns, in C. Triflievi 12 to 13 microns; in Araucaria Bidwilli 11, in Agathis bornensis 10 to 12, and in Araucaria Cookei roots only 3 microns; while these measurements rise in Pityoxylon (sp.) to 15, in Larix americana to 16, in Dion spinulosum to 19, and in Pinus strobus to from 25 to 35 microns. Lest any doubt as to the bordered pit features of C. Oweni should remain, I may emphasize the fact that the cellulose bands or "bars of Sanio" often so characteristic in various recent Abietineæ, are not present in even a rudimentary condition. The testimony of the sections is conclusive on this point. Indeed the pits can be studied to even better advantage than in some artificially stained woods. Nor are the bars absent because there is crowding. Normally the pits barely touch and no more, although the outer border does appear very distinct and it is easy to see how cellulose thickening on a contact line could arise.

figures and the attention they invite to one of the best conserved Devonian woods ever sectioned. Doubtless some details of structure have been imperfectly observed or understood by us, but the results show an advanced structural type which can stand in an ancestral relationship to other gymnosperms, or even be regarded as standing near to cycadaceous types, and slightly in advance of the actual line leading into the modern Araucarians. Moreover this wood suggests that it may well be that both Jeffrey and Thomson are virtually correct when the one assigns a high antiquity to Araucarian, and the other equal great age to Abietineous structures. The fact that the latter have undergone much variation in Cretaceous time, playing the great rôle in the Cretaceous coniferous forests, merely makes the ancestral Abietineous features harder to discern; whereas in the Araucarians primitive structures stand out in bold relief. At least it is evident that great variety of structure exists in Devonian woods, and considering the further diversity of the ancient seed types it begins to appear that if there is any past period which can be fairly singled out as the true age of gymnosperms it must be Devonian time.

Randolph-Macon Woman's College. Yale University Museum.

#### EXPLANATION OF PLATES.

#### PLATE I.

Photomicrograph 1 (above). Radial section of wood showing the radially grouped pits and the highly characteristic appearance produced by these together with the thickening of tracheidal walls and constriction between the pit groups.  $\times 100$ . Yale Museum Section No. 421. Photomicrograph 2 (below). Transverse section of wood interior to growth

Photomicrograph 2 (below). Transverse section of wood interior to growth ring, showing marked variation from large rounded to pentagonal rhomboidal and other outlines. See fig. 2. Yale Museum Section No, 420.

#### PLATE II.

Photomicrograph 3 (above). Tangential section of wood.  $\times 100$ . Yale Museum Section No. 427.

Photomicrograph 4 (below). Radial section of wood.  $\times 280$ . Focussed to bring out the *x*-figure formed by the crossed slits of paired pits of appressed tracheids. [Neither slit is in full focus in such a photograph.] Yale Museum Section No. 421.

# ART. VII.—An Occurrence of Pyroxenite and Hornblendite in Bahia, Brazil; by HENRY S. WASHINGTON.

# Introduction.

IN June, 1909, I had occasion to visit and examine a reported copper mine near Maracas, in the State of Bahia, Brazil. Although the so-called mine proved to be valueless as a commercial source of copper, yet the igneous rocks encountered were so interesting that they deserve description.

The locality is about 300 km. west of the city of Bahia, two days ride (about 100 km.) south of Tambury, a station on the Paraguassu River, on the San Felix-Bandeira da Mello railroad, 215 km. from the former. The locality is in the complex of plutonic rocks and crystalline schists, which extends in a north and south zone through the state, between the Cretaceous to the east and the (probably) Jurassic Salitre limestone and Carboniferous Lavras sandstones to the west. The general geology has been briefly sketched by Branner,\* who considers the igneous and metamorphic complex to be pre-Cambrian.

The pyroxenite-hornblendite mass is found about 5 leagues (20 miles) north-northwest of the small town of Maracas, and forms a hill called San Gonsalvo Velho about one league northwest of a cluster of houses known as Furnaca.

Surrounding it are gneisses, none of the specimens of which are now, unfortunately, available. They are, however, white or pinkish, largely composed of feldspar and quartz, with little mica, a decided schistose structure. and with apparently little crumpling, the foliation being generally more or less horizontal.<sup>+</sup>

It is assumed that the rock mass in question is an igneous inclusion and not part of the metamorphic complex, as the region shows many such instances of inclusions of various plutonic bodies in the gneisses and other metamorphic rocks, The microscopical examination also favors this view. There is an apparently similar mass of pyroxenite near Sitio Novo. This I could not visit, but I was shown specimens of the rock which seems to be a coarse-grained hypersthenite, and samples of a very long-fibered asbestos which occurs there.

The igneous mass forms a north-south ridge, about 1 km. long, 200 m. wide and 80 m. high. The upper, and apparently the central, part is a coarsely granular hornblendite, while the sides are formed of a finer grained pyroxenite, which is some-

\* J. C. Branner, Eng. Mining Jour., lxxxvii, p. 982, 1909 (Map).

<sup>+</sup>In this the formation differs from the region to the southwest, where, near Rio de Contas, I found that the foliations were often vertical, as well as to the north, where vertical foliations were observed by Branner and myself.

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what foliated parallel to the contact with the gneiss. Cutting this outer pyroxenite are many veins of white chalcedony, and here and there are "bunches" of what appears to be a somewhat altered biotite, a light brownish jefferisite or vermiculite. There are found near the borders some quartz veins, stained green by copper. A few pits have been sunk near the contact, where the pyroxenite is somewhat altered and impregnated with chrysocolla and malachite. It may be mentioned that as a copper mine the locality is quite worthless, the amount of ore being very small, and the lack of water and fuel and difficulties of transportation being prohibitive of economic working.

# Hornblendite.

This rock forms the upper part of the ridge and apparently the interior part of the mass. It is coal black, glistening and highly granular, the grains of hornblende being from 1 to 3 mm. in diameter. These grains are somewhat incoherent so that the rock crumbles more or less under the hammer and in some specimens can even be rubbed down to a coarse granular powder under the fingers. The grains are quite anhedral with well-developed cleavage and are apparently perfectly fresh. No other mineral but hornblende is to be seen megascopically.

In thin section the rock is seen to be holocrystalline and composed almost entirely of anhedral grains of hornblende with sporadic small grains of olivine and magnetite. The texture is typically granitic and there is not the slightest evidence of any of the structures produced by metamorphism or crustal movement. The hornblende is anhedral, the grains butting against each other and not interlocking. Prismatic cleavage is well developed. The color is olive green, with distinct but not very strong pleochroism; a = light greenish yellow,  $\beta =$  olive green and  $\gamma =$  olive or slightly bluish green. The absorption as usual is  $\gamma > \beta > a$ . The extinction angle is about 11°, but this as well as the refractive indices and other optical characters will be investigated later. The hornblende is absolutely fresh and its only inclusions are the magnetite grains and very rarely small olivines.

The olivine forms small anhedra generally in the interstices between the hornblende grains and less often included in the mineral. It is perfectly colorless and quite fresh except for a slight incipient iddingsitization on the borders. It rarely carries small inclusions of magnetite. The magnetite is in small anhedral grains, usually elongated and with rounded outlines. It is always present as inclusions, for the most part in hornblende, but less often in olivine. It seems to be quite fresh but is very rarely accompanied by a brownish staining. No feldspar or apatite are to be seen and I could find no grains of the pleonaste which is present in the pyroxenite.

Chemical Composition.-An analysis was made by the usual methods and the results are given below with three others of closely similar rocks.

TABLE I.					
	A	В	С	D	
SiO <sub>2</sub>	44.78	44.18	43.17	43.51	
$\operatorname{Al}_{2}O_{3}$	9.38	10.67	11.42	9.82	
Fe <sub>2</sub> O <sub>3</sub>	4.51	0.92	4.97	6.32	
FeO	7.70	10.03	6.36	9.62	
MgO	16.85	17.77	16.97	14.97	
CaO	10.85	9.75	11.62	11.83	
Na <sub>2</sub> O	2.24	2.37	1.11	1.30	
K,0	0.50	1.23	0.10	0.22	
H_0+	0.25	0.92	2.51	0.64	
H_0	0.08		0.22		
CÔ,	none	trace	0.71		
TiO <sub>2</sub>	0.74	1.30	1.23	1.02	
$ZrO_{2}$	none				
$P_2O_5$	none	0.38	0.04	0.03	
S	0.29		0.06		
$Cr_2O_3$	0.24				
MnO	1.90		0.14	0.21	
Ni0	none				
BaO	none				
LiO	none		1		
CuO	0.16				
-					
	100.07	9 <b>9·</b> 8 <b>3</b>	100.63	99.52	

A. Hornblendite ("IV.1(2).3.2.2.). Near Maracas, Bahia, H. S. Washington, analyst. Brazil.

B. Kylite (feldspathic peridotite) ((III)IV.I".3."2.2). Benbeoch, Kyle District, Ayrshire, Scotland. M. Dittrich, analyst.
G. W. Tyrrell, Geol. Mag. (V), ix, p. 122, 1912.
C. Amphibole picrite ((III) IV. (1) 2.3."2."2). Sequoia P. O.,
Yosemite National Park, California. G. Steiger, analyst. H. W.
Turner, U. S. G. S. Bull. 228, p. 242, 1904.
D. Henrele dite. (IV 10.2.2."). Notestr. New Coloderia.

D. Hornblendite ("IV. "2. 3. 2. 2). Nakety, New Caledonia. Boiteau, analyst. A. Lacroix, C. R., clii, p. 820, 1911.

From the analysis it is seen that the hornblendite is very fresh—remarkably so for so mafic a rock. In its general features it closely resembles other hornblendites as well as some peridotites which contain either hornblende or subordinate feldspar (kylite). The titanium is not high, there is a little chromium and copper but no nickel, while the percentage of

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manganese is extremely high for this constituent. Indeed this rock carries the highest amount of MnO of any igneous rock known to me in which the figures for this constituent are reliable. This feature will be discussed later.

*Classification.*—The norms of these rocks are as follows, the letters corresponding to those of the analyses :

	A	В	С	D
Or	1.11	7.23	0.56	1.67
Ab	11.00	3.67	9.43	11.00
An	15.01	14.73	25.85	20.02
Ne	4.26	9.09		
Di	31.04	24.72	25.00	30.85
Ну			3.00	
0İ	28.76	34.51	23.78	24.19
Mt	6.20	1.39	7.19	9.02
Il	1.37	2.43	2.28	1.98
Ap		1.01		· · · · · ·

From these figures it is seen that A and B fall in rossweinose (IV. 1.3.2.2) and C and D in uvaldose (IV. 2.3.2.2), the complete symbols in each case being given with the analyses. The differences are, however, not great, they all contain so much normative feldspar as to be intermediate toward the salfemane class. A and B carry such small amounts of ores as to fall in order 1 (although intermediate toward 2), while C and D carry so much that they are over the line in order 2. As regards the other divisions they are all substantially identical.

*Mode.*—The Maracas rock, being coarse-grained, simple in composition, and very fresh, measurement of the mode by Rosiwal's method is very easy. A large series of traverses gave the following results in percentage by weight :

Hornblende	91.3
Olivine	3.6
Magnetite	5.1

100.0

On comparing this with the norm, it is evident that the large amount of normative feldspar and nephelite molecules have entirely entered the hornblende, as is true of other hornblendites. In this it differs modally from the chemically similar kylite (B), which is described as a feldspathic peridotite with some augite, so that its mode is more nearly normative. The difference is evidently due to differing conditions during crystallization, and will be discussed later.

The simplicity of the mode, and the very small amounts of olivine and magnetite present, permit the calculation of the composition of the hornblende with a very fair degree of accuracy. For this the MgO and FeO of the olivine are

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assumed to have the ratio MgO: FeO=4.1, which is approximately that of the rock. The chromium oxide is assumed to form chromite, while all the titanium and manganese are assigned to the hornblende. A little TiO, may enter the ores, but its amount would be uncertain, and as its total is small, the assumption made will not seriously affect the calculated composition. The results of this are given in Table II.

		TABLE	II.		
	A	В	С	D	E
SiO <sub>2</sub>	48.62	50.08	47.49	46.08	46.14
TiO <sub>2</sub>	0.80	0.76	1.21	0.77	
$Al_2O_3$	10.19	7.97	7.07	10.56	17.07
Fe <sub>1</sub> O <sub>1</sub>	1.35	2.69	4.88	-2.88	8.45
$Cr_2O_3$	none	0.16	none		
V.O.	·		0.04		
FeO	5.89	6.71	10.69	8.30	n. d.
MnO	2.06	0.49	0.51	0.12	
NiO	none		0.02		
MgO	16.66	16.31	13.06	14.40	15.01
CaO	11.78	11.21	11.92	12.64	11.70
Na <sub>2</sub> O	2.43	1.22	0.75	1.62	1.11
K,Ó	0.22	0.46	0.49	0.34	0.10
H <sub>2</sub> O	none	1.40	1.86	2.14	
P <sub>2</sub> O <sub>5</sub>	none		none	0.18	
F			0:06	none	
	100.00	00.10	100.05	00.00	00.50

100.00 99.46 100.05 99.99 99.58

A. Hornblende from hornblendite. Maracas, Bahia.
B. Hornblende from quartz diorite. Table Mountain, California. Cf. Bull. U. S. G. S. 419, p. 266.

C. Hornblende from quartz monzonite. Mt. Hoffman, Mariposa Co., California. Cf. Bull. U.S. G. S. 419, p. 266.

D. Hornblende from hornblende gabbro. Beaver Creek, California. Cf. Bull. U. S. G. S. 419, p. 266.

E. Hornblende from hornblende hypersthenite. Madison Co., Montana. Cf. G. P. Merrill, op. cit., p. 657.

This closely resembles hornblende from diorites, monzonites, and gabbros, but is quite unlike amphiboles from alkalic, highly sodic and lenadic rocks, such as syenites and nephelite syenites. It differs from all others so far known in its high manganese content, MnO evidently replacing FeO. Further discussion of its composition and affinities will be deferred until its optical properties have been investigated.

In E is given a partial analysis by Merrill of a hornblende from a hypersthenite which is closely like the pyroxenite next to be described. The alumina is obviously high and the magnesia and probably FeO low, but making allowance for this and the presence of titanium, etc., the composition much resembles that of the hornblende of the Maracas rock.

#### Pyroxenite.

This rock forms the outer portion of the mass. The transition between the two types is gradual, and apparently the quantity of pyroxenite is much greater than that of the hornblende, though no definite estimates were made. The rock is distinctly foliated parallel to the contact with the gneiss.

The pyroxenite is a glistening dark brownish black, rather coarsely granular, made up largely of bright glistening prismoids and grains of clove-brown pyroxene from 1 to  $2^{mm}$  in diameter. It is distinctly finer grained than the peridotite. Grains of greenish black hornblende are also present, but they are not conspicuous as compared with the pyroxene. The rock is evidently very fresh, except near the contact with the gneiss, where it has undergone some alteration and impregnation with copper minerals.

In thin section the rock is seen to be holocrystalline and with granitic texture. The dominant pyroxene is orthorhombic. It may be called hypersthene rather than bronzite, following Dana and Hintze, as it contains about 13% of FeO and is pleochroic. It forms thick, stout, rather prismoidal subhe-dral as well as anhedral grains. It is of a very pale pinkish brown or flesh color, and shows decided but not very strong pleochroism;  $\alpha$ , flesh pink,  $\beta$  and  $\gamma$  colorless. Rather coarse cleavage lines are prominent and the extinction is always parallel to these. The pyroxene is perfectly clear and fresh, and carries no inclusions. A very pale olive-green hornblende is less abundant than the hypersthene. It forms usually anhedral grains, or very rarely, prismoids. In its general character it resembles that of the hornblendite, but the color is paler and its pleochroism extremely weak. It also is perfectly fresh and with fine cleavage lines well marked. The crystallization of the hypersthene and hornblende would seem to have been in great part contemporaneous, as each occurs more or less partially enclosed in or molded against the other, as well as in anhedral grains; but on the whole much of the pyroxene seems to antedate the hornblende, some of which is evidently the last product of crystallization.

There are a few small anhedra of colorless olivine which show signs of slight incipient alteration in narrow yellow borders here and there. Small anhedral grains of a dark green spinel, probably pleonaste, are rather common, but not a grain of magnetite was seen. There is absolutely no feldspar.

*Chemical Composition.*—An analysis made by me is given below, along with two others of closely similar rocks. This analysis resembles those of several other pyroxenites, two of its closest analogues being given. Like the hornblende, it is remarkable for its high manganese, and the amount of chromium is also notable.

	TABLE III.			
	A	В	C	D
SiO <sub>2</sub>	51.23	<b>51</b> .83	51.76	47.29
Al <sub>2</sub> Õ <sub>3</sub>	6.12	7.98	6.02	16.93
Fe <sub>2</sub> O <sub>3</sub>	1.96	1.48	1.64	1.58
Fe <sup>0</sup>	6.95	8.28	8.01	2.67
MgO	26.52	24.10	27.14	21.01
CaO	4.03	5.26	3.15	8.56
Na <sub>2</sub> O	0.29	0.35	0.79	1.17
K,Ó	0.12	0.06	0.32	0.38
H <sub>2</sub> O +	0.14	0.29	0.85	0.29
H_0	0.10			
TiO,	0.27	0.29		
P <sub>2</sub> O <sub>5</sub> <sup>•</sup>	none	0.03	0.02	
S	0.41		0.12	
Cr <sub>2</sub> O <sub>3</sub>	0.31	0.31		
MnO	1.46	trace		
NiO		0.11		
BaO	none			
CuO	0.51			
	100.17	100.43	99.89	99.89

A. Hornblende-hypersthenite  $(IV''.1_{(1)2}.1.(1)2.$  Near Maracas, Bahia, Brazil. H. S. Washington, analyst.

B. Hornblende-hypersthenite (IV.1.(1)2.1.2). Between Meadow and Grass Creeks, Montana. L. G. Eakins, analyst. G. P. Merrill, Proc. U. S. Nat. Mus., xvii, p. 658, 1895.

C. Bronzite rock (IV.1., 1.(1)2). Radau, Hartz Mountains. Eyme, analyst. O. H. Erdmannsdoerfer, Jb. Pr. G. L-A., xxv, (1904), p. 471, 1907.

D. Ariegite, Escourgeat, Ariego, Pyrenees. Pisani, analyst. A. Lacroix, C. R., cxxxii, p. 359, 1901.

The analysis of ariegite will be referred to later.

*Classification.*—The norms of these three rocks are as follows:

	А	В	С
Or	0.56	<b>0*5</b> 6	1.67
Ab	2.62	3.14	6.81
<b>A</b> n`	15.01	19.74	11.95
Di	3.73	5.10	2.62
Ну	62.89	60.48	57.90
0İ		8.70	15.74
Mt	2.78	2.09	2.32
Il	0.46	0.61	

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It is obvious from these, and from the symbols given with the analyses, that notwithstanding their higher silica, the pyroxenites are decidedly more femic than the hornblendes, the former being all centrally in dofemane, while the latter are intermediate toward the salfemane class. This is quite in accordance with general experience, the few hornblendites known falling either in salfemane or dofemane, while the pyroxenites are either in dofemane or more commonly in perfemane. The amount of normative ores in each is negligible and the ratio of pyroxene to olivine about the same but just on the border between the first and second sections of the order. A and C therefore fall in the subrang IV.1., 1.2, which has been recently named hilose by Daly<sup>\*</sup>; and B in IV.1., 1.2, that is, cookose; the Brazil rock being a cookose-hilose and the Montana rock a hilose-cookose.

*Mode.*—The mode of the Maracas rock was determined by Rosiwal's method:

Hypersthene	59.4
Hornblende	- 29.6
Olivine	7.5
Pleonaste	3.2
	100.0

The amounts of olivine and pleonaste are negligible, so that the rock is a hornblende hypersthenite, or a hornblende bronzitite, according to the nomenclature adopted for the hypersthenes, just as is the Montana rock described by Merrill. The type specimen of this latter, preserved in the Petrographic Reference Collection of the United States Geological Survey. very much resembles the Brazil rock. It differs in showing a somewhat mottled texture with areas of slightly different granularity and tone, but the greater part is closely like that here described, both megascopically and microscopically, the less abundant, rounded, darker and finer grained areas being finer grained under the microscope, and showing rather more hornblende. Merrill remarks on the cumbersomeness of this name, but refrains from coining a new one because the specimen described by him was at the time the only known example of this combination. As the type is now shown to be widespread, I venture to suggest the name bahiaite for this holocrystalline combination of dominant hypersthene and subordinate hornblende with negligible ores and olivine. The name would be of equal classificatory rank with lherzolite or saxonite. In some respects, they correspond to the avegacites

\* Jour. Geol., xix, 297, 1911.

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of Lacroix,\* which are composed of augite and hornblende but with much more magnetite, ilmenite and apatite, so that they care lower in silica and magnesia, and higher in lime and iron oxides.

## General Remarks.

Petrographically, these Bahian rocks are of interest because of their bearing on certain features of classification. As has been seen, both the hornblende and pyroxenite are absolutely free from feldspars, though their norms show respectively about 30 and 18 per cent. Closely allied chemically to each are feldspar-bearing types represented respectively by the kylite of Tyrrell, which shows considerable plagioclase along with augite, olivine, and a little hornblende; and the Radau rock, which also shows considerable bytownite with much bronzite. These types are therefore distinctly more normative in their modes than the Brazil rocks.

A similar shifting of the mode from a less to a more normative character through the appearance of feldspar and the nonformation of hornblende, is shown in some rocks from Garabal Hill, recently studied by Wyllie and Scott.<sup>+</sup> They show that bordering an intrusion of tonalite is a mass which forms a diorite near the contact, with about 70 per cent of sodi-calcic feldspar and 7 per cent of hornblende, and which gradually changes to an almost pure hornblende (with pyroxene), with about 84 per cent of hornblende and 5 per cent of feldspar. These two extremes closely resemble each other chemically as shown by the analyses here given.

$\mathbf{A}$	В
52.83	53.29
11.74	8.81
6.66	4.68
6.13	6.66
6.41	9.07
8.05	8.99
2.67	3.21
2.06	- 1.87
1.20	1.51
0.50	0.12
none	none
1.82	1.41
0.08	trace
99.85	99.67
	52.83 11.74 6.66 6.13 6.41 8.05 2.67 2.06 1.20 0.20 none 1.82 0.08

A. Diorite, Garabal Hill, Scotland. Analyst not stated. Wyllie and Scott, Geol. Mag. (V), x, p. 540, 1913.
B. Hornblendite, Garabal Hill, Scotland. Analyst not stated. Wyllie and

Scott, Geol. Mag. (V), x, p. 540, 1913.

\* A. Lacroix, VIII Cong. G. Int., C. R., p. 832, 1901. † Wyllie and Scott, Geol. Mag. (V), x, p. 539, 1913.

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Since high alumina in one is connected with low magnesia in the other, the difference being almost exactly the same, while the other components of the rock are almost identical in both, one is inclined to suspect the common error in the determination of these two constituents in the diorite. If this were the case, the close resemblance between the two would have been still greater.

The two authors determined the modes at several points regularly distributed between the two extremes, and have plotted them on a diagram. This shows very clearly the inverse behavior of the hornblende and feldspar, while the minor constituents, as quartz and biotite, remain comparatively constant. The significance of this is not commented on by the authors, but it is clearly evident, both from their diagram and from the norms, that much of the actual feldspar of the diorite has lost its modal existence, and become incorporated in the complex hornblende as one approaches the border.

In 1901, Lacroix\* described some pyroxenites from the Pyrenees, an analysis of one of which is given in Table III. These pyroxenites, called by Lacroix "ariegites," which contain varying amounts of hornblende or garnet with magnetite. and only traces of olivine, are distinctly lower in silica and iron oxides, and much higher in alumina and lime than that from Bahia. Lacroix calls attention to their chemical affinities with the gabbros, and on this account he undertook some experiments in recrystallizing them from a fused condition. On reheating (at a temperature not stated) the glass obtained by fusing the rocks in a platinum crucible, he obtained masses made of "microlites of augite imbedded in larger crystals of bytownite." Olivine was also formed readily in the melt. On referring to the norms of these rocks,<sup>+</sup> it will be seen that they correspond well with the modes of these artificially recrystallized melts. We may, therefore, consider that, even for rocks of such complicated abnormative modes, the norm as calculated in the quantitative system is justified as a basis of comparison. Lacroix himself points out (p. 360) the theoretical interest of his experiments as demonstrating that the differing modes are due solely to differing conditions during consolidation (as well as, almost undoubtedly, to the presence or absence of gases or water vapor), and remarks that had his ariegites solidified as volcanic lava flows, they would have formed pyroxene-rich basalts.

Mr. G. A. Rankin, of the Geophysical Laboratory, to whom I desire to express my thanks, very kindly undertook similar

\* A. Laeroix, C. R. xxxii, p. 358, 1901.

+ H. S. Washington, U. S. G. S. Prof. Paper 14, 1903, pp. 335, 337, 339, 347.

experiments on the Bahia hornblendite. Unfortunately, the time at our disposal was rather limited, owing to my impending departure for Naples, and the results are not wholly in harmony with those of Lacroix. Further work along these lines will be undertaken later.

On melting a rather large sample of the hornblendite in a gas furnace, and cooling slowly, a holocrystalline mass was obtained. This showed in thin section many very thin plates, appearing as long thin needles in the section, of a colorless monoclinic pyroxene with extinction angles up to about 30° and with rather indefinite and fuzzy borders. There are also many similar thin plates of a colorless olivine or possibly orthorhombic pyroxene with sharp and clearcut borders and many phenocrystic grains of magnetite. These lie in a greenish, somewhat cloudy groundmass which is resolved by high powers into a felt of very small prisms of greenish augite, and many minute grains of magnetite. The augite prisms here and there are arranged in branching or feather-like patches. The base in which these are imbedded appears to be in great part holocrystalline, colorless and with lower refractive index than pyroxene. It appears to be feldspar, in part at least, though the absence of twinning lamellæ and crystal forms, and the difficulty of determining the optical constants, render this identification somewhat uncertain.

Another sample of the hornblendite, on heating in an electric furnace, was found by quenchings to have a melting interval of from about 1200° to 1400°. After heating to 1450° (that is, above its melting point) for some time, and then being cooled slowly to 1250° and held at this temperature for 5 hours, thin sections show beautifully sharp phenocrysts of a colorless olivine. Dr. H. E. Merwin kindly examined these and found the refractive index to be  $\gamma = 1.680, \alpha = 1.643, \pm .003$ , corresponding to forsterite. They are somewhat skeletal in development, carrying elongated central cores of greenish groundmass. They are elongated parallel to a pinacoid and show sharp domal terminations at either end, the domal angle varying between 80 and 90°. No phenocrysts of monoclinic pyroxene were seen. The groundmass here is yellowish-green, somewhat resembling the other. It is composed largely of minute prisms of augite, not felted as in the previous case but arranged in oblong featherlike aggregates, each small patch outlined by a narrow row of minute magnetite grains. The basis between these could not well be made out, but there seems to be nothing which can be considered to be feldspar, and the small aggregates appear to be wholly of an augitic pyroxene. These results are, as has been said, somewhat inconclusive, and the evidence is not strongly in favor of the

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formation of feldspar in these melts under the conditions obtaining. It may be recalled, however, that the ariegites of Lacroix are much higher in alumina and lime, so that their chemical composition is more favorable to the formation of calcic feldspars, as is also shown by the greater abundance of the anorthite molecule in their norms. Further investigations along these lines are to be undertaken later on.

## The Manganese and Copper Content.

It has already been noted that the percentage of manganese shown in my analyses is exceptionally high for igneous rocks. There are, it is true, some other instances of similarly high figures for manganese such as the mijakite of Petersen,\* but there is little doubt that in such cases the high figures for manganese are due to incomplete precipitation of alumina in the sodium acetate method and the weighing of the unprecipitated Al<sub>o</sub>O<sub>o</sub> as MnO. In the Bahian rocks, manganese was determined by the colorimetric method, which is far less subject to sources of error than, and is as accurate as, the gravimetric methods for small amounts of these constituents.

The high manganese content shown by these rocks is especially interesting in view of the fact that the crystalline zone of Bahia abounds in deposits of manganese ores. The largest and best known of these are those near Nazareth, about 250 km. east of Maracas, as well as those near Vilha Nova da Reinah, some 300 km. to the north. At both of these (which have been visited by me), there are extensive deposits of psilomelane of excellent quality. There are also smaller deposits at Cachoeira, some 200 km. to the east, and elsewhere in the state, but always in the metamorphic and crystalline belt. The high manganese of the rocks studied suggests the source of these valuable deposits.

The distinctly high amounts of copper found in the analyses explain the considerable staining of the somewhat altered rock near the contact by secondary copper minerals. While prominent on account of their bright colors, the amount of copper present is not sufficient to warrant its extraction, quite apart from the small size of the mass and other considerations.

Geophysical Laboratory, Carnegie Institution of Washington,

Washington, D. C., April 25, 1914.

\* Jb. Hamb. Wiss. Anst., viii, 1891, p. 511.

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# SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. The Atomic Weight of Lead from Ceylon Thorite.-F. SODDY and H. HYMAN have carried out a preliminary atomic weight determination upon the lead extracted from Ceylon thorite. The authors found in this mineral 54.5 per cent of thorium, 0.35 per cent of lead, and 0.72 or 1.6 per cent of uranium, according to two methods of determination, the first chemical, the other calculated from the radium present in the mineral. According to recent theories of radio-activity a mineral rich in thorium and poor in uranium may contain lead with an appreciably higher atomic weight than ordinary lead, for if the end products of both uranium and thorium are, as is supposed, the isotopes of lead, the former should have an atomic weight of 206, and the latter 208.4, while the accepted value for ordinary lead is 207.1. Rather more than a gram of purified lead chloride was obtained from about a kilogram of the mineral. This was compared with ordinary lead chloride, and titration with silver nitrate solution was the method used. The results indicated that the thorite lead had an atomic weight of 208.4 if the ordinary lead was 207.1, while the value calculated from the composition of the mineral, if all the lead in it was derived from the radio-active elements, was 208.2. The authors say that the results so far carried out do not settle the question, but show a difference in the expected direction of the right order of magnitude .-- Chem. News, cix, 159. H. L. W.

2. The Extraction of Germanium from the Waters of Vichy. -J. BARDET, by spectroscopic examination, has found a great many heavy metals in mineral waters, and among them gallium and germanium were almost constantly present. Since there are few available sources of germanium, as the deposit of argyrodite at Freiberg is exhausted, and as the extraction of this metal from the blendes in which it was discovered by Urbain is a long and expensive operation, Bardet has undertaken the experiment of extracting germanium from the residues of the evaporation of mineral waters. It was found that in the manufacture of Vichy salts from the natural waters the first heating of the water causes the decomposition of the bicarbonates and the precipitation of the alkali-earth carbonates, and that this precipitate, which is chiefly calcium carbonate, contains the greater part of the heavy metals, including the germanium. From about 100 kg. of this precipitate pure germanium oxide weighing 0.060 g. was extracted by a comparatively simple process. It was calculated that this represented some 250,000 liters of the original Vichy water, and corresponded to  $\frac{24}{100,000}$  m.g. of germanium oxide per liter. This estimate is a minimum on account of losses during extraction

and purification, but the conclusion is reached that these residues may become a practical source of the rare metal.—C. R., cliii, 1278. H. L. W.

3. The Acid Salts of Dibasic Acids.-It is customary to assume that bivalent acids form acid salts readily on account of the presence of two hydrogens in the acid molecule, and this idea is expressed in the formulas usually given to these acid salts. For instance, the acid potassium sulphate and oxalate are indicated by the formulas HKSO, and HKC<sub>2</sub>O, E. JUNGFLEISCH and P. LANDRIEU have shown, however, that acid camphorates are not compounds of this type but are formed by the union of the free acid with the neutral salt. They have also carefully investigated the acid potassium oxalate, and find that it does not crystallize unchanged from its solutions. They conclude, therefore, that the formula of this salt should be written K.C.O.H.C.O. instead of in the usual manner previously mentioned. This con-clusion of these investigators is perhaps not entirely free from criticism, but it is strengthened by the known existence of acid nitrates and acid salts of other univalent acids.-C. R., clviii, 1306. H. L. W.

4. Fluorsulphonic Acid.-OTTO RUFF and H. J. BRAUN have found that this acid, which has the formula SO HF, may be conveniently prepared by distilling a mixture of fluorspar with fuming sulphuric acid. The best yield is obtained when the fuming acid contains about 60 per cent of the free anhydride, SO.. The operation can be carried out in a simple retort made of wrought iron pipes, but in order to make it perfectly pure it must be redistilled in platinum. The pure acid boils at 162.6° C. at atmospheric pressure. With solid sodium chloride or fluoride, it forms sodium fluorsulphonate with violent evolution of hydrochloric or hydrofluoric acid. It is remarkably stable towards heat and does not decompose, apparently, even at 900° C. However, reducing agents act upon it when heated, forming HF and SO<sub>2</sub>. Finely divided sulphur is acted upon by it at its boiling temperature with the formation of the compounds just mentioned.—Berichte, xlvii, 646, 656. H. L. W.

5. The Density and Atomic Weight of Neon.—A. LEDUC, starting with about 8 liters of this gaseous constituent of the atmosphere, which was already nearly pure, purified it further by fractional absorption by charcoal at the temperature of liquid air followed by fractional expulsion until the final sample was believed to contain less than  $\frac{2}{1000}$  of impurities, chiefly nitrogen. As a result of density determinations he found the value 0.695 instead of 0.674 as found by Ramsay and Travers. He found, further, that the atomic weight of this element is exactly 20 times that of hydrogen, or 20.15 compared with oxygen as 16. This value agrees closely with 20.2 given in the last International table.— C. R., clviii, 868. H. L. W.

6. A Chart of the Carbon Compounds; by CHARLES W. CUNO. Poster about  $2\frac{1}{2} \times 3\frac{1}{2}$  ft. (Published by the Author,

University of Denver.)—This chart gives a survey of the most important classes of organic compounds. Many structural formulas are given, and many methods of synthesis and characteristic reactions are included. The arrangement is systematic and ingenious, and it should be useful to students in reviewing the more fundamental and important facts of the subject. H. L. W.

7. A New X-Ray Spectrograph.-An extremely simple apparatus for photographing Röntgen-ray spectra has just been devised by MAURICE DE BROGLIE. The entire dispersing system consists of a cylindrical core, about 3cms in external diameter, around a portion of which a sheet of mica is tightly wrapped. The axis of the cylinder is rigidly fixed parallel to the lead slit and eccentric with respect to the line of collimation of the beam of X-rays. In a word, the narrow beam meets the cylindrical mica surface almost tangentially. The photographic plate is placed with its plane at right angles to the axis of collimation and at a suitable distance beyond the cylinder. The glancing angles at the mica surface of different portions of the X-ray beam increase continuously from zero up to a certain finite limit. It follows, therefore, from the well-known law of "reflection" of X-rays, that the constituent radiations will be spread out as a sharply-defined spectrum on the photographic plate. If great accuracy in the deter-mination of the relative positions of the spectral lines is of primary importance, then the mica cylinder does not compare favorably with the type of X-ray spectrograph in which a suitable crystal is slowly rotated, for (a) the spectrum is not normal, (b) both positive and negative orders of spectra do not occur, so that an error in the determination of the position of the central image cannot be eliminated in the usual way, (c) the dispersion is less than when a plane sheet of mica is revolved, and (d) the dispersion of mica is less than that of rock salt, say in the ratio of 1:3.58. On the other hand, the apparatus involving the mica cylindrical surface is rigid and incomparably simpler than the apparatus requiring a rotating mechanism. The cylinder can be readily used in a closed vessel susceptible of evacuation. The new spectrograph records all of the spectral lines simultaneously, and hence it admits of shorter times of exposure than the rotating crystal system. The geometrical distribution of the lines on the photographic plate is (theoretically, at least) not complicated. The author calls attention to the fact that if the mica sheet were given the form of a concave cylinder whose sectional generatrix is an equiangular spiral, a point source situated at the pole of the spiral would produce an extended source of monochromatic radiation. The spectra reproduced in the plate are very clear and sharp.-Jour. de Phys., April, 1914, p. 265. H. S. U.

8. The Ultra-violet Limit of the Solar Spectrum.—The results obtained by Miethe and Lehmann have been confirmed and extended by ALBERT WIGAND, hence a brief account of the latest investigation will be sufficient. The spectrograph used had quartz lenses and crossed calcite prisms. The absorption of these prisms began to be appreciable at  $265^{\mu\mu}$ , which wave-length is ade-quately shorter than the observed end of the solar spectrum, namely  $290^{\mu\mu}$ . The instrument was set for the mercury line 292  $\cdot 58^{\mu\mu}$  and calibrated with the mercury arc spectrum. All measurements were started at the sharp absorption line t,  $299.45^{\mu\mu}$ . With a slit width of  $0.01^{\text{mm}}$  the exposures took from a few seconds up to 10 minutes. Nothing was gained by lengthening the exposure time, because of the ever-increasing density of fog due to light of greater wave-length scattered by the optical surfaces. The failure of Wigand's first experiments was caused by this scattered light, and the success of his later attempts to photograph shorter wave-lengths than had been previously recorded depended on the recognition of this fact and the removal of the disturbing cause. It was found that bromine vapor afforded the required light-filter. The saturated vapor was confined in a glass tube 20<sup>cms</sup> long and 3.5<sup>cms</sup> in diameter. The incidence end of this tube was closed by a plano-convex quartz lens of 22<sup>cms</sup> focal length. The end of the tube nearer to the slit of the spectrograph was made of a plane-parallel quartz plate. The bromine vapor absorbed completely all radiations from the yellow-green as far as some distance in the ultra-violet. On the other hand, it was entirely transparent in the interval  $303^{\mu\mu}$  to  $265^{\mu\mu}$ . This absorbing screen practically removed all undesired light and greatly increased the contrast, sharpness and detail of the spectrograms.

The best negatives taken at Halle (100 meters above sea level) gave  $289.73^{\mu\mu}$  as the very shortest solar radiation recorded. On September 9, 12 good negatives were obtained by the investigator when in a free balloon at an elevation of about 9000 meters (5.5 miles). All of these plates gave inferior limits of the solar spectrum less than  $290.75^{\mu\mu}$ , the shortest wave-length recorded being  $289.60^{\mu\mu}$ . Thus the solar spectrum has been extended by  $1.5^{\mu\mu}$  as compared with earlier data obtained by the photographic method. The fact that the extreme ultra-violet limit of the solar spectrum is sensibly the same at elevations of 100 and 9000 meters shows that the conclusion of Cornu and others-that the limit of the spectrum increases steadily towards shorter wave-lengths as the altitude increases—is untenable. Also the lack of agreement between the data obtained by other investigators (save Miethe and Lehmann) was due, in part at least, to light scattered within the spectrographs employed. A table is given of 52 absorption lines from  $t 299.45^{\mu\mu}$  to  $291.18^{\mu\mu}$ . The two most refrangible lines are new, and they were recorded on the negatives taken at Halle as well as from the balloon.

Hartley has ascribed the abrupt ending of the transmitted solar spectrum to the absorption exerted by ozone. If the limit is due to any constituent of the earth's atmosphere then the observed lack of dependence of this limit upon the altitude requires the assumption that most of the absorber lies above 9000 meters. This hypothesis is not strengthened by the fact that at

# Chemistry and Physics.

an elevation of 9000 meters 2/3 of the total air mass is left below. Again, the relatively cool outer atmosphere of the sun may absorb all radiations of wave-length shorter than about  $289^{\mu\mu}$ . The most plausible explanation of the existence of an approximately abrupt ultra-violet limit to the solar spectrum seems to be given by Rayleigh's theory of the scattering of short waves by molecules and small suspended particles, which accounts for the blue color of the sky, etc. To test this point, Wigand has done some preliminary work by focusing the bluest part of the skylight on the slit of the spectrograph. Four different negatives gave the following limits: 289.87, 289.80, 289.60 and 289.39<sup> $\mu\mu$ </sup>. It is thus evident that the limit is at least as low for blue skylight as for direct sunlight, as would be expected if the true explanation is to be found in the scattering by small particles.—*Phys. Zeitschr.*, Nov. 15, 1913, p. 1144. H. S. U.

9. Change in a Lunar Crater.-Most, if not all, of the changes which have been observed in the moon and accepted as thoroughly verified are of a periodic nature. A marked case of a non-periodic change is recorded in a short article by WILLIAM H. PICKERING. The author says: "It is indeed the most marked non-periodic change that the writer has ever detected." The crater in question is named Eimmart and is situated at the northwest border of Mare Crisium, in latitude  $+24^{\circ}$  and longitude 295°. This crater is about  $40^{\rm kms}$  in diameter. The general nature of the phenomenon observed is that while formerly, at each lunation, the crater apparently filled up gradually and overflowed with a white material, the source of which was a point at the foot of the northern interior slope, this change no longer occurs. The last "eruption" observed occurred in January, 1913. Only one observation was made in February and March, but less activity was then shown, while in April and May the phenomenon was so reduced in intensity as to be scarcely noticeable. Interesting drawings of the appearance of the crater during and after its maximum activity are reproduced in the paper, but the author does not discuss the geological or physical aspects of the results obtained with the Draper refractor.-Astron. Nachrichten, No. 4704, p. 414. H. S. U.

10. Propagation of Light in Dispersing. Media.—According to the Principle of Relativity it is impossible for a velocity to exceed that of light in free space. This applies to the convective velocity of an electron or ordinary body as well as to the velocity of propagation of a mechanical or electrodynamical signal. On the other hand, it has often been shown experimentally that, in the immediate vicinity of an absorption band, a region exists throughout which the index of refraction is less than unity. Consequently the "velocity of light" (no matter whether this term is taken to mean the group velocity or the phase velocity) in such a region is greater than c, the velocity of light *in vacuo*. This apparent contradiction between experiment and theory has been exhaustively discussed and satisfactorily explained in two long, mathematical papers, one by A. SOMMERFELD and the other by L. BRILLOUIN.

To begin with, great care must be taken in defining the various kinds of velocities which may be associated with the propagation of transverse vibrations. If the train of waves is unlimited in both directions, it is not possible in general to define the velocity of propagation. In this case a phase velocity is obtained, and this arises in interference experiments and in the majority of optical phenomena. What is generally understood by the "velocity of light" in an ordinary optical medium (velocity in free space divided by the index of refraction,  $c/\mu$ ) is nothing but this phase velocity. Only in a vacuum does the phase velocity equal the velocity of propagation. In any other medium it only shows how the phase of the light is retarded by the interaction of the medium, but it teaches nothing about the process of propagation. In order to be able to state anything about the propagation a limited train of waves must be considered. That is, the medium is at rest up to a certain instant, then a uniform succession of vibrations sets in, which either breaks off, after a time, or persists indefinitely. Such a train of waves is called a "signal." The velocity of the "head" of the wave-train must not be confused with the signal velocity, that is, with the velocity with which the main part of the light motion is propagated in a dispersing medium. It turns out that as the signal progresses it does not retain its original form. At a given depth in the medium a very weak light-motion first arrives (the "forerunners") which gradually increases to a value corresponding to the intensity of the incident light. Brillouin proves that the signal velocity practically agrees with the group velocity when the period of the vibrations is different from the natural period of the dispersing medium, that is, outside of the region of anomalous dispersion. Sommerfeld shows that the "head velocity" is identical with the vacuum velocity, c, under all circumstances, no matter whether the medium disperses normally or anomalously, whether it is transparent or absorbent, whether it is single refracting or double refracting. Consequently, if white light falls normally upon a dispersing plate, the less refrangible ("fast") components do not hasten ahead of the more refrangible ("slow") components, so that, at the first instant of emergence the light is colored red. On the contrary, the wave-fronts of all the components of the white light traverse the plate with the same velocity c, and, at the first instant, all contribute in the same manner to the energy of the emergent light. Furthermore, the "forerunners" do not show the colors of the constituents from which they have arisen, but have an ultra-violet wave-length and an extremely small intensity determined by the dispersive power and thickness of the plate. During the passage of the light through the plate its character is changed so fundamentally-while the ions are being set in vibration-that in general no similarity exists between the incident and the first emergent light. Also so much energy is held back

in accelerating the ions that the first emerging energy is very small in comparison with the incident energy. The preceding statements have been generalized for the case of oblique incidence.

A curve is given in the second paper showing the form of two "forerunners" and the arrival of the "signal." In another diagram three curves are drawn for the region of anomalous dispersion. Frequencies are laid off as abscissæ and the ordinates denote the ratio of the velocity of light in free space to the velocity of propagation in question. Hence, in a certain sense, the ordinates mean indices of refraction. The three velocities involved in the denominator of the ratio just mentioned are the phase, group, and signal velocities. The curves for the group and phase velocities follow the familiar course, having maximum values greater than unity and minima less than 1. The graph corresponding to the signal velocity has two maxima and one minimum, but nowhere falls below unity. At the minimum the signal velocity attains the value of the vacuum velocity. It is shown that the portions of the group and phase velocity curves which have ordinates inferior to unity do not correspond to physical reality (as velocities) because the underlying definitions break down. Consequently the apparent lack of agreement between the experimental data and the Principle of Relativity has been satisfactorily removed by these two very important mathematical investigations .- Ann. d. Physik, vol. xliv, pp. 177-240, May, 1914. н. s. u.

11. Dialogues concerning Two New Sciences; by GALILEO GALILEI. Translated from the Italian and Latin by Henry Crew and Alfonso de Salvio. Pp. xxi, 300. New York, 1914 (The Macmillan Co.).-The following sentence, quoted from the translators' preface, shows very clearly why the arduous task was undertaken, namely : "For more than a century English-speaking students have been placed in the anomalous position of hearing Galileo constantly referred to as the founder of modern physical science, without having any chance to read, in their own language, what Galileo himself has to say." The text of the National Edition of the Works of Galileo has been strictly followed. The English translation is enhanced by the inclusion in it of an "Introduction" by Antonio Favaro of Padua, who has devoted the best years of his life to the production of the twenty volumes of the National Edition. Le Mechaniche and De Motu Accelerato by Galileo have been wisely omitted from the present volume since the former contains little but the Statics which was current before the time of Galileo, and the latter is essentially included in the "Dialogue" of the "Third Day." No pains have been spared by the translators to reproduce as accurately as possible Galileo's thoughts, having due regard, at the same time, to all details which make for elegance of presentation.

As regards the original text, lack of space precludes the possibility of doing justice to the subject. Moreover, the book ought to be read by all who are engaged in teaching physics. There-

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXVIII, NO. 223.-JULY, 1914.

fore, it will be sufficient to state that the book contains four "Dialogues" which deal with the following subjects: "I. First new science, treating of the resistance which solid bodies offer to fracture. First Day;" "II. Concerning the cause of cohesion. Second Day;" "III. Second new science, treating of motion [movimenti locali]. Third Day. Uniform motion. Naturally acclerated motion;" and "IV. Violent motion. Projectiles. Fourth Day." H. S. U.

12. The Norwegian Aurora Polaris Expedition, 1902-1903. Vol. I. On the Cause of Magnetic Storms and the Origin of Terrestrial Magnetism; by Dr. BIRKELAND. Second section. Pp. ix, 319-801, pls. XXII-XLII. Christiania, 1913.-The first section of this extended work by Dr. Birkeland, based upon observations made during the polar expeditions of 1896-1903, was published five years since and noticed at length in this Journal at the time (volume xxix, p. 272). The second section, now issued, carries forward the subject, Part II being devoted particularly to "Polar Magnetic Phenomena and Terrella Experiments"; and Part III to "Earth Currents and Earth Magnetism." Numerous special plates accompany the volume; these are devoted in part to the perturbations observed from October 15, 1882, to July 15, 1883; also others to earth currents and magnetic elements at Kaafjord, Bossekop, Parc St. Maur, Greenwich, etc. The author's point of view and conclusions can be best brought out by the following quotations from the preface :

"In order further to make it clear whether our results from the working-up of the above-mentioned observations from the most varied parts of the world could be brought into theoretic harmony with my previous assumptions, I have carried out a long series of experimental investigations with a magnetic globe in a large vacuum-box intended for electric discharges. I have hereby been enabled to obtain a representation of the way in which cathoderays move singly, and group themselves in crowds about a magnetic globe such as this. Special study has been made of those crowds of rays that produce magnetic effects analogous to those observed upon the earth during positive and negative polar storms." \* \*

"I hold that I have demonstrated that the magnetic storms on the earth—the positive and negative polar storms, and the positive and negative equatorial storms—may be assumed to have as their primary cause the precipitation toward the earth of heliocathode rays, of which the magnetic stiffness is so great that the product H.  $\rho$  for them is most usually about  $3 \times 10^6$  C. G. S. units.

"On account of the magnetic condition of the earth, these new solar beams which I have discovered will especially make their way towards the earth in the polar regions in the two auroral zones, where they also certainly produce other effects which play an important part in various meteorological phenomena."

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# Geology and Mineralogy.

"The experimental investigations which at first were designed to procure analogies capable of explaining phenomena on the earth, such as aurora and magnetic disturbances, were subsequently extended, as was only natural, with the object of procuring information as to the conditions under which the emission of the assumed helio-cathode rays from the sun might be supposed to take place. The magnetic globe was then made the cathode in the vacuum-box, and experiments were carried on under these conditions for many years. It was in this way that there gradually appeared experimental analogies to various cosmic phenomena, such as zodiacal light, Saturn's rings, sun-spots and spiral nebulæ. The consequence was that attempts were made to knit together all these new discoveries and hypotheses into one cosmogonic theory, in which solar systems and the formation of galactic systems are discussed perhaps rather more from electromagnetic points of view than from the theory of gravitation. One of the most peculiar features of this cosmogony is that space beyond the heavenly bodies is assumed to be filled with flying atoms and corpuscles of all kinds in such density that the aggregate mass of the heavenly bodies within a limited, very large space would be only a very small fraction of the aggregate mass of the flying atoms there. And we imagine that an average equilibrium exists in infinite space, between disintegration of the heavenly bodies on the one hand, and gathering and condensation of flying corpuscles on the other."

# II. GEOLOGY AND MINERALOGY.

1. Geology of Saratoga Springs and vicinity; by H. P. CUSHING and R. RUEDEMANN. N. Y. State Mus., Bull. 169, 1914, pp. 1-177, pls. 1-20, text figs. 1-17, 1 map.—This report treats in detail of the difficult geology of the region about the widely known watering place, Saratoga Springs, New York. The Adirondack complex basement and the slightly folded but much faulted early Paleozoic strata of the western area are described by Cushing; while the almost undisturbed shale series of the western basin and the greatly overthrust and highly complicated structure of the eastern trough are wrought out by Ruedemann. How far the eastern mass of closed folds and isoclinal structure overrides the western in "Schuppen" or shingle structure, is not known, but the contained fossils in the two series of strata show clearly that they are the sediments of two distinct water areas separated from one another by a land barrier. Marked folding took place toward the close of the Ordovician (Taconic revolution), but when the major thrust-faulting occurred is not as yet known. It may have taken place during the closing periods of the Paleozoic. C. S.

2. Notes on the Ontogeny of Paradoxides, with the descripion of a new species from Braintree, Mass.; and Notes on the Ontogeny of Isotelus gigas Dekay; by PERCY E. RAYMOND. Bull. Mus. Comp. Zool., vol. lviii, No. 4, pp. 225-244, with 1 plate; No. 5, pp. 247-263, with 3 plates, 1914.-In these excellent papers the author presents all that is known regarding the ontogeny of the genus Paradoxides and the species Isotelus gigas. his studies being based largely on a wealth of material in the Agassiz Museum of Harvard University. Incidentally a number of species are more clearly delimited or described as new. In the youngest or protaspis stage of Paradoxides, this genus is seen to be closely related to Olenellus. On the other hand, when Isotelus gigas has a length of from 3 to  $5^{mm}$  it has "almost exactly the same form as an adult specimen of Basilicus barrandi, thus providing an excellent example of recapitulation, for the beginning of the range of Basilicus antedates that of Isotelus. Another interesting fact is that while *Isotelus gigas* is the most specialized species of the genus, it is one of the first to appear, and apparently one of the first to die out, while the ones which survived to the end of the Ordovician were the more primitive forms, Isotelus maximus and I. iowensis" (p. 247). I. gigas in its development passes through the Basilicus, Ogygites and Isotelus stages into that of the species I. gigas.

3. Acceleration of development in fossil Cephalopoda ; by JAMES PERRIN SMITH. Leland Stanford Junior Univ. Pub., Univ. Ser., 1914, 30 pages, 15 plates .- Professor Smith in this paper discusses, with an abundance of illustrations, the principles of the biogenetic law as shown among the goniatites and ammonites. The more this study is pursued, the more intricate it becomes, and the author fears that he will be thought to be leaving the "Hyatt school" of paleontologists. In conclusion, however, he adds : "The writer is still a firm believer in the biogenetic law, but that law is not such a simple thing as it was once thought to be. In the youth of every theory everything is beautifully clear, and ideally simple. As time goes on we are compelled to drop one idea after another, until it almost seems that the whole will be lost. When sceptics concerning the recapitulation theory throw up to us that ontogeny does not always recapitulate phylogeny, we are prepared to admit this, even to go further and admit that it does not often recapitulate. In fact, the writer would be prepared to go still further, and to state that, in the sense in which the term has been used by most adherents of the theory, it never recapitulates. Our over-zealous friends have claimed too much, and have done more to prevent general acceptance of the theory than a host of enemies " (p. 26). C. S.

4. The Stratigraphy and Paleontology of the Tanner's Creek section of the Cincinnati Series of Indiana; by E. R. CUMINGS and J. J. GALLOWAY. Thirty-seventh Ann. Rept. Dept. Geol. Nat. Res. Indiana, 1912. 1913, 87 pages, 20 pls., 18 figs.—This paper is especially valuable for the great care with which the fossils are zoned in the Cincinnati Series and with which the 389 species found in the state of Indiana have been listed. The chief bulk of the material consists of Bryozoa (176 forms, 18 new) and Brachiopoda (48). The authors do not draw the top of the Maysville at the Mt. Auburn but at the top of the Arnheim. They say in part :

"We do not agree either that the Arnheim should be placed in the Richmond, or that the Richmond belongs in the Silurian. There is no lithologic or faunal break at this level, at least in the present section. Most of the Arnheim species range without interruption from within the Corryville to the middle Arnheim, and many of them throughout the Maysville. . . "At the top of the Arnheim the rocks are irregularly bed-

ded and nodular and almost barren of fossils. At this point limestones cease to predominate and are replaced by soft, argillaceous shale and thin beds of limestone. Shale predominates throughout the Waynesville, which is 105 feet thick. There is also a marked faunal break at the top of the Arnheim. Not less than 30 species of Bryozoa fail at this point or abruptly become Over 20 species make their first appearance at this horizon. rare. The Waynesville fauna is quite distinct from the Arnheim and shows a change of life conditions. There are also numerous migrants from other regions, especially from the northwest, indicating a pronounced epeirogenic movement at this time. At no horizon throughout the Maysville is there any faunal or lithologic change comparable with the one at the top of the Arnheim. Hence, we maintain that the Arnheim should be classed with the Maysville sediments and that the Richmond should begin with the lower Waynesville. On the other hand, we believe that the Richmond is most intimately associated with the subjacent Ordovician, both lithologically and faunally, and that it should be retained in the Ordovician System" (p. 8). C. S.

5. Mud Cracks open under Water; by E. S. MOORE.—An interesting occurrence of mud cracks, remaining open under water for at least several weeks, was recently observed by the writer. In a small pond, a mile and three-quarters west of Julian, along the Bald Eagle Creek, in Centre County, Pennsylvania, an area at least ten feet in diameter on the bottom of the pond was found to be covered with large mud cracks, wide open. The water was about a foot deep and many of the cracks as much as an inch and a quarter wide. The water was not occasioned by a recent rainfall, which formed a temporary pond, as water has been seen in this area during different months of the year, although the mud cracks were only recently observed. These were first seen on April 4th, 1914, while passing this pond, but they were again observed on April 29th of the same year and appeared to be in practically the same condition as when first seen.

Owing to the fact that geologists usually consider that mud cracks cannot remain open under water for any length of time, this seems to be a rather striking occurrence of this feature. Some other explanation than that of baking by the sun must be offered to satisfy the conditions, as this mud certainly had not been exposed to the drying influence of the sun for several months,—at least since the previous summer and possibly not even then. The only explanation seems to be that the cracks are due to the ground freezing, with expansion, and later thawing, with contraction, beneath the water. It would thus seem possible to explain in this way the occurrence of mud cracks in some other areas where it has been found difficult to account for their presence, by the sun's action.

State College, Penn.

6. Engineering Geology; by HEINRICH RIES, Ph.D. and THOMAS L. WATSON, Ph.D. Pp. xxvì, 672; pls. 104, figs. 225. New York, 1914 (John Wiley & Sons).-The authors of Engineering Geology have produced a book which should find wide use. It is neither an economic geology nor the conventional geologic text, but combines many of the best features of both. The engineer with little geologic training may find here an appropriate scientific basis for his work, and the geologist may gain an appreciation of the bearing of his science on problems relating to water storage, sewage disposal, and other features of engineering work. In the chapters on minerals, rocks, structure and metamorphism, soils, surface waters, underground waters, wave work, lakes, glaciers, the treatment given these subjects in the elementary textbooks of geology is supplemented by instruc-tions for field use in determination of thickness and depth of beds, position of faults, flow of streams, strength of materials, etc. The book includes special economic chapters on landslides, building stones, limes, cement and plaster, clay and clay products, coal, petroleum, road materials, and ore deposits. H. E. G.

7. United States Bureau of Mines; JOSEPH A. HOLMES, Director.—The following BULLETINS have recently appeared (see vol. xxxvii, p. 351):

No. 42. The sampling and examination of mine gases and natural gas; by G. A. BURRELL and F. M. SEIBERT. Pp. 116; 2 pls., 23 figs.

No. 57. Safety and efficiency in mine tunneling; by DAVID W. BRUNTON and JOHN A. DAVIS. Pp. 271; 6 pls., 45 figs.

No. 67. Electric furnaces for making iron and steel ; by D. A. LYON and R. M. KEENEY. Pp. 142 ; 36 figs.

No. 68. Electric switches for use in gaseous mines ; by H. H. CLARK and R. W. CROCKER. 1913. Pp. 38 ; 6 pls., 1 fig.

No. 79. Abstracts of current decisions on mines and mining, March to December, 1913; by J. W. THOMPSON. Pp. xv, 140.

In addition to the above a number of TECHNICAL PAPERS and MINERS CIRCULARS have also been issued.

8. Canada Department of Mines. Geological Survey, R. W. BROCK, Director.—Recent publications are here noted (see vol. xxxvii, p. 352):

GUIDE BOOKS.—No. 5. Excursions in the Western Peninsula of Ontario and Manitoulin Island. Pp. 108; with numerous illustrations.

No. 8. Parts I, II and III. Transcontinental Excursion C1. Toronto to Victoria and return via Canadian Pacific and Canadian Northern Railways. Pp. 101; 105-274; 277-386; with illustrations. 1913.

No. 9. Transcontinental Excursion C2. Toronto to Victoria and return via Canadian Pacific, Grand Trunk Pacific, and National Transcontinental Railways. Pp. 164, with illustrations.

No. 10. Excursions in Northern British Columbia and Yukon Territory and along the North Pacific Coast. Pp. 179. 1913.

MEMOIRS.-No. 18 E. Bathurst District, New Brunswick ; by G. A. Young. Pp. 96; 1 fig., 4 maps.

No. 25. Report on the Clay and Shale Deposits of the Western Provinces (Part II) : by HEINRICH RIES and JOSEPH KEELER. Pp. 99; 40 pls., 6 figs.

No. 26. Geology and Mineral Deposits of the Tulameen District, B. C.; by CHARLES CAMSELL. Pp. viii, 188; with 33 pls., 2 figs., 4 maps.

No. 31. Wheaton District, Yukon Territory; by D. D.

CAIRNES. Pp. x, 153; 10 figs. No. 36. Geology of the Victoria and Saanich Map-areas, Vancouver Island, B. C.; by CHARLES H. CLAPP, 1913. Pp. 143; 18 pls., 6 figs., 4 maps (not yet published).

No. 44. Clay and Shale Deposits of New Brunswick; by J. KEELE, 1914. Pp. 94; 16 pls., 7 figs., 1 map.

No 48. Some myths and tales of the Ojibwa of Southeastern Ontario; collected by PAUL RADIN, 1914. Pp. 83.

Also the following maps: 43A .- Sooke Sheet, Vancouver Island, British Columbia. Topography. 98A .- Rainy Lake,

Rainy River district, Ontario. Geology. 9. A New Geologic Map of the State of New Jersey.—It is announced by the State Geologist, H. B. KÜMMEL, that a new geologic map of New Jersey has recently been issued; the preceding one bore the date of 1888. The new map shows in colors the location of the different varieties of rock, clay, sand, etc., within the State and the various periods of geologic history to which they belong. By means of eighteen different colors and various patterns of dots and lines, fifty-seven different rock formations are distinctly represented and their location shown; in the earlier map only twenty-four formations were indicated. The scale is about 4 miles to an inch, sufficiently large to permit considerable detail; the size is  $2 \times 4$  feet. The compilation has been done by Prof. J. Volney Lewis, of Rutgers College, and the State Geologist, from published folios and manuscript data in the possession of the Survey. Copies can be obtained of the State Geologist, Trenton, N. J., on payment of 50 cents.

10. Bulletin of the Hawaiian Volcano Observatory, Dr. T. A. JAGGAR, Jr., Director.-A weekly bulletin is now being issued from the Volcano Observatory on the borders of Kilauea. Nos. 1 to 20 of volume II, of dates January 7 to May 20, 1914, have recently been received. The bulletin is in charge of Professor Howard M. Ballou as editor. These notes, first published in the Pacific Commercial Advertiser of Honolulu, give a most interesting and useful record of the constantly changing conditions, particularly at Kilauea, and will have therefore a permanent value to all volcanologists and seismologists.

11. Simple Directions for the Determination of the Common Minerals and Rocks. A Laboratory Course in General Geology; by WILLIAM H. HOBBS. Pp. vii, 31. New York, 1914 (The Macmillan Co.).—This pamphlet, a reprint of matter from the author's "Earth Features and their Meaning," will be found useful by many teachers and students.

12. The Minerals of the Black Hills; by VICTOR ZIEGLER. Pp. 250; 31 pls. and 73 figs. South Dakota School of Mines. Bulletin No. 10. Department of Geology and Mineralogy. Rapid City, February, 1914.—The Black Hills region has been so rich in its mineral products, both as regards the variety and the economic importance of its species, that this record of Professor Ziegler will be welcomed by all interested in mineralogy. The opening forty pages are given to a general account of minerals for the local reader, and then follows a description of the individual species arranged according to the usual classification. Much interesting matter is contained here, and the value of the publication is largely increased through the twenty-seven halftone plates of typical minerals, which are reproduced with an unusual degree of success. There is also a general map of the Black Hills and a special map of the Harney Peak region, showing the many important localities of tin and tungsten, also lithium; further, bismuth, mica, and barite.

13. Kristallberechnung und Kristallzeichnung; by B. GOSSNER. Pp. vii, 128; 109 text-figures with 1 plate. Leipzig, 1914 (Wilhelm Engelmann).—This book gives, with the aid of many figures, a clear and concise account of the various methods of projection and calculation in common use by crystallographers. In addition it explains the different methods for drawing crystal figures. It should prove a valuable text-book for students of crystallography, as well as a convenient reference book for those engaged in crystallographic investigations. W. E. FORD.

## III. BOTANY AND ZOOLOGY.

1. The Weed Flora of Iowa; by L. H. PAMMEL and five collaborators. Pp. xiii, 912; 564 text figs. Iowa Geological Survey, Bull. No. 4. Des Moines, 1913.—This elaborate work was undertaken in the hope that the immense damage done by weeds in Iowa might be diminished if farmers had accessible information about these destructive plants. The first chapter, a descrip-

# Botany and Zoology.

tive manual, is by Professor Pammel himself, and provides full descriptions of the weeds represented, together with figures, notes on distribution, and directions for extermination. The second chapter describes the gross structure of the seeds of the weeds, the third chapter the microscopic structure of certain selected seeds, and the fourth chapter includes a full account of the morphology of the leaves and flowers of weeds. In the remaining chapters the dissemination of weeds, the morphology of the underground portions, the injuriousness of weeds, and the migration of weeds are among the topics treated. The numerous illustrations, which are partly original and partly taken from other publications, add greatly to the value of the volume.

2. Researches on the Irritability of Plants; by JAGADIS CHUNDER BOSE. Pp. xxiv, 376; 190 text figs. New York, 1913. (Longmans, Green & Co.)-In this volume Dr. Bose continues his interesting and original studies on the responses of plants to stimuli and describes improved and delicate apparatus by means of which the responses may be more accurately recorded. The plants most used in his investigations were the sensitive plant, Mimosa, and the remarkable Desmodium gyrans, and the stimuli employed were of many different kinds. By means of his apparatus he was able to demonstrate the latent period of a response as well as its various phases, and most of his figures represent actual records of responses made by himself and by his students. One interesting conclusion which he draws from his investigations is that the various manifestations of irritability shown by plants are identical with those shown by animals, and he suggests that many difficult problems in animal physiology may find their solution in the study of the more simply organized plants. A. W. E.

3. Introduction to Botany; by JOSEPH Y. BERGEN and OTIS W. CALDWELL. Pp. vii, 368; 246 text figs. Boston and New York, 1914. (Ginn & Company.)-In this elementary text-book, designed for pupils in secondary schools, the authors aim to present those features of plant life which are of interest to all people. The plant is considered as an independent organism, which has its own living to make under varied circumstances. The forms selected for description and illustration are for the most part those seen in everyday life and those of economic importance. The figures, many of which are original, are unusually clear, and an interesting feature of the work is the introduction of portraits of famous botanists. The book maintains the high standard set by the authors in their earlier publications and may be cordially recommended to teachers. A. W. E.

4. Wissenschaftliche Ergebnisse der Deutschen Zentral-Afrika-Expedition 1907–1908, unter Führung Adolf Friedrichs, Herzogs zu Mecklenburg. Leipzig, 1914 (Klinkhardt and Biermann).-Vol. II, Botany, edited by Dr. J. MILDBRAED, Berlin. Lieferung 7, pp. 603-718. The earlier parts of this valuable work have already been reviewed in this Journal (see xxxv, 335). In the present part, which concludes the volume, the vegetation of the region visited by the Expedition is discussed by the editor, Dr. Mildbraed. The treatment is largely ecological and the various formations represented in equatorial Africa are taken up in considerable detail. Attention is called in conclusion to the strong resemblance between the flora of the eastern part of Africa and that of the western coast.

Volume V, Zoology III, edited by Dr. H. SCHUBOTZ. Lief. 1, 2. Of the nine large volumes in which the results of this important expedition are being published (see above), volume V is devoted to zoology. Of this, Lief. 1, on the Orthoptera, is by JAMES A. G. REIN; it occupies pp. 1–223 and discusses 226 species of these insects, including 81 species and 10 genera new to science. Lief. 2 is devoted to Fishes, and is by P. PAPPENHEIM und G. A. BOULENGER. This includes pp. 225 to 260, with 10 plates and describes 21 new species of fishes.

A. W. E. and W. R. C.

5. The Elementary Principles of General Biology; by JAMES FRANCIS ABBOTT. Pp. xvi, 329, with 114 illustrations. New York, 1914 (The Macmillan Co.).—The modern conception that the essential principles governing the life and growth of organisms are identical in both plants and animals is well illustrated by this book. In the general treatment of the subject the author therefore selects his examples impartially from both kingdoms, choosing those which most clearly illustrate the principal phenomena. None of the species either of animals or plants are treated as structural entities, the activities rather than the mechanism of organisms being considered of chief importance.

The principal phenomena exhibited by organisms, such as metabolism, growth, differentiation, development, variation, heredity, organic response, and evolution are treated in such a clear and logical manner as to furnish a comprehensive survey of the field either for the student or the general reader.

The use of a book of this character, when accompanied by suitable laboratory exercises, should mark a distinct advance over the disjointed college courses in botany and zoology. W. R. C.

the disjointed college courses in botany and zoology. W. R. C. 6. Biology, General and Medical; by JOSEPH McFARLAND. Pp. 457, with 160 figures. Second edition, thoroughly revised. Philadelphia and London, 1913 (W. B. Saunders Company).—Of the numerous text-books which have appeared in this field during the past decade this is one of the few that have enjoyed a popularity so great as to require the printing of a new edition within three years of the first publication. In addition to the general discussion of the principal biological phenomena, the author lays special emphasis on those phases of the subject which concern the human welfare and which are particularly important for a broad comprehension of the medical sciences. Such topics include the blood relationship of animals, parasitism, infection and immunity, mutilation and regeneration, grafting, senescence, decadence, and death of organisms. W. R. C.

# Botany and Zoology.

7. Monograph of the Shallow-water Starfishes of the North Pacific Coast, from the Arctic Ocean to California. Smithsonian Institution, Harriman Alaska Series, vol. xiv. Part I. Text, 408 pages: Part II, 110 plates, April, 1914; by A. E. VERRILL.—This work, which has been delayed for several years, owing to various causes, stated in the preface, includes descriptions and illustrations of practically all the families, genera, and species now known to occur between San Francisco and the Arctic Ocean in waters less than 60 fathoms deep.

The Introduction includes a general account of the morphology, habits, classification, variations, hybridism, peculiarities and relations of the fauna, etc.

As a very large proportion of the species belong to the Forcipulosa, and especially to the family Asterridæ, nearly half of the work is devoted to that group, of which the structure and development, as well as the classification, are discussed in detail. Much use is made of the structure of the pedicellariæ, of which an unusually large number are figured. About 100 species are described from this region, besides about 20 named varieties. Analytical tables are supplied for the larger and more difficult families. The Geographical Distribution is discussed and faunal lists are given on pp. 337–374. This includes a comparison with the Patagonian and Antarctic faunæ, with revisions of many of the genera and species of that region.

Seventeen new genera are established, as well as numerous new species. The Bibliographical List which includes a large number of titles, covers 14 pages. Many titles relate to the arctic faunæ, for many arctic and circumpolar species occur on the northern coasts of Alaska.

The volume of plates includes general figures, as well as details, of nearly all the species. The general figures are heliotype plates, from photographs. Among these are figures of the original types of the various species described by Dr. Wm. Stimpson, many years ago and never before figured. The microscopic details of pedicellariæ, spines, etc., which occupy many plates, are from camera-lucida drawings by A. H. Verrill, and will prove to be of great value in the identification of species.

A few typographical errors have been noticed: On page 204, Alvelata should read Avelata; page 178, line 12 from bottom should be omitted, for No. 1181 is the Asterias Katherinæ, described on p. 112.

8. Memoirs of the Queensland Museum. Vol. II; edited by the Director, R. HAMLYN-HARRIS. Issued December 10, 1913. Pp. 339 ; 22 pls. Brisbane.—The papers in this volume are in part ethnographical, in part devoted to Natural History. The memoir on Queensland fishes, profusely illustrated, is of especial interest; also one on the Australian Hymenoptera Chalcidoidea by A. A. Girault; this is a supplement to a paper in Vol. I of the Museum Memoirs. 9. Catalogue of the Ungulate Mammals in the British Museum (Natural History). Vol. II. Artiodactyla; by R. LYDEKKER assisted by GLBERT BLAINE. Pp. xvi, 295; 33 figs. London, 1914.—This second volume deals with a considerable portion of the African antelopes, including the Bovidæ subfamilies Bubalinæ to Reduncinæ; the remainder, embracing the Gazelles, the Prongbuck, the Giraffes and the Okapi, are reserved for a third volume.

10. Field Museum of Natural History. Annual Report of the Director, Dr. FREDERICK J. V. SKIFF, to the Board of Trustees for the year 1913. Publication 173. Vol. IV, No. 4, pp. 275-363. Chicago, 1914.-The work of the Field Museum during the past year has been largely in the way of preparation of material for exhibition in the new building. This has been carried on so rapidly that the present quarters are now much over-crowded with the installations that have been made. The cost of maintenance amounted to \$170,000 and the total expended was \$237,000, about the same as that of the preceding year. Numerous additions have been made, both to the collections and to the library, and among other points may be mentioned the reinstallation of the meteorites with the incorporation of some 1600 specimens of the unique Ward-Coonley collection. The total number of visitors for the year was upwards of 214,000, and the outside work of the institution is also shown in a variety of public lecture courses. In addition to the museum work at home, the Joseph N. Field Ethnological Expedition to the South Seas, under Dr. Lewis, has now concluded its three years' studies and collections, while the South American Zoological Expedition is still in the field, and is yielding important results. A collection of 24,000 birds' eggs has been left by the will of the Hon. R. M. Barnes.

The following publication has been recently issued : No. 172, Botanical Series, Vol. II, no. 9. I. The Genera Pedilanthus and Cubanthus, and other American Euphorbiaceæ; by CHARLES F. MILLSPAUGH. II. Two New Stonecrops from Guatemala; by RAYMOND HAMET. Pp. 353-381.

11. International Kongress für Vererbungs- und Züchtungsforschung.—At the last Congress held in Paris, it was decided by the International Committee that the next—the fifth—should later place at Berlin in 1916 in the early part of September. The members of the Committee have already been announced and the committee's address is Invalidenstrasse 42, Kgl. Landwirtsch. Hochschule, Berlin, N4., Germany.

Der Mensch und seine Kultur: Neue Ausblicke auf ihre Entwicklung; von NEOPHILOSOPHOS TIS. Pp. 100. Konstanz, 1912 (Verlag von Ernst Ackermann).

# IV. ASTRONOMY AND MATHEMATICS.

1. An Introduction to Celestial Mechanics; by F. R. MOUL-TON. Second revised Edition. Pp. xvi, 437; 62 figs. New York, 1914 (The Macmillan Co.).—The issue of a second edition of Professor Moulton's work points not only to a continued interest in celestial mechanics but also to the fact that the volume satisfies a need. The gap between a text-book on descriptive astronomy like that of Young and the big treatise of Tisserand in four quarto volumes requires filling by just such a publication. The student who has mastered it and desires to specialize in any of the departments of celestial mechanics will have received the necessary foundation and will be enabled to go forward without having continually to return in order to supply some lacuna in hjs information.

A few additions have been made but this second edition is not very largely increased. The author has, however, rewritten several portions, as suggested by experience in using the book in the class-room, and has brought those subjects which have advanced in the interval of eleven years, up to date. Two excellent features of the work are the problems and the bibliographies at the end of each division. E. w. B.

2. Memorabilia Mathematica, or the Philomath's Quotation-Book; by R. E. MORITZ. Pp. vii, 410. New York, 1914 (The Macmillan Co.).-A volume containing over a thousand quotations from more than three hundred writers should be a boon in these days of addresses and public lectures. Here is material referring to the values and excellencies of mathematics gathered from poets, philosophers, historians, scientists and mathematicians, grouped under twenty heads and cross indexed under nearly seven hundred topics. Professor Moritz's collection is essentially a dictionary of quotations, but unlike most dictionaries the curious reader can open it almost anywhere and peruse several pages in succession without suffering from mental conges-While every student of mathematics must welcome the tion. appearance of a volume which can set forth in non-technical language the excellencies of his subject, one cannot help feeling, on glancing through it, that many of the quotations might have been omitted without loss. A commonplace remark apart from its setting, and there are many such printed, is apt rather to repel than to attract. Nevertheless, it should stimulate an interest in the history of the subject and should for that reason be within easy reach of the student. E. W. B.

3. Publications of the Allegheny Observatory of the University of Pittsburgh.—The following have been recently issued (see vol. XXXVI, 89): Volume III, No. 4. The Orbit of  $\lambda$  Tauri; by FRANK SCHLESINGER. Pp. 23-30.

No. 5. Spectrographic Observations of  $\phi$  Persei; by FRANK C. JORDAN. Pp. 31-41.

No. 6. Thermo-Electric Measurements of Stellar Radiation; by A. H. PFUND. Pp. 43-48.

No. 7. The Orbit of R Canis Majoris; by FRANK C. JORDAN. Pp. 49-52.

No. 8. Anomalous Refraction at the International Latitude Stations in 1902, 1903 and 1904; by FRANK SCHLESINGER and CHARLES J. HUDSON. Pp. 55-57.

No. 9. The Determination of Star Positions by means of a wide-angle Camera; by FRANK SCHLESINGER and CHARLES J. HUDSON. Pp. 59-75.

No. 10. The Orbit of 18 Aquilæ; by FRANK C. JORDAN. Pp. 77-82.

4. Publications of the United States Naval Observatory, Capt. J. L. JAYNE, U. S. N., Superintendent. Second series. Volume VIII has the following title : Vertical Circle Observations made with the five-inch Alt-Azimuth Instrument, 1898–1907; by F. B. LITTELL, G. A. HILL and H. B. EVANS; reduced by F. B. LITTELL, Pp. xxxvii, 463; 3 pls. Washington, 1914. 5. Leander McCormick Observatory of the University of

5. Leander McCormick Observatory of the University of Virginia, S. A. MITCHELL, Director. The following publications (reprinted from the Astrophysical Journal) have recently been separately issued: Vol. II, part 2: Wave-Lengths of the Chromosphere from Spectra obtained at the 1905 Eclipse; by S. A. MITCHELL. Part 3. The Depth of the Reversing Layer; by S. A. MITCHELL.

6. Carother's Private Astronomical Observatory, Houston, Texas.—Bulletin No. 2, recently issued, is as follows : Confirmation of the Solar Hypothesis for "The Central Law of the Weather."

7. Napier Tercentenary Celebration and Mathematical Colloquium.—A circular signed by C. G. Knott, General Secretary, announces that immediately following the Napier Celebration, a Mathematical Colloquium will be held at Edinburgh on July 24–27 (see vol. xxxvii, p. 288), under the auspices of the Edinburgh Mathematical Society. Lectures will be given on Nomography, by M. D'OCAGNE, of Paris; on Infinity in Geometry, by H. W. RICHMOND, of Cambridge; on Critical Studies of Modern Electric Theories, by E. CUNNINGHAM, of Cambridge; on The Solution of Algebraic and Transcendental Equations in the Mathematical Laboratory, by E. T. WHITTAKER, of Edinburgh.

The fee for the Colloquium is 15s. Those who desire to become members are requested to communicate as soon as possible with P. Comrie, 19 Craighouse Terrace, Edinburgh. A remittance of  $\pounds 1$  will cover ordinary membership of both the Napier Celebration and the Mathematical Colloquium.

8. Logarithmic Reduction Tables for Students of Analytical Chemistry; by CHARLES J. MOORE. Pp. 78. Boston & New York (Ginn & Co.).—The object of this little book is well stated in the preface, as follows: "The aim of the author has been to supply students of analytical chemistry with accurate tables, covering gravimetric, volumetric, and gas analysis, for which they have constant use. In order to meet the needs of the beginner, the method of using each table is fully explained. \*\* Six-place

# Miscellaneous Intelligence.

logarithms are used and a table of logarithms of numbers from 1 to 10,000 is included. \* \* The table of atomic weights contains the nearest known approximations of the exact values."

# V. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Report on the Progress and Condition of the United States National Museum for the Year ending June 30, 1913; by RICHARD RATHBUN, Assistant Secretary of the Smithsonian Institution in charge of the National Museum. Pp. 201. Washington, 1914.—The National Museum in its present development is remarkable at once for its great extent, the completeness of its collections in the different departments, the admirable nature of its installations and the large amount of original scientific work which it sends out. Hence this annual report by Dr. Rathbun is most interesting in the details given with regard to the Museum as a whole and in its several activities.

Of the numerous publications from the Smithsonian Institution which have appeared recently, the following must be specifically noted:

BULLETINS of the National Museum. No. 50. The Birds of North and Middle America; by ROBERT RIDGWAY. Part VI. Pp. xx, 882; 36 pls.

No. 84. A Contribution to the Study of Ophiurans of the United States National Museum; by RENÉ KŒHLER. Pp. vii, 173; 18 pls.

Classified List of Smithsonian Publications available for distribution, April 25, 1914 (Publication 2268). Pp. vi, 32.

Bureau of American Ethnology. Bulletin 56. Ethnozoology of the Tewa Indians; by JUNIUS HENDERSON and JOHN P. HAR-RINGTON. Pp. x, 76.

2. United States Coast and Geodetic Survey; O. H. TITTMANN, Superintendent.—The following are recent publications:

Hypsometry. Fourth general adjustment of the precise Level Net in the United States and the resulting Standard Elevations; by WILLIAM BOWIE and H. G. AVERS. Special Publication No. 18. Pp. 328; 5 illustrations.

Terrestrial Magnetism. Results of Magnetic Observations made by the Survey between July 1, 1911, and December 31, 1912; by R. L. FARIS. Special Publication No. 15. Pp. 102.

Results of Observations made at the Magnetic Observatory at Sitka, Alaska, 1911 and 1912; by DANIEL L. HAZARD. Pp. 100; 17 figs.

3. Publications of the Carnegie Institution of Washington.— The following publications of the Carnegie Institution have been recently received (see vol. xxxvii, p. 362):

No. 90—B. Department of Historical Research, J. FRANKLIN JAMESON, Editor. Guide to the Materials in London Archives for the History of the United States since 1783; by CHARLES P. PAULLIN and FREDERIC L. PAXSON. Pp. xi, 642.

No. 182. Department of Marine Biology, ALFRED G. MAYER, Director. Papers from the Tortugas Laboratory. Vol. V, pp. iii, 222, including eleven memoirs with numerous illustrations.

No. 191. A reconstruction of the nuclear Masses in the lower portion of the Human Brain-Stem; by LEWIS H. WEED. Pp. 76; 6 pls.

No. 192. The Climatic Factor as illustrated in arid America; by Ellsworth Huntington; with Contributions by Charles Schuchert, Andrew E. Douglass, and Charles J. Kullmer. Pp. vi, 34; 12 pls., 2 maps, 90 text figs.

No. 194. The daily march of Transportation in a Desert Perennial; by EDITH B. SHREEVE. Pp. 64; 27 figs.

No. 196. Size Inheritance in Rabbits; by E. C. MACDOWELL, with a prefatory note and appendix; by W. E. CASTLE. Pp. 55; 19 tables. (Laboratory of Genetics, Bussey Institution, Forest Hills, Mass.)

No. 200. Reports upon the present condition and future needs of the Science of Anthropology; presented by W. H. R. RIVERS, A. E. JENKS, and S. G. MORLEY, at the request of The Carnegie Institution of Washington. Pp. 91; 11 pls.

4. Annual Report of the Board of Scientific Advice for India for the year 1912-13. Pp. 190. Calcutta, 1914.—This volume, like its predecessors, gives a digest in very concise form of the scientific work accomplished for the Indian Government by members of the Board-some twelve in number-with their associates. The entire range of science, both general and economic, is included, so that the information here briefly summarized is of very varied character and of much interest. The chapter on Geodesy, by the superintendent of the Trigonometrical Survey, Lieut.-Col. G. P. Lenox-Conyngham, is particularly interesting, and some of the conclusions from the measurements of gravity by pendulum observations during the year are quoted here. These determinations were made at fourteen stations along a line extending from Bhopal to Khurja, near Bulandshahr, including Kalianpur, the station of origin of the Indian triangulation. This completes a chain of stations along the meridian of 78° from Mussoorie (Lat 30° 28') to Amraoti (Lat. 20° 56'), a distance of about 650 miles. The results stated briefly are as follows :

"From Mussoorie to Gesupur (Lat.  $28^{\circ} 33'$ ) the defects of gravity decrease rapidly from '11 to '02 dynes. Between Gesupur and Khurja we find a rise to '04 and from thence to Agra the negative residuals again decrease, becoming positive at the latter station. Between Agra and Bina we find two belts of deficient gravity or "valleys" separated by a positive area or "ridge." From Bina to Amraoti we have a succession of positive values with only two small negatives at Bhopal ('004) and Shahpur, latitude  $22^{\circ} 12'$  ('005.)

"The existence of this area of excessive gravity, often called the hidden chain, was deduced by Colonel Burrard in 1901 from the evidence of the deflections of the plumb line. The pendulum has verified it, and this year the northern edge has been located between Kalianpur and Goona. This fact lends strong probability to the assumption that the deflection of the plumb line at Kalianpur is southerly.

"It is interesting also to note that the positive areas at Sipri and Agra and the sudden change between Khurja and Gesupur are indicated by the plumb line deflections in these localities. This seems to show that the variations of density which produce these abnormalities are situated near the surface."

5. The American Philosophical Society.—The general meeting of the American Philosophical Society, held in Philadelphia on April 23 to 25, was one of the most successful in its history The list of papers presented included nearly fifty titles, and in addition an evening lecture was given by Dr. A. L. Day of the Geophysical Laboratory upon "Some Observations of the Volcano Kilauea in Action." The following is a list of new members elected : Charles G. Abbot, Washington; James W. Bright, Baltimore; Bradley M. Davis, Philadelphia; Thomas McCrae, Philadelphia; William D. Matthew, New York; Alfred G. Mayer, Washington; Samuel J. Meltzer, New York; John C. Merriam, Berkeley, Cal.; Robert A. Millikan, Chicago; William A. Noyes, Urbana, Ill.; Stewart Paton, Princeton; Richard M. Pearce, Jr., Philadelphia; Palmer C. Ricketts, Troy; Harold A. Wilson, Houston; Fred. E. Wright, Washington.

The following foreign members were also elected :

Shibasaburo Kitasato, Tokyo ; Heike Kamerlingh Onnes, Leyden ; Vito Volterra, Rome.

6. The San Francisco Meeting of the American Association for the Advancement of Science.—The American Association for the Advancement of Science has decided to hold a general meeting in San Francisco and vicinity on the occasion of the Panama-Pacific International Exposition, in 1915, and has appointed a Pacific Coast Committee of thirty-two members to make the necessary arrangements. This Committee has recommended, and the American Association has approved, that the sessions of the meeting shall begin on Monday, August 2d, and terminate on Saturday, August 7th. The general sessions and the general evening lectures will be held in San Francisco. Sessions for the presentation of addresses and papers will be held chiefly at the University of California, Berkeley, but on one day at Stanford University.

The Pacific Coast Committee hopes that the 1915 meeting of the American Association, at a point so far removed from the usual meeting places of the general and special scientific societies of America and from the homes of their members, may be remarkable for the number of members of these societies in attendance and for the wide interest and high standard of the addresses and papers presented. Address correspondence to Albert L. Barrows, Associate Secretary, University of California Library, Berkeley, California.

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 223.—July, 1914. 8

# Scientific Intelligence.

7. British Association for the Advancement of Science.—The next meeting of the British Association will be held in Australia during the month of August. The presidential addresses will be divided between Melbourne and Sydney and the sectional addresses between these cities and also Adelaide and Brisbane. The members going from England are expected to number about 400; numerous interesting excursions have been planned.

8. A Theory of Interest ; by CLARENCE GILBERT HOAG, A.M. New York, 1914 (The Macmillan Co.).—This book is an attempt at an original solution of the problem of interest. In many ways the method of approach is new and striking. It is doubtful, however, if the presentation offered brings us any nearer to a final solution of the problem than we were before.

Perhaps the most characteristic feature of the book is the way of defining "principal." The principal of a loan is commonly supposed to be an equal amount lent at one time and repaid at another. The interest is an addition to the principal and is reckoned as a per centage of it. This equality of the principal is defined by the author of A Theory of Interest as equality of "nominal value." The thought is, that the present sum and the future sum (minus interest) are equal, not from the viewpoint of the present, for they are not, the future principal being subject to discount in present valuation; but that the equality is equality to a changing market. The future sum has as high a value to its time as the present sum has now. It is as satisfactory, however, and perhaps clearer to the average man, to think of the principal as a fixed number of money units, e.g., dollars, which are assumed to remain constant in general purchasing power during the period of the loan.

In the working out of his theory the author introduces interesting geometrical diagrams and algebraic formulæ, but the theory set forth is essentially that of Fisher, less fully elaborated. In particular, the discussion of the influence of productivity on the rate of interest goes no further than to repeat in other words Fetter's and Fisher's criticisms of Böhm-Bawerk.

Considered as a restatement, in original form, of a theory of interest held by not a few economists, the book has much to commend it. But it cannot be regarded as offering a theory which is new in anything but phraseology. H. G. BROWN.

9. Franklin Institute award of the Elliott Cresson Medals.— Under date of May 20, 1914, the Secretary of the Franklin Institute announces that acting through its Committee on Science and the Arts, it has awarded its Elliott Cresson Gold Medal, the highest award in the gift of the Institute, to the following gentlemen : Prof. Edgar F. Smith, Dr. Orville Wright, Prof. Dr. Josef Maria Eder, Prof. Dr. Karl Ritter von Linde.

10. The Science Reports of the Tohoku Imperial University, Sendai, Japan. Second Series (Geology).—Nos. 4 and 5 of the first volume, recently issued, contains the following interesting papers : Mezozoische Pflanzen von Omoto von H. Yabe.

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# Obituary.

On a Staurolite-garnet-mica-schist from Lian-tung ; by M. Oyu. Ein neuer Ammonitenfund aus der Trigonia sandstein-Gruppe von Provinz Tosa ; von H. Yabe.

Riebeckite-bearing Soretite-trachyandesite and its allied glassy variety (Monchiquite) from Kozaki, Prov. Bungo, Japan; by S. Kôzu. On some occurrences of audalusite in the environs of Hitachi mines; by M. Oyu.

# OBITUARY.

EDUARD SUESS, dean of modern geology and geologists, passed away on April 26, 1914, in the fullness of his eighty-three years, revered by all students of his chosen earth science and loved by all who came under the influence of his warm personality.

The son of a German merchant of Jewish extraction, Suess was born in London on August 20, 1831. Here his parents resided until 1834, when they removed to Prague, and eleven years later to Vienna, where the youth was destined to rise to great eminence in the University, in the council of the city, and in the Austrian parliament. While in the Polytechnic School, it became apparent that his natural bent was wholly toward natural history studies, and at nineteen years of age he published his first paper, a short sketch of the geology of Carlsbad and its mineral waters. In 1851 he was appointed as assistant in the Geological Department of the Royal Natural History Museum at Vienna, where for the next eleven years he devoted himself to paleontology, and chiefly to brachiopods of the Paleozoic and Mesozoic eras.

At the age of twenty-six, Suess was appointed extraordinary professor and in 1867 full professor in the University of Vienna, and there he remained for forty-four years, a great and enthusiastic teacher, until his retirement at the age of seventy. Among his students may be mentioned Neumayr, Mojsisovics, Fuchs, Waagen, and Penck.

The greater part of Suess' long life was devoted to working out the evolution of the features of the earth's surface. The problem of mountain-building presented itself to his mind during his many excursions in the eastern Alps, and in 1875 he stated his views thereon in the small volume called *Die Entstehung der Alpen*. This work, according to Geikie, "contains the germ of those later contributions to science which have placed him on so conspicuous an eminence among the geologists of the day. . . To thoughtful students of the science this treatise, in his firm hold of detail combined with singularly vivid powers of generalisation, was full of suggestiveness. But the interest and importance of its subject did not obtain general recognition until it was followed ten years afterwards (1885) by the first volume of the great *Antitz der Erde*—the work which has chiefly given Suess his place among his contemporaries, and by which his name will be handed down to future time. In its striking arrangement of subjects, in its masterly grouping of details which, notwithstanding their almost bewildering multiplicity, are all linked with each other in leading to broad and impressive conclusions, and in the measured cadence of its finer passages, the *Antlitz* may be regarded as a noble philosophical poem in which the story of the continents and the oceans is told by a seer gifted with rare powers of insight into the past." CHARLES SCHUCHERT.

Dr. ALFRRD E. BARLOW of Montreal died on May 28, having perished with his wife in the wreck of the "Empress of Ireland." His death is a great loss to Canadian geology and mineralogy, to which he had made important contributions.

Dr. ALEXANDER FRANCIS CHAMBERLAIN, professor of anthropology in Clark University, died on April 8 at the age of fortynine years.

Professor JESSE J. MYERS, of the Michigan Agricultural College, died on May 28 at the age of thirty-eight years.

Dr. P. H. PYE-SMITH, F.R.S., late Vice-chancellor of the University of London and a consulting physician of Guy's Hospital, died on May 23 in his seventy-fifth year.

Sir JOSEPH WILSON SWAN, the emiment English electrician and investigator, died on May 27 in his eighty-sixth year.

M. PHILIPPE E. L. VAN TIEGHEM, the eminent French botanist, died on April 28 at the age of seventy-five years.

Dr. KARL CHUN, professor of biology at the University of Leipzig, has died at the age of sixty-two years.

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# ART. VIII.—A Study of Some American Fossil Cycads.\* Part VII.—Further Notes on Disk Structure; by G. R. WIELAND.

A FOREWORD to the present addition to the series of pre-liminary notices on the Cycadeoideæ, which from time to time have been brought out in this Journal, is on the one hand quite as necessary as it is on the other inherently difficult to give. Not since these investigations were begun have any structures been found so baffling to reasonable interpretation as those now brought to light. It is, in the writer's judgment, not enough to simply ascribe these peculiar features of the staminate disk as an isolated instance of adaptation. They have to do with bud structures, with reduction from more megaphyllous forms, with prefoliation as well as prefloration, and consequently lay an emphasis upon the fact that it is at last necessary to hypothesize great strobilar variety of form and sexuality in that distant period when the early land plants by means of simple stems and by megaphylly raised their crowns above the soil to make the world's first forests. No difference what interpretation we give these flower buds, exteriorly so like various of the so-called Neuropteris seeds, they constitute evidence that fusion and emplacement of sporophylls coupled with reduction were notable factors in gymnosperm evolution and thus point to an initial hypothesis for the origin of the complex seed coats of early Paleozoic time which no mor-

\* Parts I-III of these studies of American fossil cycads appeared serially in this Journal for March-May, 1899, Part IV in June, 1901. Part V in August, 1911, and Part VI in February, 1912. See also December, 1904— The Proembryo of the Bennettiteæ; February, 1908—Historic Fossil Cycads; December, 1911—On the Williamsonian Tribe; September, 1913—The Liassic Flora of the Mixteca Alta of Mexico, its Composition, Age, and Source.

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phologist bent on making the fullest use of the paleontologic record can afford to ignore. They do suggest a means of simplifying our conception of the evolution of the early land forests; and they do go far to show how a great variety of floral structures could have been rapidly developed in late Silurian and earlier Devonian land plants, a variety permitting development of later types of plants by a frontal or abreast course of development along more or less parallel lines. And certainly such a conception of the main course of plant evolution is more consonant with general facts of distribution and theories of climatic change than is any view of descent by a series of dichotomies.

There is, in short, a broad suggestion of parallelism and periodicity in plant evolution. It has hitherto been difficult to reconcile the meager record of Silurian plants with the sudden appearance of varied Devonian types well advanced and so persistently lacking in forerunners. But this paucity of record is more easily accounted for if the direct evolution of new structures be held to have reached a climax in the first rapid covering of the land by homosporous types. From the leafy crowns of these earliest of all forest forms must in time have been derived the early heterosporous types, and from these in turn by continued sterilization emplacements, fusions, reduction and branching, a profusion of early seeds and the flowers. Such would be, hypothetically speaking, the line of least resistance in early plant evolution. We know that evolution of the early land plants may well have been rapid just as many phyla of invertebrates develop diversity of form early in their history, and just as in recent geologic time where islands have been freshly populated plant forms elsewhere herbaceous quickly develop variety of species and tree-like stature.

That ancient seeds then have such a leafy structure appears to find the simplest explanation in the fact that a seed is as much a branch or derivation of a crown of fertile fronds as flowers have been conceived to be. And the striking character of the staminate disk of *Cycadeoidea* raises the question whether in the sporophyll fusions and reductions resulting in seed coats, whorls of sterilized microsporophylls, or of bracts, may not in some forms be merged as seed coat components, it being clearer now than ever that no one course of evolution can account for all the varied types of seed integuments. In some such manner the double nature of the integument in those forms where there is a series of inner testal bundles separated from an outer by the middle stone might be accounted for.

Finally, it is clear that if seed and flower have this dual homology and were thus successively derived from primitive

# G. R. Wieland-Cycadeoidean Flower-bud Structure. 119

homosporous crowns by one and the same general process of sterilization, fusion of leaves, and reduction, the relation of gymnospermous cones to angiospermous flowers will be found a much closer one than has hitherto been conceived possible. Especially too will it be seen that *Cycas* is in reality specialized and very closely apposed to other cycads when it is observed that instead of producing numerous compound branches or cones the seeds are simply distributed laterally along flat blades instead of spirally along cylindrical strobilar axes. Any known form which could qualify as an Angiosperm ancestor must therefore combine some of the characters of *Cycas* with those of *Cycadeoidea*, and this in a remote sense the Gnetaleans do.

As every one knows who has examined at all attentively the Yale, State University of Iowa, or National Museum collections of Cycadeoideans, or the long series of silicified trunks which from first to last has been obtained from Italy and from the Isle of Portland, the number of fruits of larger size preserved in entirety is very small. The tendency is for the fruits to be broken away; entirely where the peduncles were of some length, or partly where the fruit, though borne on a shorter peduncle, reaches any considerable size. Moreover, on studying those lesser fruits which appear to be quite wholly enveloped by ramentum, a considerable number prove to be very young; others, a very large number, are found to be young ovulate cones; while a far from inconsiderable number of the axes are found to contain cavities lined irregularly by quartz druses, or to have their tissues broken down. Again, there is much difficulty of fruit study in the case of many important trunks, due to that natural dislike that an investigator must have, to a certain extent, of injuring a great specimen by cutting away one or two fruits instead of studying it systematically after sawing through it longitudinally and obtaining the segments most favorable for completer studyan operation requiring time and resources. Also, the number of conserved disks being at best but small in proportion to the ovulate cones, knowledge of the staminate disk variations in form and structure has accumulated relatively slow.

It thus transpired that, as related in Part VI of these studies, the very reduced size of some of the flower buds of relatively large trunks long remained a rather hidden character notwithstanding the fact that small and young fruits were amongst the first of the subjects considered important and to which much attention was given; though inasmuch as the general characters of the trunks indicate marked specific variety, it has not been at any time a source of surprise to find considerable variation in the size of the disks and the number of microsporophylls composing them.

In the flower type here to be considered, however, there is an added interest not only because of the large amount of reduction in the fertile segments both ovulate and microsporangiate, but especially because of the great relative bulk of the microsporophylls and their very peculiar form. This is, moreover, of importance in enabling us to criticize previous restorations where the apical region of the flowers is less complete. Not only so, but the restorations given herewith are suggestive of certain larger hypotheses as to the true nature of both ovulate and microsporangiate floral structure of undeniable significance which it will be of much interest to briefly take up following the present preliminary descriptions.

While preparing material for my volume on the structure of the fossil Cycads (Carnegie Institution Publication 34) I noted as a specimen of especial interest an upper portion of a trunk of the Yale Collection numbered 549+550. A half dozen or more medium-sized flower buds enveloped by large bract groups, and the distinctly rhombic-shaped leaf scars of lesser to small size, were the particular features which arrested attention. In general, the characters suggested C. dacotensis. to which species Professor Ward had indeed referred both these trunk fragments which I later found to fit together as a single large more or less apical segment of a trunk or perhaps branch. But the lesser variations from C. dacotensis as usually seen led me to cut a section from one of the flowers, which although it proved to be indifferently conserved, indicated the structureless outlines or casts to be new and distinct. It was noted that the microsporophylls were very heavy and thick in the upper part of the flower; but as the single section cut so lacked finer structural detail, little could be said about the floral features; while on examining several other of the axes, exteriorly more promising, little further was learned of the structures present. As is often the case in the fossil cycads, petrifaction had resulted in the replacement of the original tissue by silica in much too granular to quartzose a condition for the clear preservation of histologic details. The further study of this specimen was therefore deferred, and attention was not again directed to it until much later, when the sections shown in figures 1 and 4 were cut from an isolated flower bud I had collected at Minnekahta in the Fall of 1902. This flower bud has a complete summit and at once recalled the trunk apex and section just mentioned. For so nearly alike are the general features, and the type of conservation, that it is not impossible that the isolated fruit really pertained to the two larger trunk fragments, and escaped attention when they were

collected some two years earlier at the same locality. My own search for new material was, of course, carried out with far more care than that of the earlier collectors, who quite without exception had mainly sought huge or otherwise striking specimens.

### Specific position of specimens.

For trunk and floral characters of the type before me, we may then use both the earlier trunk fragment and the isolated specimen in full confidence that both are of precisely the same species. Furthermore, both may be provisionally referred to the same species as the great type *Cycadeoidea colossalis* of the U.S. National Museum. In the original descriptions of this specimen no very clear distinction from the prototype of the Minnekahta series of species, Cycadeoidea dacotensis, is definitely pointed out. But a close reading of the measurements shows that the leaf bases are very small, and the floral axes of only medium size. In C. dacotensis the lateral and vertical diagonals through the leaf bases measure from 16 to  $26^{\text{mm}}$  and 10 to  $16^{\text{mm}}$  respectively as compared with 13 to  $16^{\text{mm}}$ and 8 to 12<sup>mm</sup> in the C. colossalis. This is a really great and striking difference, when it is recalled that the largest of the trunks or branches definitely proven to belong to Cycadeoidea dacotensis weighs a scant hundred kilograms, whereas the great National Museum type exceeds 300 kilograms in weight, being one of the largest single stems, if not "the largest," in the world. The huge columnar trunk of the Yale Collection C. ingens, which yielded the first flower buds with disk features studied, has the greatest recorded weight, 303.91 kg.,\* and after it comes the famous Dresden trunk Cycadeoidea Reichenbachiana. The largest known single branch is the superb specimen shown in Plate V, fig. 1, of my American Fossil Cycads with a weight of 147 kg., and the greatest weight yet determined in a branching aggregate is 844 pounds, (382 kgs.) seen in the group figured in Plates XII and XIII of the American Fossil Cycads.

No further facts need be given to show that the type of *C. colossalis* has distinctive features, even in the absence of the closer knowledge of its actual woody cylinder and other of the more searching details of trunk structure so much to be desired. Nor do I now need to go on *seriatim* with other forms related to *C. colossalis* and show how they differ in first one, then another of the known features.

\*In the late Fall of the year 1898 I re-examined the exact spot where *C. ingens* was collected (cf. American Fossil Cycads, Plate XLIX, upper figure), finding a few additional fragments from the apex of the trunk increasing the weight of this great type to over 304 kilograms.

With respect to the floral structures of the type of *C. colos*salis, we are as yet largely in ignorance, but as noted there is some indication that these also will be found of essentially the type here described. Just as in the case of the Yale trunk fragment and the isolated fruit now considered, the flower buds are of slightly lesser size than in *C. dacotensis*, but have an enormous development of the bracts, the outer of which even closely approach in size the relatively small leaf bases. It is, therefore, with considerable confidence that future closer study may fully justify my provisional reference of these Yale Museum specimens to *Cycadeoidea colossalis*, that I now go on to the description of their very singular floral features.

# Description of Structure.

The preservation of structures as indicated by the sections so far cut from the above mentioned isolated bisporangiate

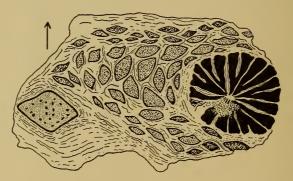


FIGURE 1. Cycadeoidea colossalis.—Trial transverse section through isolated bisporangiate flower bud, surrounded by a thick husk of heavy hairy bracts and retaining still attached a single one of the leaf bases from between which the fruits emerge.

The section passes above the central ovulate cone, and cuts the sterile prolongations of the ten rachides into which the staminate disk divides. This figure is copied directly from an enlarged photograph and here reduced to about natural size.

axis is very uneven, but yields the details affording the restoration given in figures 2–7. An attached leaf base, however, very fortunately shows remarkably fine preservation of structure, some of the bundles clearly showing all details and possessing more development of enveloping sclerenchyma than has been seen in any other American specimen. Also an occasional bract is well conserved, and the appearance of the material from which supplementary sections remain to be cut,

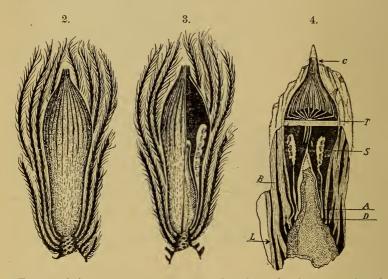
#### FIG. 1.

indicates that considerable further structural details may yet be observed, and thus later permit accurate specific determination. For the present, however, that which mainly concerns us is the plan of the flower and its outer form, both being clearly exhibited and quite accurately determined.

The first or trial section cut from the isolated bud was that drawn in figure 1. It clearly shows the characteristic small size and lozenge-shaped transverse section of the nearest adjacent leaf base well crowded to the side by the series of relatively very large bracts. The outer bracts appear the larger because cut at a much higher level than those next the essential organs, the bracts being slender near their insertion and increasing in size toward and beyond their mid-length. 'As they are still large where truncated by the eroded outer surface of the fossil, about a centimeter above the level of the trial section, the actual terminations as in most fair-sized fruits cannot be observed. It is nevertheless clear enough that the bracts were long and heavy, and formed a dense protecting husk projecting well above the extreme apex of the flower proper. At the center of the bract series, as one notes in figure 1, only the disk features may be seen since the section is cut well above the apex of the ovulate cone, and also passes above the highest of the synangia. All the tissues cut at this level, which was intended to and actually does traverse the broadest part of the flower bud, are therefore rachidal. And furthermore, as one attentively studies the section it is plainly seen that the closely appressed and transversely cut rachides have the appearance of a series of heavy V's with their sides close together and their vertices outlining a very small circle or point near the center of the flower, except that in several instances the arms of the V's barely touch at the center, while in one case the V section of a rachis is seen to unite near the inner or vertical point with the arm of the adjoining rachis, the other arm of which is thus left entirely free. But at the center be it noted that there is not the least trace of the decurved tips of fronds clearly observable in the longitudinal and more basal transverse sections, so that there can be no mistaking the fact that this entire section shows only the development of the heavy Obviously enough, therefore, the series of sector-like rachides. rachidal sections pairing into, as one may readily count, ten V's with arms mostly joined but sometimes free, or again fused with an adjacent member, indicates one of two possibilities. Either the disk divides irregularly into outer or ventral winglike expansions of the rachides, the number of which would in this case be somewhat uncertain, or it divides at quite exactly the level of this section into ten distinct rachides, each of which is deeply incised by a median ventral furrow so as to

form normally twenty divisions at the summit of the flower. This latter is the true structure, as would indeed be fully confirmed without further sections, although there are some slight departures from entire symmetry of form.

The presence of outer median rachidal furrows had already been noted in the very different flower of *Cycadeoidea Marshiana* described in Part VI of these studies. This latter, however, is a much smaller species of flower than the form before us, and the microsporophyll surfaces are much more crinkled and rugose; while the apex was not found present. But a small median outer furrow is present in each rachis, as one readily sees on referring to Part VI of these studies (fig. 3A).



FIGURES 2-4. Cycadeoidea colossalis. Drawings showing external and structural features of the bisporangiate flower bud with enveloping bracts either removed or indicated diagrammatically. About natural size.

FIG. 2. Exterior view of bud in part diagrammatic and drawn in approximate proportions, the base being somewhat narrow. Note resemblance to so-called *Neuropteris* seeds in both form and surface grooving.
FIG. 3. Same as preceding with one quarter of fruit bud cut away to

FIG. 3. Same as preceding with one quarter of fruit bud cut away to bring to view central ovulate cone.

FIG. 4. Drawing of longitudinal section through flower-bud dome (C) extending up to plane (T) of trial section (fig. 1) and surmounted by dome-shaped apex of disk (C) which is shown in full relief, just as it appears after splitting away a portion of the bract husk.

C, dome formed by extension of paired and closely appressed rachidal appendages; T. plane of trial section (fig. 1); S. synangia; A. decurved tip of staminate frond extending just to base of the ovulate zone of the central seed cone, which is shown relatively large, being very young and small; D, disk insertion; B, L, onter bracts next to leaf base.

Failing the deep incision now observed, the full significance of that small notch was by no means at first appreciated, though it could not escape observation when the drawings were made. As reference to the figures shows, the groove was only seen near its lower and shallower end at a height of a full centimeter or more above the central cone. But fortunately, all the upper portion of the bud before us is present, save a very small slender tip, and the bracts are so broken away on one side as to disclose the entire outline of the bract-enveloped disk apex, which as the drawing (fig. 4) shows rises in the form of an absolutely symmetrical spired dome.

With the trial section just described completed, it was possible to locate and cut to the best possible advantage the supplementary longitudinal section. This as drawn in figure 4 in conjunction with the view of the dome-shaped summit yields nearly all further larger details of the floral structure and plan. It brings to view the very heavy bracts, somewhat irregularly appressed in position, the large peduncle and ovulate cone of inverted pear-shape with a very minute and limited seed zone, the exact thickness of the disk and its insertion, the decurved microsporophyll tips, and finally the rather limited fertile or synangia-bearing space, with the immense expansion of the sterile rachidal region just at the base of the terminal dome. Special features are the relative narrowness of the seed zone. to the basal portion of which the microsporophyll tips exactly reach as a complete enclosing curtain, and the high position of the synangial region above the fertile zone of the seed. This latter feature is partly paralleled in C. Marshiana, but quite different from the condition seen in C. dacotensis, where the synangia grow far down in the campanula toward the base of the ovulate strobilus.

### Comparison with other Cycadeoidea Flower Buds.

This is indeed a flower of singular aspect. And it is safe to say that the prolongation of its sterile spinose pairs of median rachidal wings into a dome-like expansion, not only taking up all the space between the outer husk of bracts but carrying them up as a high summit, would never have been suspected without actual observation. The long bush of terminal sterile scales visible in nearly all ovulate cones not having the short cushion easily led to the belief that the ovulate cone formed a summit above the always decurved microsporophylls and thus took up any unfilled space between the fertile organs and the bracts rather than that any open tent-shaped space was left between these organs and the floral envelope of hairy bracts. The casts of *Williamsonia gigas* figured by Williamson seemed to lend further support to such explanation of the outer form, which it may well prove is partly or wholly correct in the case of some species. However this may be, it is only the actual evidence to which one may turn, and it is always best in any study of fossils rightly carried out to exactly state to what extent supposedly correct interpretations of structures are brought under suspicion by newly found or better understood features. It is, therefore, well to add that in the case of Cycadeoidea ingens nearly the entire flower is present, and that in my original descriptions I noted the radial structure that appeared very vaguely at the summit, and rather happily termed the fruit a "capsular male fructification." But it was then thought that as the summit was quite small only a few millimeters could have been eroded away, which if true would leave the restoration essentially correct as given. But now it seems probable that a small dome was present; though it is not to be overlooked that this may have been rounded, not *spired*, in which case the restorations first given are essentially correct.

The case of *Cycadeoidea dacotensis* is more doubtful. It might have had a greater or a smaller dome than the hypothetical one of *C. ingens*, or none. The huge rounded and wholly bract-covered fruits of the original type in the State University of Iowa collection must be ovulate cones from which the staminate disks have been shed. Those with disks end roughly and are thus partly eroded at the summit. It is clear at least that if, as first supposed, the ovulate cone is much elongated no dome can be present. Speaking from the viewpoint of symmetry both structures would not be found together. So far the apical region of a well-preserved flower of *Cycadeoidea dacotensis* has never been seen; but now that the subject has assumed such a tangible interest the actual dome structure will be searched out and studied.

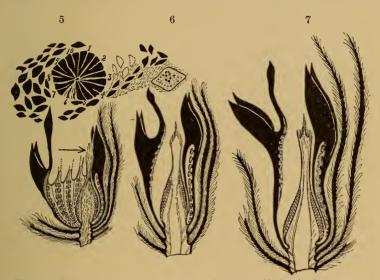
In C. Marshiana, as described in Part VI, the flower is very small, and so far the disk apices have not been noted. The figures given show structure only and are all absolutely correct in all details, so that any one may judge for himself as to whether there was development of a dome. It seems to me quite certain that there was a distinct dome to that flower.

### Expansion of Flower and Mode of Fertilization.

What a flower with such strange appendages may have looked like in the different species when mature is easier fancied than accurately drawn; and for this reason I have given in figs. 5–7 several restorations in imagined expanded positions. But it is readily seen that, having a form so doubly unique for a gymnosperm, it was much easier for the disk to dehisce out

of its close packing of bracts than to actually expand at the time of maturity, unless indeed there was an immense later growth as yet little suspected.

Had both pollen and ovules reached maturity before the splitting away of the disk, the arrangement would have facilitated close fertilization to an extraordinary degree, provided



FIGURES 5-7. Cycadeoidea colossalis. Series of distinctly diagrammatic restorations of fruit shown in the preceding drawings, given for the purpose of further bringing to view the flower bud structure as it might appear were such a flower freely expanded.

In figure 5 a generalized sketch of the trial section is introduced to show the ten V-shaped transverse sections of rachides as cut at base of the terminal dome, the level of this section being indicated by the arrow near summit of flower arbitrarily shown in expanded form with front half cut away. Figs. 6 and 7 are merely repetitions of fig. 5. In all three figures the seed zone and synangial region are represented much above the proportionate size, while the peduncle appears relatively small, the object being merely to bring sharply into view special features rather than to give a final restoration. With regard to improbability of expansion of the dome-forming disk see text.

only that there were free-swimming antherozoids. For otherwise the manner in which the decurved tips of the staminate fronds lie appressed to the outer surface of the ovulate zone and thus shut off the synangial region from it would have tended to prevent direct pollination. Neither of these conditions, as already explained in earlier papers, are probable, so far as the species are known, the very immature condition of the ovulate region as compared with synangial development making it probable that in most cases the shedding of pollen took place early and that cross fertilization was the rule, aided very likely by motile antherozoids. The pollen may even have undergone growth and development after shedding. This, at any rate, is the view I earlier proposed and still hold. Since then Lignier has suggested the possibility of parthenogenesis in *Cycadeoidea*. However, this ingenious hypothesis is quite entirely lacking in direct evidence.

## General Discussion.

There yet remain several highly interesting general considerations as to the actual significance of the mid-ventral appendages that form the remarkable dome of the flower before us. In the first place it is, of course, most difficult to say whether this structure is, first and last, simply a result of growth response due to the appressed position of the flower, and thus comparable to those thousand and one modifications seen in Angiospermous flowers, or whether it has antiquity or otherwise indicates inherent variety of form. For my part, I think the form is an adaptation filling spatial and purely mechanical requirements in a bizarre side line of the cycads, which I have never regarded as quite representative of the race to which it belongs. Not only so, but in all the Williamsonia flowers in which staminate organs have been found, and such have now been studied by Nathorst, Hamshaw-Thomas, and myself, there is no evidence of auriculate or extraordinarily furrowed rachides.

But in the first place, whether the condition here described is primitive or not, the vista of modification in Cycadeoidean and Williamsonian sporophylls is much enlarged. And once more, the *Cycadeoideas* are seen to present analogous characters to the existing cycads. For in what ultimate respect do these auriculate and horn-like appendages differ from the pair of horns present alike in the *Ceratozamia* mega- and microsporophyll? However one may view this point, it is clearer than ever that not even on the basis of the sporophylls can we separate these two groups from each other.

Secondly, a consideration of far-reaching and fundamental importance comes into view if the grooved and winged character of these microsporophylls is in reality primitive, or even in case approximately such a condition could primitively arise. For in either case, stamens being primarily homologous to the megasporophylls, some light, even if we take a purely mechanical view-point, must eventually be shed on the relation between the micro- and megaspore-bearing structures in the primitive gymnosperm races, if not, indeed, on that very central paleobotanic problem the origin of the seed coats.

With exactly this possibility in view, I have in describing the apical region of the flower as a dome, which it in reality is, had in mind the further thought of analogy to the "canopy" of the seeds of the Paleozoic cycadofilicaleans. Moreover, if one but considers the sterile tips of these fronds in a semiexpanded position they would, if considered as meeting and fusing edge to edge, correspond to the lagenostome of old gymnosperm seeds. This in Lagenostoma, where its most typical form is seen, comes to the surface, rising as high as the elements of the canopy. Continuing, therefore, the analogy already suggested by the use of the terms 'dome' and 'canopy,' for the outer apex of flower and seed, the staminate frond tips taken collectively would be correctly named the cycadostome. If any true homology should ever be established between these structures these terms might still be used, no better nomenclature suggesting itself, the important point being that sterilized megasporophylls enclosing a megaspore may also be conceived to take the same outer form as the staminate disk.

For the present, suffice it to say then, the comparisons invited by these striking features are highly suggestive. Any solution or hypothesis of seed origin is of the most excessive difficulty because seeds with the highly developed coats are already present in the Devonian. In fact, the lack of fossil forms giving any definite hint of the mode of seed coat origin beyond the assuredly significant fact that the oldest seeds are the most complex has seemed to make seed coat origins doubly difficult of explanation. And yet the enormous structural gap between the oldest pteridophytes and the earliest gymnosperms has not deterred investigators from suggesting that seed and pollen-bearing organs are, broadly speaking, mega- and microsynangial structures. With a somewhat different possibility in mind, I have already pointed out the fact that the seeds of Neuropteris are of the most leafy type known, and appear to be in some way related to the microspore-bearing disk Codonotheca, one of the most fundamentally important ancient fruits ever discovered, and one which should be familiar to every paleobotanist. It must be significant that the pollen of *Codonotheca* is the largest known, but the general fact that ancient pollen is large and shows evidence of prothallial structure was long since sufficiently proven by Renault and also illustrated by Brongniart.

Is it not, then, fully significant that as we go back into the remoter Paleozoic, seed structures are leafy and have highly developed vascular bundles while likewise pollen is of relatively enormous size? Does not such fossil evidence as is afforded by the seed-like exterior of *Codonotheca* with the large size of

its (?) microspores go to show that with continued sterilization of a megaspore-bearing crown of whorled, equitant, opposite or circularly emplaced sporophylls finally reduced to bract-like form, these might unite to enclose a single spore, the nucellus, and thus surround and fuse with it as a ribbed, bundle-supplied, apically chambered, protecting wall? This indeed is the analogy which must best explain the seed and show why ancient seeds are the more complex, are leafy, and have their major and secondary ribs, their canopy and lagenostome. The seed is, in short, as much a branch, or better a compacted and sterilized crown of sporophylls as a simply staminate flower; while a seed and its stamens is thus primarily analogous to a bisporangiate strobiloid crown, and either taken alone, to a simple monosporangiate crown. Just as the strobilus and the flower are the homologues of primitive crowns of simple, spore-bearing leaves, so it seems that the seed is the first resultant of a process of reduction from an apical group of fertile fronds,—a dyad in case of platyspermic forms; a triad, quatrad or pentad of such fronds in the case of more complex seeds like those of the *Conostoma* group.

To further illustrate the explanation of the seed canopy and lagenostome here given I may best briefly refer to a fine new type of seed from the Calciferous sandstone series of the Lower Carboniferous rocks of Pettycur, Fifeshire, Scotland, very recently described by Miss Benson.\* This seed is about four millimeters in length and enclosed by a cupule. Eight bundles traverse the tissues of the cupule and the same number the inner flesh. That is to say, the seed wall may be conceived to arise from fusion of two alternant whorls of eight members each. But easily the most striking feature of this seed is its finely developed apical frill and its wholly reduced lagenostome, clearly brought to view in fig. 8; while in fig. 9 I have modified Miss Benson's figures slightly so as to emphasize the frill region. Also the dotted line (L) outlines the hypothetical position of the lagenostome of this same seed in its more primitive condition before marked reduction had set in. And it will at once be noted that the general form and relation of parts thus had is essentially that seen in *Physos*toma elegans, which I am thus bound to consider a simple and primitive, but at the same time much reduced type of seed, in one sense much, rather than little, specialized as hitherto held. Indeed after studying original sections from my own collection this interpretation of the apical relations in *Physostoma* hardly seems to admit of any doubt. As observed

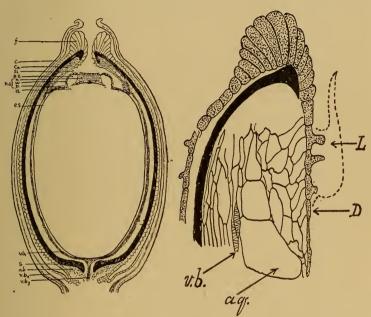
\* Sphærostoma ovale (Conostoma ovale et intermedium Williamson), a Lower Carboniferous Ovule from Pettycur, Fifeshire, Scotland; by Margaret J. Benson. Trans. Roy. Soc. of Edinburgh, vol. L, Part I (No. 1), pp. 15 and 2 pls. Jan., 1914.

by Oliver,\* the integument even rises free from the nucellus before dividing into the canopy and the thin lagenostome extension which as in Sphærostoma wholly lacks the specialization into the distinct regions so marked in Lagenostoma and Conostoma.

In order to give more precision to discussion and description of the complex testal forms of Paleozoic time, Oliver and

FIG. 8.

FIG. 9.



FIGURES 8, 9. Sphærostoma ovale Benson, a seed about four millimeters in length from the Lower Carboniferous of Scotland.

FIG. 8. Longitudinal section of seed and enclosing cupule. From Benson.

f,	frill
с.	cupu

- ca, canopy
- si, sinus
- pc, pollen chamber
- n, column
- w, lagenostome

- p, plinth a, archegonium
- es, embryo-sac
- vb1, integument bundle
- ab, abscission layer
- vb2, cupule bundle
- $vb_3$ , ovule bundle

Frill region of seed with hypothetical position (L) of lageno-FIG. 9. stome. Modified from Benson.

Sclerotic sheath in solid black; vb, extreme apex of one of the eight integumental bundles; aq, aqueous tissue; D, continuation of epidermal secretory cells.

\* Ann. Bot., vol. xxiii, No. lxxxix, Jan., 1909 (cf. p. 92, fig. 7).

Salisbury\* have introduced an elaborate and very usable terminology for the seed apices. But this should not mislead us into reading into these structures undue complexity of origin. For Oliver and Salisbury themselves in their paper on the Affinities of the Paleozoic seeds of the Conostoma group, just cited, explicitly describe a continuity of the tissues in the Lagenostome region: "\* \* Thus we see that the epidermal laver of the interior of the seed is in complete continuity throughout and that the various regions termed the micropylar tube, micropylar funnel, plinth jacket, plinth, and lagenostome walls are merely different and specialized portions of one and the same layer." The italics are mine and in my judgment this continuity does permit and does suggest as the most reasonable hypothesis the origin of the seed wall from eared fronds like the units which go to make up the Cycadeoidea disk, by a simple process of sterilization and reduction in the case of most Paleozoic seeds. Certainly it is possible that the Cycadeoidean or similar disks are very ancient structures, and that a theory of reduction from such disks as the result of sterilization and megaspore protection by reduced fronds, rests under less burden of demonstration than does any theory of seed coat origin which calls into requisition much direct evolution of new structures. Especially so when the particular structures from which such evolution could have proceeded are now seen to be but hypothetical at best.

Furthermore, reproduction being so completely dependent on nutritive processes primarily and on the use of protective coverings secondarily, it is certain that as megaspores increased in size, the simplest mode of protection would be inside a whorl of leaves at the center of a more or less scaly bud or crown. And alike in the Devonian as in the Mesozoic the development of apical domes would best overcome the spatial requirements due to circinate or conduplicate prefloration. At least this is the explanation that comes first to hand, it being clear enough that such an outer covering would at once enable the plant to greatly increase the size of its megaspores, protect them in an economical manner from insects, rain and wind, and then, following the assumption of microphylly with later cycles of branching and budding, greatly increase the number of fruits. So I conceive the seed habit was made possible and acquired by a process of reduction and sterilization with final enclosure of a giant apical spore after the forward course of evolution which first enabled plants to invade and cover the land and then raise their stems above the soil, had culminated.

\* Aun. Bot., vol. xxv, No. xcvii, Jan., 1911.

If indeed such a conception or theory of the seed has in it elements of truth, the characterization of a seed as a "megasynangium," which I would understand to carry with it the idea of a course of direct evolution, rather than the process of reduction just outlined, either fails to express the main fact or is wrong. Only the nucellus can theoretically correspond to the synangial structures. Moreover, if seed coat origins, like floral origins, have largely been processes of reduction which began in Silurian or early Devonian time, the gap between ferns, the evolution of which must conversely be regarded as a more distinctly ascendant process, and the primitive gymnosperms largely disappears.

\*

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It does seem then, that there is a certain analogy between a staminate flower and a seed of the older gymnospermous type, that indeed both have a common history as derivatives of homosporous crowns. But necessarily the conception of the course of change which had carried these reproductive structures far apart even in Devonian time can only be cleared by the discovery of fossil evidence. So vast and multitudinous must be the course of change involved that it appears nearly impossible to hypothesize given stages in floral and seed evolution, though certain factors of change do come into view. In the first place, it seems that up to a certain point the process was one of nearly universal forward evolution, after that one of reduction, or of sterilization, whichever one chooses to call it, coupled with branching or budding,-nature taking the course of least resistance, rather than accomplishing the end directly by the continual evolution of new structures. According to this new view the actual amount of structural evolution is far less than once seemed could possibly have sufficed. The stony layer of the cycad seed is simply the modified outer sclerenchyma of a series of component rachides, the "blow-off" layer of various forms, the persistent fern chaff or ramentum, and the Lagenostoma cupule, as I have earlier supposed, a bract component. The seed canopy is formed by the original crown of fronds, while the lagenostome even has to do with the prefloration of these. On such an hypothesis of structure the bundles and the ribs are likewise easily explained features, especially if fusion between two whorls be considered to have taken place where there is both an inner and outer flesh traversed by bundles.

It would then seem clear that the first great crest in the successive waves or pulsations in the evolution of plant, and especially of floral structures, was marked by what could be hypothesized as the *Eo-forest*, or primitive forest,—the first in AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXVIII, No. 224.—AUGUST, 1914.

which plants clothed the land and by megaphyllous and then simple stem-growth raised their structures above the moist soil into the air and sunlight. And it is there in that oldest forest that after the direct evolution of stem, vascular and leaf structures the primitive strobilar crown was organized and a point established where branching and sterilization could set in and thus inaugurate that vast course of aërial flower and seed growth evolution, which has gone on unceasingly since early Devonic time.\*

It is hypothesized, therefore, that as the earliest forest types gradually grew larger and finally reached the normal size of forest trees the segregation of the sporophylls in special axes became more and more pronounced. Thus arose the seed and the flower. But, as yet, it is most difficult to discern more closely modes of early floral origin. There is only much suggestion of "unequal rates" of evolution. For example, *Lyginodendron*, very ancient of type and still semi-procumbent, is characteristically gymnospermous in its seeds, but remains Marattia-like in its sporophylls in strong contrast to the much older *Cordaites*, so far as we know the first great forest type to achieve microsporophyll reduction.

But too few forms are as yet known to satisfactorily illustrate any hypothesis. Because of the difficulty of the study, progress is being made in large part by restudy and revision. At best it is a most difficult task to say the last word about the best conserved fossils, and except in the isolated "coal balls," the Paleozoic forms are doubly difficult of interpretation. Yet a fund of notable facts has been brought to light in the past

\*So far, nearly all the general outlines of ancient plant life have quite failed to take into account not only the great rôle played by early seaweeds, but the extreme antiquity of gymnospermous seeds and woods of high organization and cosmopolitan distribution. In consequence, after the extremely important position the early land plants and first forests are now seen to occupy in any larger scheme of plant evolution it is far from a mere digression to here modify the outline of plant development in geologic time long since given by Brongniart, as follows:

1	(Hypothetic)	$\left\{ \begin{array}{l} { m Oldest\ Precambrian} \end{array}  ight\}$
II	Reign of Algæ	∫ Precambrian } Cambrian
III	Reign of Early Land Plants	( Ordovician (?) ) Silurian
IV	Reign of Gymnosperms	Devonian
V	Reign of Acrogens	} Carboniferous } Permian
VI	Reign of Proangiosperms	(Triassic ) Jurassic
VII	Reign of Angiosperms	{ Cretaceous { Tertiary

ten years. The latest contribution on the Paleozoic Cycadofilicaleans is a most interesting paper by Bertrand, which has just now come to hand. This paper deals with Neuropteris. New facts are brought out in regard to peculiar orbicular leaves bearing the pollen, and seeds of what I call the leafy type are figured. But I regret to find that once more a European student fails to draw comparisons with the Codonotheca (Sellards, 1903). Sellards' original paper gives a good description of the outer form of the fruit, shows the probable bundle pattern of the sporophylls, and suggests pointedly the probable Neuropterid affinity. As in the case of the Neuropteris seeds so far described the finer structure of the sporophylls is not determined, but the very large microspores are remarkably conserved. I have before suggested the need to reconcile this form with other and later described *Neuropteris* seeds, so called. Taken in conjunction with the forms reconstructed by Bertrand, Codonotheca shows that the fruits of the Paleozoic "quasi-ferns" must have exhibited an extraordinary range of structure, and it would appear that some of the fossils considered to be *Neuropteris* seeds are in reality bisporangiate buds. At least, it is to be observed that the internal structure of the Neuropteris seeds of large leafy form is little understood ; although these remarks do not, of course, apply to distinctly small and winged seeds like those of Pecopteris Pluckeneti.

In closing the presentation of this hypothesis for the origin of the seed canopy and lagenostome, I may add that I do not see that there is any really fundamental divergence from earlier views, especially because hypotheses based on a relative absence of evidence usually contain their own sufficient negation. Thus a seed must be much more than merely a "megasynangium." Moreover, these newer views of seed coat origin go far to explain the large size of the seeds and the relatively small number of flowers in cycadaceous plants; while the ovulate crown of *Cycas* in turn assumes a certain complexity of structure more in accord with other cycad strobili, and also with the Gnetalean strobili. Evidently *Cycas* only appears ancient and primitive because it still retains in full the old *impulse* to fruit from a leafy crown.

For, in a way, it would seem that *Cycas*, though so ancient of aspect, is also the most specialized cycad, with ovules arising from adventitious bud meristems of the axis of the socalled carpellary leaf, which is thus complex rather than primitive. To coin a term, *Cycas* may be a compoundly branched and *platystrobiline* form in which the fertile ovulate crown corresponds in a larger sense to a crown of strobili of the usual cylindrical type. However, not to go into a long diversion, at best only speculative, I content myself with say-

ing that if the Cycas carpels bear any relation to Angiospermous carpels, then *Cycas*, despite its seemingly ancient form, is not the least but must be the most specialized member of the *Cycadacea*. Similarly the quadrate group of seeds in *Genetop*sis would be intermediate between a "flower" and a "cone." While in the sense here perhaps rather dimly glimpsed, all cones of present day gymnosperms are at least once compound axes, and the conception of the ovulate strobilus of *Cycadeoidea*. as a compound axis with interseminal scales analogous to bracts, so insistently held by Lignier, may possibly prove to more nearly express the truth than my own view that the strobilus is simple, the interseminal scales resulting directly from sporophyll sterilization. In either case the *Cycadeoidea* seed pedicel is a far more ancient structure than any of the modern carpellary leaves of cycads, which is the more important point. But however these structures be viewed, the thought comes to mind that no closing words of my own can be quite so helpful or explanatory as an opinion of Thiselton-Dyer, which I again quote: ". . . . . . an ovule is a sporangial structure and it is not easy to see anything in a pinna which is directly comparable to it. Morphological conceptions must not enslave us, and I see no reason why sporangial structures, like buds, may not appear anywhere."

Thornton and Hayden-Separation of Zirconium. 137

ART. IX.—The Separation of Zirconium from Iron and Aluminum with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron"); by WILLIAM M. THORNTON, Jr., and E. M. HAYDEN, Jr.

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

In connection with a study of potassium ferrocyanide, Schröder\* has stated that both titanium and zirconium could be quantitatively precipitated by the "cupferron" reagent from their acidified solutions and that experiments were in progress for estimating these two elements. Schröder gave no experimental data and, as far as the authors of this paper can ascertain, has not published further upon the subject. Bellucci and Grassit have shown the "cupferron" reagent to be a quantitative precipitant for titanium and that a clean separation of titanium from aluminum could be brought about in solutions notably acid with either sulphuric or hydrochloric acid. Following the work of Bellucci and Grassi, one of ust has pointed out that, after throwing down the iron as ferrous sulphide from a solution containing sufficient ammonium tartrate to hold up titanium, and after acidifying the iron free filtrate, the titanium can be quantitatively precipitated by the "cupferron" reagent notwithstanding the presence of tartaric acid; and, further, that, if the above-mentioned filtrate be strongly acidified with sulphuric acid and contain also a sufficient quantity of tartaric acid, titanium can be quantitatively separated from both aluminum and phosphoric acid in one operation.§ On account of the great similarity in chemical nature between titanium and zirconium it appeared probable that in a similar way zirconium could be parted from the three substances mentioned above. Experiments with a view to accomplishing these separations were very successful as far as iron and aluminum were concerned. In the case of phosphoric acid, however, it was found that the zirconium derivative of nitrosophenylhydroxylamine, + even when the former was

 $\begin{array}{c} \uparrow \begin{bmatrix} C_6H_5 - N = N - O - \\ \parallel \\ O \end{bmatrix}_{\begin{array}{c} \text{II} \\ 4 \end{array}} \begin{array}{c} \text{assuming a formula analogous to the one} \\ \text{Second Barrier} \\ \text{Second Barri$ 

present with the zirconium in relatively small quantities, carried down very appreciable masses of phosphoric acid; although the test solution contained 40°m3 of sulphuric acid (1:1) and 5 grm. of tartaric acid in a total volume of  $400^{\text{cm}^3}$ .

Gazzetta Chimica Italiana, Anno xliii, Parte I, 570, 1913.
This Journal, xxxvii, 173, 1914.
Ibid., xxxvii 407, 1914.

<sup>\*</sup> Zeitschr. anorg. Chem., lxxii, 89, 1911.

On account of the great difficulty in handling these two substances when together in solution the authors decided to abandon the attempt to separate them in aqueous solution but to recommend instead that, in the analysis of phosphatic materials containing zirconium, the phosphoric acid be separated at the beginning of the analysis by fusion with sodium carbonate and a little sodium nitrate and leaching with water, whereupon sodium phosphate dissolves, leaving the residual sodium zirconate which is soluble in sulphuric acid.\*

Two solutions of zirconium sulphate were used in these experiments. The first was prepared by dissolving Merck's zirconium sulphate in dilute sulphuric acid, filtering, and making up to definite volume. Four experiments were made with the object of setting the standard of this solution. In experiments (a) and (b) the zirconium was thrown down in the hot solution by redistilled ammonium hydroxide—the precipitation being performed in a platinum basin. In experiments (c) and (d) the zirconium was precipitated by the "cupferron" reagent from a volume of  $400^{\text{cm}3}$  containing  $20^{\text{cm}3}$  of sulphuric acid (made by diluting acid of sp. g. = 1.84 with an equal volume of water). The following results were obtained:

Zirconium sulphate solution

#### Zirconium oxide

(a)	$25^{\text{cm}^3} = 25.9545$	grm	0.1088	grm. 0.4157%
		grm		
		grm		
		grm		

Since the values obtained in (b) and (c) by two different methods agree so closely, (c) was arbitrarily taken as correct. The second solution was prepared by acting on twice crystallized potassium fluozirconate with sulphuric acid (1:1), warning gently until all hydrofluoric acid had been displaced, pouring into cold water, and making up to definite volume. This solution was standardized by precipitation with the "cupferron" reagent, which had already been shown to agree well with results obtained by the reliable ammonium hydroxide precipitation. Duplicate determinations gave the following results :

Zirconium sulphate solu	tion	Zire	onium	oxide
(a) $25^{\text{cm s}} = 26.550$	grm	0.1101	grm.	0.4147%
$(b) 25^{\text{cm}^3} = 26.559$	orm.	0.1099	grm.	0.4138%

The mean of these two values was taken as correct.

The first series of experiments was performed with the object of ascertaining satisfactory conditions for the separation of zirconium from aluminum. Known quantities of zirconium

\* See Hillebrand, Bull. U. S. Geological Survey, No. 422, p. 139, 1910.

and aluminum were taken by weighing off portions of the standardized zirconium solution and dry recrystallized ammonium aluminum sulphate respectively. The solution was made neutral to methyl orange with ammonium hydroxide, which had been redistilled and kept in bottles of Jena glass. Measured volumes of sulphuric acid (1:1) were then added and the solution made up to  $400^{\text{cm}3}$ . About  $20^{\text{cm}3}$  of a 6 per cent "cupferron" solution was added gradually with constant stirring. Thereupon the zirconium came down as a very bulky and flocculent white precipitate. Without much delay the precipitate was filtered on paper with the aid of gentle suction and washed thoroughly with hydrochloric acid (made by diluting  $100^{\text{cm}3}$  of acid of sp. g. = 1.20 to one liter). The precipitate was placed in a tared platinum crucible, dried at  $110^{\circ}$  C., and carefully ignited to zirconium oxide. Table I contains the results of four experiments.

#### TABLE I.

The Separation of Zirconium from Aluminum.

No.	ZrO <sub>2</sub> taken grm.	Al <sub>2</sub> O <sub>3</sub> taken grm.	$ m ZrO_2$ found grm.	Error g1m.	${{\rm H_2SO_4}\atop{{\rm (1:1)}\atop{{ m cm^3}}}}$	$egin{array}{c} Volume \ of \ soln. \ cm^3 \end{array}$
1.	0.1091	0.1127	0.1090	-0.0001	40	400
2.	0.1088	0.1127	0.1090	+0.0005	40	400
3.	0.1086	0.1157	0.1090	+0.0004	60	400
4.	0.1091	0.1127	0.1094	+0.0003	60	400

In the second series of experiments zirconium was separated from iron. Known quantities of iron were introduced by weighing off portions of Kahlbaum's ferrous ammonium sulphate. Since the technique is the same for the separation of zirconium from iron only as for the separation of zirconium from both iron and aluminum, the procedure will be described below for the more general case. Table II embodies the results of two experiments.

#### TABLE II.

#### The Separation of Zirconium from Iron.

No.	$ m ZrO_2$ taken grm.	Fe <sub>2</sub> O <sub>3</sub> taken grm.	$ m ZrO_2$ found grm.	Error grm.	Tartaric acid grm.	${{\rm H_2SO_4}\atop{{\rm (1:1)}\atop{{ m cm^3}}}}$
5. 6.	$0.1088 \\ 0.1090$	$0.1018 \\ 0.1018$	$0.1091 \\ 0.1093$	+0.0003 +0.0003	2	40 40

In the third series of experiments known mixtures of iron, aluminum, and zirconium were analyzed. The iron and aluminum were introduced into the solution by weighing dry portions of ferrous ammonium sulphate and ammonium aluminum sulphate just as was done in the two series above. In Table III are put forth the results of four experiments.

### TABLE III.

The Separation of Zirconium from Iron and Aluminum.

	$\rm ZrO_2$	$Fe_{2}O_{3}$	$Al_2O_3$	$ m ZrO_2$		Tartaric	$H_2SO_4$	Volume
No.	taken	taken	taken	found	Error	acid	(1:1)	of soln.
	$\operatorname{grm}$ .	grm.	grm.	grm.	grm.	grm.	$\mathrm{cm}^3$	$\mathrm{cm}^3$
7.	0.1087	0.1018	0.05635	0.1086	-0.0001	2	40	400
8.	0.1089	0.1018	0.05635	0.1088	-0.0001	2	40	400
9.	0.1101	0.2036	0.1127	0.1110	+0.0009	2	40	400
10.	0.1100	0.2036	0.1127	0.1103	+0.0003	2	40	400

The technique of the analysis is here connectedly given. Tartaric acid is added to the solution in amount equal to five times the aggregate weight of the three bases to be held by it in solution. It is desirable that the initial volume of the test solution should not much exceed 100<sup>cm<sup>3</sup></sup>. To facilitate reduction of the iron the solution is made neutral to litmus paper with ammonium hydroxide and then acid again with  $2^{cm^3}$  of sulphuric acid (1:1). Hydrogen sulphide is then passed in until the iron has all been reduced to the ferrous state. The solution is now made slightly ammoniacal and more hydrogen sulphide introduced till the iron has been completely thrown out as ferrous sulphide, leaving the solution, however, alkaline to test-paper. The ferrous sulphide is thrown on a filter and washed ten times with very dilute colorless ammonium sulphide. The filtrate is acidified with 40<sup>cm<sup>3</sup></sup> to 60<sup>cm<sup>3</sup></sup> of sulphuric acid (1:1) and the hydrogen sulphide thus liberated boiled The solution is then cooled (best by iced water), the out. volume made to 400<sup>cm<sup>3</sup></sup>, and the "cupferron" reagent added gradually in the cold with constant stirring. Without delay the filtration is proceeded with, using a paper filter and mild suction. The filtrate should be tested as to completeness of precipitation by adding thereto a few drops of the reagent. A white turbidity will appear immediately if the solution still contain zirconium-otherwise a small white precipitate of nitrosophenylhydroxylamine which disappears on standing. After a little experience the analyst will have no difficulty in distinguishing these two precipitates, which are very different in appearance. The precipitate is washed at least twenty times with hydrochloric acid  $(100^{\text{cm}^3} \text{ of acid of sp. g.} = 1.20 \text{ diluted}$ to one liter), agitating the filter contents as much as possible and not allowing the washing fluid to run through too fast to accomplish much solvent work. After having been sucked free from drainage liquid at the pump, the precipitate along with the filter is placed in a tared platinum crucible and dried

at 110° C. If it be desired to save time, the ignition can be started with the precipitate moist—exercising great care, however, to avoid loss by spattering. With the lid not quite covering the crucible, the volatile matter is cautiously smoked off, the residual carbon burned away, the Meker burner applied for one half hour, and the zirconium oxide weighed. The ignition should be repeated, of course, until a constant weight is obtained.

In order to determine to what extent the zirconium derivative of nitrosophenylhydroxylamine includes fixed alkalis when salts of the latter are present in the solution, zirconium determinations were made in the presence of a large excess of potassium sulphate. The mode of experimentation was the same as that employed in the case of the separation of zirconium from aluminum. Table IV shows the results of two experiments.

#### TABLE IV.

The Separation of Zirconium from Potassium.

No.	$ m ZrO_2$ taken	${ m K_2O}$ taken	$ m ZrO_2$ found	Error	$H_{2}SO_{4}$ (1:1)	Volume of soln.
1.01	grm.	grm.	grm.	grm.	grm.	$cm^3$
11.	0.1088	2.7027	0.1097	+0.0009	40	400
12.	0.1089	2.7027	0.1096	+0.0002	40	400

It will be observed that the gain of weight undergone by the zirconium is not very large, and when one considers that the amount of potassium present (calculated as oxide) is nearly twenty-five times as great as the zirconium (also reckoned as oxide), the tendency of the precipitate to carry down alkalis need not be regarded as serious.

It remains now only to call attention to the chief points of merit possessed by this method of analysis. The precipitation of zirconium by the "cupferron" reagent is quantitative. From solutions strongly acidified with sulphuric acid, a clean separation of zirconium from aluminum can be effected. Tartaric acid does not interfere with the precipitation so that the acidified filtrate from the ferrous sulphide is in fit condition for the separation of zirconium from aluminum—a fact which obviates the necessity for oxidizing the organic oxyacid. The precipitate comes down immediately in flocculent and readily filterable condition, is little prone to include alkalis, and after drying can be converted into zirconium oxide of a high degree of purity. The manipulation is extremely simple and the sources of error are few.

May 26, 1914.

# ART. X.—The Crystal Form of Some of the Hydrated Halide Salts of the Alkali Metals; by C. W. Cook.

Some years since, an attempt was made to prepare, for the purpose of crystallographic study, a complete suite of crystals of the alkali halides. The proper conditions for crystal growth were not obtained, however, so that the crystals which resulted were imperfect and for the most part not suited for study. In a number of instances, hydrous instead of anhydrous compounds were formed. With the exception of the lithium salt of hydrobromic acid, these compounds upon exposure to the air lost their water of crystallization so rapidly that the crystals became opaque and their surfaces so dull that accurate measurements could not be made. In two cases, those of sodium bromide and potassium fluoride, the loss of water was less rapid than for most of the compounds, so that a few measurements were possible. While these measurements are not complete and probably not accurate, the results are given in hopes that they may be of assistance to future investigators.

### Hydrated Potassium Fluoride (KF, 2H, O?).

This compound was prepared by treating a solution of potassium carbonate placed in a lead dish with hydrofluoric acid and allowing it to crystallize through slow evaporation at room temperature (cir. 20° C.).

The crystals which were obtained were about 7 to  $S^{mm}$  in length with smooth well-developed faces. On exposure to the air, they rapidly became opaque and the faces assumed a pitted appearance. The substance crystallizes in the prismatic class of the monoclinic system and the crystals under discussion possessed a decidedly prismatic habit. The elements of crystallization are:

a:b:c = 1.0565:1:0.70608  $\beta = 109^{\circ} 15',$ 

which are based upon the following observations:

$$a: m = (100) : (110) = 44^{\circ} 52'$$
  

$$a: c = (100) : (001) = 70^{\circ} 25'$$
  

$$c: a = (001) : (011) = 33^{\circ} 38'$$

Five forms were observed as follows:

 $a\{100\}, b\{010\}, c\{001\}, m\{110\}, g\{011\}.$ 

Definite signals were obtained from all of the faces except those of the basal pinacoid, so that the observations except for the value of  $\beta$  are probably fairly accurate. The value of  $\beta$  is based upon maximum schimer and may vary therefore from the true value.

### Hydrated Sodium Bromide (NaBr, 2H<sub>2</sub>O).

This compound was studied crystallographically by Mitscherlich<sup>\*</sup> in 1829. He states that the crystals are stable below 30° C. The crystals obtained by the author, however, lost their water of crystallization quite rapidly at the temperature of the room, so that complete measurements were not possible. Observations in the prism zone confirm the work of Mitscherlich, as may be seen from the following comparison:

> $m: m''' = (110): (1\overline{1}0) = 61^{\circ} 28'$  (Mitscherlich)  $m: m''' = (110): (1\overline{1}0) = 61^{\circ} 24'$  (Cook).

In addition to the above, a new form,  $o\{120\}$ , was observed, which on account of the close agreement of the observed and calculated angles may be considered as well established. The angles are :

	Observed	Calculated
b: o = (010) : (120) =	$40^{\circ} 2'$	$40^{\circ} 4'$

The prism faces were characterized by a pronounced skeletal development.

### Hydrated Lithium Bromide (LiBr, 2H, O?).

The hydrated lithium bromide is a very stable compound, some of the crystals which have been kept for four years showing but slight efflorescence. The crystals examined were 2.5 to  $5^{\text{mm}}$  in length and well developed, the faces giving excellent reflections.

The compound crystallizes in the prismatic class of the monoclinic system, the elements of crystallization being :

$$a:b:c = 0.83665:1:1.1188$$
  $\beta = 107^{\circ} 18' 30''$ 

The crystals show in general a short prismatic or tabular habit, two variations of this type of development being observed.

Type one, which may be characterized as basal tabular, is represented in fig. 1. This type was assumed by four of the five crystals measured, and possessed the following forms:-

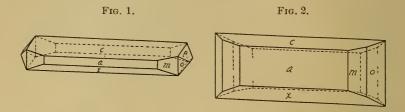
$$a\{100\}, c\{001\}, m\{110\}, o\{120\}, x\{\overline{1}02\}, p\{011\}.$$

A pyramid in the zone (120) (001) was also observed, but the reflections from it were so poor that no attempt is made to

\* Mitscherlich, E., Pogg. Ann., xvii, 385-388, 1829.

### 144 C. W. Cook—Crystal Form of Alkali Halides.

locate it definitely. The pinacoid  $c\{001\}$  is always the predominating face, is well developed, and gives good reflections. The orthopinacoid  $a\{100\}$  appears as a rather narrow face elongated parallel to the *b*-axis. Of the prisms,  $o\{120\}$  was always found to be present and to be better developed than the unit prism, although both prisms were generally present.



The clinodome  $p\{011\}$  is not always present, but when it does occur it possesses small triangular faces giving excellent reflections. The hemi-orthodome  $x\{102\}$  is always present and gives good reflections.

Type two shows a tabular development parallel to the orthopinacoid (fig. 2). This type of development was observed but once and exhibited the following forms :

### $a\{100\}, c\{001\}, x\{\overline{1}02\}, m\{110\}, o\{120\}.$

The close agreement between the observed and calculated angles may be seen from the following table :

	Observed	Calculated
a:c = (100):(001) =	72° 41' 30″*	
a:m=(100):(110)=	38° 37'*	
$c : x = (001) : (\overline{1}02) =$	38° 33′*	
a:o = (100): (120) =	$58^{\circ} 4'$	57° 58′ 30″
c: p = (001) : (011) =	$46^\circ~52'$	$46^\circ~53'$
c: o = (001) : (120) =	80° 45′	80° 55'

The quantity of material available was not sufficient to permit of the determination of the exact amount of water of crystallization, so that the formula which is given is based upon the formula that Mitscherlich established for the sodium bromide.

In conclusion the author wishes to express his thanks to Dr. E. H. Kraus for valuable suggestions and criticisms.

University of Michigan, Ann Arbor, Mich., April, 1914.

# ART. XI.—The Dinosaurs not a Natural Order; by F. R. VON HUENE.

In 1888 the well-known British investigator, H. G. Seeley, demonstrated\* for the first time that Owen's order "Dinosauria" should be divided into two large natural groups, especially on account of pelvic differences. Seeley called these groups Saurischia (= Theropoda + Sauropoda) and Ornithischia (= Orthopoda). This classification he kept until he died in 1909, but nobody followed him. † In 1907, the writer, however, accepted Seeley's classification and gave new evidence for it. but was still of the opinion that the two groups were only ramifications of one natural unit, the Dinosauria. But several years ago he came to the conclusion that the Dinosauria are not of monophyletic origin, but have developed from two different stocks and therefore should be considered as consisting of two distinct natural orders. Superficial similarities have been valued too highly, as for instance, the general form of the body, bipedal locomotion in two large groups, certain similarities in the formation of the foot, the femur, the humerus, and the shoulder girdle. The name "Dinosauria" should be abandoned absolutely, as have been such names as "Enalosauria."

The most striking difference between the Saurischia and the Ornithischia is in the pelvis, as is generally well known. Even in the oldest known representatives of these two groups there is no convergence in this respect at all. In the Ornithischia the facial part of the skull is prolonged and without preorbital openings, except in the most primitive forms, which have here a small fenestra. The dentition has become more numerous and more specialized, the anterior end of the jaws is toothless (except in the primitive Hypsilophodon) and in the lower jaw (in one group also in the upper jaw) a new symphysial bone has been formed, the premaxilla is of enormous size and its posterior extremity is intercalated between maxilla and nasals, even reaching the lacrymale adlacrymale. The enormous size of the internal bony or nasal openings and the different formation of the rest of the palate, the freedom of the quadrate, the supraorbital forming part of the roof of the skull (as shown by the writer in the Stegosauria, the Trachodontidæ and the Ceratopsia) and the high processus coronoideus in the lower jaw: all of these features in the skull of the Ornithischia are differences from

\* Rept. Brit. Assoc. Adv. Sci., 1888, pp. 698-699.

+ Barr in 1891 reached the same conclusion regarding the invalidity of the order, but divided it into three groups : Iguanodontia, Cetiosauria and Megalosauria. See American Naturalist, vol. xxv, pp. 434-454.

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the Saurischia and at the same time show the higher degree of adaptation and specialization of the former group. Already in 1908 I stated that we do not know any Ornithischia in the same degree of primitiveness which we know in the oldest Saurischia.

In the vertebral column, Saurischia of the highest degree of specialization do not possess ossified tendons as do all bipedal Ornithischia, even the relatively primitive Hypsilophodon. This must be due to a different manner of locomotion and of feeding. The different kind of motion must be referable to the same cause as the transformation of the pelvis and its stronger fixation at the vertebral column. Also, abdominal ribs are not yet known in Ornithischia, but they do occur in Saurischia, even in some of the latest forms.

In a recent paper the writer has tried to demonstrate that the Saurischia and the Ornithischia came from the Pseudosuchia, the former directly from their most primitive representatives by minor specializations, the latter from more specialized Pseudosuchians by a stage of bipedal hopping creatures, in which the pelvis became adapted to this new locomotion by retroversion of the pubis and development of a praepubis. (From this stage—as the writer suggests—the birds also were formed by becoming climbers on trees, then becoming adapted to flying by means of expansions of the skin known as patagia, subsequently acquiring feathers and ultimately learning true flight. These are Abel's ideas combined with those of the present writer.)

In 1908 the writer showed that the Sauropoda have developed from the Plateosauridæ, an opinion he stills sustains though some minor changes in the knowledge of the Saurischia have taken place. He now makes two large suborders within the Saurischia: Cœlurosauria and Pachypodosauria. In the former there are four families: Hallopoda, Podokesauridæ (Podokesaurus, Procompsognathus, Saltopus, Cœlophysis and Tanystrophæus), Compsognathidæ and Cœluridæ (including Ornithomimus). The second suborder would again comprise two lines of development, one leading from Thecodontosaurus to the Plateosauridæ and Sauropoda, the other from Palæosaurus to the Megalosauridæ. For further information on this subject the writer refers to some of his latest papers : "Beiträge zur Geschichte der Archosaurier," Geol. u. Palæont. Abhandl., vol. 13 (17), H. 1, 1914; "Ueber die Zweistämmigkeit der Dinosaurier, mit Beiträgen zur Kenntnis einigen Schädel," N. Jahrb. f. Min., etc., Beil. Bd. 37, 1914, pp. 577-589; "Das natürliche System der Saurischia," Centralbl. f. Min., etc., 1914, pp. 154–158.

Tübingen, March 10, 1914.

### J. M. Blake-Method of Ruling Used by Nobert. 147

# ART. XII.—On the Possible Method of Ruling Used by Nobert; by JOHN M. BLAKE.

NOBERT'S ruled test-lines at one time were the subject of much interest and discussion. They were regarded as marvels of mechanical skill. The rulings designed and used as a test of the performance of microscopic objectives were looked upon as the most wonderful of his productions.

It has been stated that after his death, an investigation of his apparatus did not reveal his method of work. Possibly, the apparatus which he actually used appeared to the investigator so crude, and so far from what preconceived notions of what such an apparatus *should* be, that it was passed by as unworthy of notice.

The late William A. Rogers of Cambridge, Mass., devoted much time and thought to the shaping of diamond points and edges for ruling purposes, and had much success in ruling fine and close lines. He took a great interest in what had been done by Nobert, and made measurements of the latter's bands of lines. Mr. Rogers' observations were published in the "Proceedings of the American Academy of Arts and Sciences."

At that time the writer was interested in Mr. Rogers' work and it struck him forcibly that Nobert's bands could not have been ruled on a machine like that used by Rogers. Quite a different principle must have been employed. The writer went so far as to plan out an apparatus involving the supposed principle. This apparatus he hoped sometime to make and put to the test. Its main features will be described, for we will assume that some interest in these rulings still remains and that no better explanation of a method of ruling such bands of lines has yet been published.

The proposed method dispenses with all sliding ways, joints, and screws. The ruling point is to be held by a light springbar, its motions controlled by electro-magnets; and the spacing of the lines accomplished by change of temperature of bars of dissimilar metals at measured time-intervals.

In carrying out these conditions, a chronograph cylinder would be used with contact points suitably disposed on its surface. Provision would be made for heat storage in a medium surrounding the machine. This apparatus would be placed in a room that could be kept at a constant temperature.

With this much provided, a preliminary trial of the ruling apparatus would be made, and a line ruled at each revolution of the chronograph cylinder during the fall in temperature. These preliminary lines would be expected to diminish in distance apart from the beginning to the end of the selected timeinterval, and they would afford the data for calculation and measurement by which the final working electric contact-points could be located. Success would depend upon the possibility of repeating the temperature conditions, provided the chronograph worked with precision.

The ruling point is a vital part of the apparatus. Mr. Rogers' experience tended strongly to the use of ground and shaped points and edges. It is expected, however, that with the light pressure needed in ruling these short bands covering a very small area, and with the pressure controlled by a very light spring, that a suitable working-point might be selected irom minute chance-broken fragments of diamond. A very delicate point might remain intact for a long time since no heavy moving parts would be involved, as in a ruling machine.

The errors in spacing and the curvature of the lines on a Nobert diffraction grating were revealed by placing two photo copies so that the film-surfaces were in contact, and the lines on the two made nearly parallel. Shaded irregular bands were thus produced indicating the errors in spacing. The writer has described this method in this Journal, July 1874.

These errors had apparently no periodicity as would be expected to result from the screw motion on a ruling machine of the ordinary type. It also became apparent that the lines were curved, and it was estimated that the radius-bar or springpole holding the ruling point was approximately eight feet in length.

We can see that this gives an insight into Nobert's methods; and the inference is that his most delicate ruled bands did not require the use of a screw or a sliding mechanism. The curvature of lines shown in his rulings would result from the ruling point being carried by a spring. The diminishing depth of ruling as the closest lines are approached may have been accomplished by placing the ruled surface in an oblique position, rather than by a diminished magnetic pull on the spring carrying the diamond.

The indications are that in ruling his finest bands of lines, Nobert depended entirely upon changes of temperature through measured time-intervals to give the required spacing. Derby—Crown Structure of Psaronius Braziliensis. 149

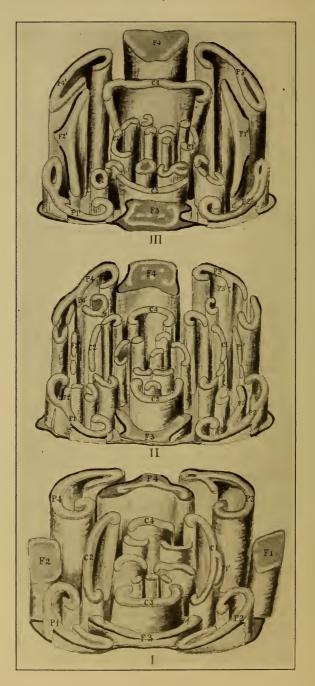
# ART. XIII.—Observations on the Crown Structure of Psaronius Braziliensis; by ORVILLE A. DERBY.

[Preliminary note in advance of the "Annaes do Serviço Geologico e Mineralogico do Brasil"]

In the restorations of certain of the stem features of Psaronius brasiliensis (this Journal, Nov. 1913) several vascular strands are represented as rising from the plane of the lowest cross section at hand, into the higher lying portions of the stem in the case of fig. 2, and into the air in that of fig. 3. The latter figure suggests the idea that when in the living plant the top of the stem stood at this level, all its vascular strands here passed, in a similar manner, from the stem into the members of the crown, standing free in the air, that they supplied. In other words, the plane of this cross section was then that of the junction of stem and crown, which though not an absolutely level horizontal surface may be presumed to have had its irregularities limited to so narrow a zone that, for all practical purposes, this plane in the fossil may be considered indifferently as that of the top of the stem or of the base of the crown. It thus represents the plane, or narrow zone, that was at one time occupied by the vegetative cone, or perhaps more properly disc, of the growing plant. With continued growth the vegetative disc would rise along the stalks of the crown organs that protruded above it, partially burying them in the rind-enclosed central parenchyma that, below it, was being added to the stem.

If this conception of the mode of growth of the plant be admitted, a schematic restoration of the basal portion of the crown of the living plant becomes possible. Any cross section of the fossil stem may be regarded as representing the plane of the vegetative disc at some moment in the life of the plant and the portions of the strands that stand above this plane can be plotted as rising free in the air. In life the aërial portion of each strand must have had a parenchymous covering which was modified on its outer surface into a more or less tenuous derinal layer that only when sclerotized to an appreciable extent would be preserved in a recognizable condition in the fossil stem. Thus in an attempt at restoration, the representation of the strands can be made with a fair degree of accuracy, provided that the successive cross sections of the fossil are not too widely spaced, while that of the parenchymous covering and of its relation to the fossil stem must be more or less hypothetical. Such an attempt has been made in the accompanying figures (I, II, III, about two-thirds natural size), in which Mr. Francisco Basto has skillfully plotted on three of

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150 Derby-Crown Structure of Psaronius Braziliensis.

Psaronius brasiliensis restored ; about  $\frac{2}{3}$  nat. size.

the cross sections at hand, taken as the top of the living stem, an imaginary cut, at an angle of 45 degrees, from front to back of the portion of the crown that stood immediately above it. The basal planes for these figures have been selected with reference to showing the three phases of the plant that are represented in the material at hand, viz., the stem with lateral members of the crown at its sides (I), at its front and back (III) and without such members (II).

In fig. I the basal plane is the lower face of the Strasbourg slice and the inclined cut rises to the top of the London 2 slice. It represents the last stage of a period of growth that terminated with the maturing and falling away of the free portions of the F1 and F2 organs whose persistent basal portions are cut at about mid-length. These and the P organs may be considered as constituting an old and mature crown of the plant, while all the others may be referred to a new crown, or crowns, in early stages of preparation.

The two external F organs are shown rising in deep grooves of the sclerotized stem rind, which, as will be seen by an inspection of the corresponding cross sections in fig. 1 of my preceding paper, did not close in completely behind them until a higher level of growth (the interior of the London 2 slice) was reached. These external organs have no sclerotized dermal layer. Their vascular system can be best discussed in connection with that of the other pair shown in fig. III.

The P organs, which are here also in a mature stage of growth, at least so far as their stalk portions are concerned, are assumed to rise flush with the stem rind and to have on their outer face a sclerotized layer continuous with the stem rind and destined to become incorporated with it. The justification of this assumption will appear later. Three of these organs present what may be considered as their normal adult character, but the fourth (P3) shows an anomaly which comes from the reunion of the two parts into which it was divided in its lower concealed part.

Of the members of the new crown the farthest advanced in development are those constituting the front and back pair of F organs, which may be considered to be at about middle age. They rise just within the upper rim of the rind and have a sclerotized layer on their outer face except along a median keel-like portion. A future F organ (F1'), destined to succeed F1, appears sprouting from the outer face of C1, being a little in advance of its companion, which only presents itself on C2 above the level of the inclined section. As will be seen farther on, the members of the C group, of which only the outer ones are numbered, hold a somewhat dubious position between the old and new crown. C1 and 2 are certainly nearly mature and are at the point of fulfilling their function of giving rise to a new pair of F organs, while C3 and C4 have still to grow considerably to attain that point.

Figure II, which is plotted on the top face of the London 1 slice as a base and rises to the level of the top of the Rio slice, shows a segment of the stem free from lateral organs. The plant had grown above the level of the top of the stubs left by the fall of F1 and F2 and was in a phase in which the P organs were undergoing important changes. These consisted of a subdivision into two or more parts and the appearance, on their inner face, of a sprout which developed rapidly into a long curved branch which soon split up into two or three parts. Of these the free internal one, with the aspect of a small C organ but that did not become incorporated in the magic quadrangle of the C group, seem to have soon ceased to grow, since no one of the four can be traced upward as far as the top of the Paris slice. The proximal portion of these branches remained attached to the parent organ and developed a sclerotized layer ou their outer face, which may be presumed to indicate that they were destined to a longer life and more important function than the detached parts. It seems reasonable to assume that this function was the substitution of the parent organ, already mature and ready to fall away, and in accordance with this view they have been lettered P1', etc. In this case, however the substitution must have been a rapid one and none of the cross sections of the fossil happen to fall at the proper level to give positive evidence that it actually took place.

The F3, F4 organs show a marked change of shape which at the highest level (F4) had become quadrate, but otherwise they had undergone no essential modification, except the appearance of a few small circular markings in their central part which are here interpreted as vascular strands, but which, as Zeiler remarked in his description of the Paris slice, may prove to be something else,-a point that can only be determined by a microscopic examination that cannot be made at present. The F1', F2' organs present themselves in two parts which may have come from a subdivision of the original sprout from the C organs, but more probably from an additional sprout. These parts are still small and, except for their position outside the group of C organs, present no characteristic features to distinguish them from the members of that group. In the case of F2' the two parts that are destined to fuse higher up are aligned with detached parts of the adjacent P organs as if these were destined to also take part in the future fusion.

The older pair of C organs (C1, C2) show subdivisions that may be taken as an old age feature, since their absence in higher cross sections proves that they soon ceased to grow. The younger pair (C3, C4) present no essential modifications, while the central members of the C group show changes in shape, size and position which possibly may be due to the substitution, by new sprouts, of old members that ceased to grow in the interval between one cut and the other.

Fig. III is plotted on the upper face of the Rio slice as a base and rises to the top of the Paris one. The nearly mature F organs are cut at the beginning of the lateral emergency of the front one and somewhat below the top of the persistent stub of the back one. The circumstance that F3 did not reach the level of the upper face of the Paris slice shows that it was slightly in advance (10-20<sup>mm</sup>?) of its fellow. Its condition a little before the level of the front of the cut was attained must have been similar to that of F4 in fig. II and its position was just within the stem rind but not quite flush with it. Its slightly rounded front face seems to have commenced to bulge outward over the rim of the stem rind, interrupting the upward growth of the latter, and its lateral sclerotized layers, being brought in contact with the stem rind, commenced to fuse with it. Between this level and that of the lower face of the Paris slice but at a point too high to be included in the cut, the central part of the organ seems to have grown away from the sclerotized layers and from the central parenchyma, leaving the former behind and fully incorporated with the stem rind but with an interval between their inner margins which soon became sclerotized (see Strasbourg to London 2 cross sections in fig. I; op. cit.) so as to make the stem rind complete behind the organ which still continued to grow upward parallel to the stem before bending outward and assuming characters that have not been preserved in the fossil. In this same interval of growth (see lower face of Paris slice in fig. I, op. cit.) the vascular strand became greatly modified through the dropping out of its broad central portion, leaving two irregular lateral strands that doubtless assumed the form shown by F1 and F2 in fig. I and eventually, just before bending outward, that of F4 in fig. III.

The P organs, which as stated above are assumed to be a new set and are accordingly lettered P1', etc., are still somewhat abnormal at the base of this segment, as is shown by the front ones, but at the higher level all four of them had become normal, as is shown by those at the back of the cut. Compared with the corresponding sections in fig. 1, a very close general agreement is noted, but with a reversal of the position of the close and open inrolled margin. This reversal is evidently due to the position of these organs relative to the sclerotized face of the neighboring F ones. The small organs originating from the curved inner ends of the branches appear at the base of this segment (to the right and left of C3), but they did not persist to the higher level and thus are lacking at the back of the figure.

The younger F organs (F1', F2') have here fully developed their middle age characters, which must have appeared in the comparatively short interval of growth between the highest level attained by the oblique cut of fig. II and that of the upper face of the Rio slice where their detached youthful elements appear united (presumably including, as already suggested, sprouts originating from the inner face of the neighboring P organs) and with sclerotized layers formed on their outer face. They are here in essentially the same stage of development as that shown in fig. 1 for the older pair whose adult characters begin to appear in fig. II.

In the C group of organs the detached parts of C1 and C2 had ceased to grow before the level of the upper face of the Rio slice was reached. Up to this level the succeeding pair (C3, C4) showed no important modifications, but from here on its members increased greatly in width and assumed the form shown by C4 in the figure, and a succeeding pair (C1', C2') began to be differentiated amongst the irregularly placed central members of the group, preparatory to giving birth to a new pair of F organs.

If, barring some details, the above interpretation and restoration of the preserved portions of the crown be accepted as substantially correct, they afford a safe starting point for more or less plausible conjectures regarding the unpreserved portions. While looking about among the plants growing around me for analogies to guide such conjectures, a decapitated female example of *Cycas circinalis* came under observation, that afforded an opportunity for watching the development of a new crown from the low vegetative cone exposed on the truncated top of an apparently lifeless stump.

At the beginning of its growing season the cone rose rapidly upward for a few inches until it assumed the form of the top of a small conical cabbage head. It was then seen to consist of a closely compacted mass of flattened finger-like scale leaves. From the apex of this cone the tip of the flower cone appeared and soon developed into a larger pineapple-like second cone superimposed on the first one. Later on, a few lance-like frond sprouts shot upward with extreme rapidity from the apex of the second cone, forming an extremely elongated third cone. The base of the whole crown complex then widened in such a way as to transform the three successive cones into concentric rings of detached sprouts, which, as they developed, commenced to spread outward at the top and eventually from their point of emergence upward, giving the plant its characteristic adult aspect.

An inclined cut rising from the top of the stem across the stalks of this new Cycas crown at the stage in which its immature members stood erect just within the rim of the stem rind would present strong analogies with that of *Psaronius brasiliensis* as represented in fig. II, if we imagine the order of the component members of the crown to be reversed so that its weakest ones (the scale leaves) would stand on the inner, and its strongest ones (the fronds) on the outer ring. Whether this comparison has any deeper significance than that of a superficial analogy, or not, is a question that must be left to the botanists to decide. It has certainly been helpful in the attempt to solve the riddles of *Psaronius brasiliensis* and for this reason it has seemed worthy of being recorded here.

Returning now to our fossil plant, it may safely be conjectured that the strong persistent stubs of the external F organs were prolonged by a tolerably large and heavy free portion which extended outward obliquely and so could not be embalied in the rising stem, and that the still stronger P stalks must also have had large and heavy prolongations that also bent outward, but at too high a level above the stem top to be reached before they fell away. On the other hand, the weaker C organs seem to have had no free portions that were not embalmed, or in other words, they retained throughout their entire life a simple sprout-like character and probably at no time rose to any great height above the vegetative disc. If the above comparison with the immature Cycas crown be admissible, the missing portion of the P stalks would correspond to the fronds, those of the F organs to the flowers and the entirely preserved C organs to the scale leaves.

Thus far the stem of our plant has been considered as divested of its sheath of adventitious roots, and only inferentially has any evidence, and that of a purely negative character, been evolved bearing on the original of this feature that is so characteristic of the Psaronius tribe. It seems evident that except sporadically (as shown by occasional root-like strands traversing the rind in some of the cross sections) the roots cannot be derived from the stem rind, since such an origin would involve an oblique, or horizontal, course in the proximal portion of the middle and outer ones, whereas the cross sections show them as standing vertically. The same argument applies to the current hypothesis that they are derived exclusively from the P organs, since this involves an oblique course for about half their number in order to cover the intermediary spaces fronting the F organs. An hypothesis, that seems easily reconcilable with the view presented above of the structural features of stem and crown, is that they descend from the first part of the outspreading portions of both the P and F organs.

An argument in favor of this hypothesis can be drawn from the history of the F organs as traced above. Those in middle life have their front nearly covered by a sclerotized layer which cleaves away when they commence to bulge over the rim of the stem rind, while at the same time the section of the vascular strand that lay behind the bulging front shows a sudden interruption. It seems reasonable to assume that this interruption may be due to the subdivision of the band-like strand into numerous filaments to supply radicular appendages to the lower face of the outspreading stalk, while the lateral portions of the original U-shaped strand continue for a farther distance outward before subdividing to supply the more essential appendages of the stalk. When the organ fell away the breaking point would be at the outer margin of the root-bearing portion, but the part of the stalk above the lower face would be exposed to the air and would decay, while the vertical portion behind it would be protected by the roots and thus preserved as persistent stubs. If this was so, the stem would grow upward free from roots until the succeeding organ of the same row sent down a fresh lot to tie on to the retarded upper rim of the root sheath. In the case of the P organs the central part of the vascular strand may be presumed to subdivide in a similar manner at the point of outbending, while the lateral portions go on to supply the pinnules that are only developed farther away. The well-known occurrence of modified pinnules (?), known as Aphlebia, on the stalks of many fossil ferns (?) may perhaps furnish an argument in favor of this hypothesis.

Rio de Janeiro, March 15th, 1914.

# ART. XIV. -- Nodules with Fishes from the Coal Measures of Kansas; by W. H. TWENHOFEL and CARL O. DUNBAR.\*

THE rarity of vertebrate remains in rocks of Pennsylvanian age makes each new discovery of great interest. The American localities where vertebrate fossils of this period occur in sufficient completeness to be of value are so few that they may almost be counted on the fingers of one's hand, while in Kansas such have been among the rarest of fossils. Two noted localities are Mazon Creek, Illinois, and the mines about Linton, Ohio. The former locality has long been famous because of the excellent preservation of its plants, crustacea and insects, and the fossils possess an added interest because of their occurrence in nodules.

#### Kansas Nodule Horizons.

Fossil-bearing nodules have also been collected in the Kansas Coal Measures. The Labette shales, near Sherman City, carry many, of which great numbers contain the brachiopod, Orbiculoidea nitida (Phillips). This fossil also occurs abundantly in the nodules of the Cherokee shale. The LeRoy shales have nodules which are fossiliferous and others are also quite common in the Vilas shales, but of the many from the latter horizon which have been broken open by the writers, not one has contained anything of value. At Twin Mound, about ten miles southwest of Lawrence, what appear to be the Kanwaka shales carry great numbers of nodules. Doctor R. L. Moodie has broken open hundreds from that locality and in only a few was anything discovered. Local collectors, however, have obtained one or two specimens of *Prestwichia dana*.

#### A New Nodule Horizon.

To the localities and horizons noted above, another must be added, which is of exceptional interest by reason of the remarkable abundance and splendid preservation of the fish remains. The discovery was accidentally made by the junior writer while searching for Pennsylvanian invertebrates. An oblong gray nodule, which he carelessly cracked, contained a complete and well-preserved skull. Naturally, invertebrates were neg-lected and careful search was made for nodules. The first afternoon's collecting netted three fish skulls and over a dozen other bones. Since then the place has been repeatedly visited and skulls have been found each time.

\* Published by permission of the Director of the Kansas Geological Survey.

# 158 Twenhofel and Dunbar-Nodules with Fishes.

Locality.—The outcrop from which the fossils were obtained is almost within the city of Lawrence, at a small quarry and pond near the southeast corner of Oak Hill cemetery. The outcrop has been in existence for some years; but the nodules have not previously been noted, due to the fact that they are not of the ordinary form, but have more the appearance of weathered pebbles. At the time of discovery there were several hundred lying upon the surface of the ground.

Manner of Occurrence and Stratigraphic Position.—The nodules occur in a thin bed of yellowish-gray shale which lies immediately above the Kickapoo limestone, the thickness of the shale not exceeding two inches. The surface of the limestone is irregular, the elevations rising practically to the upper surface of the nodule-bearing shale. The irregularities are due to differential deposition, however, and not to any action of surface weathering. The Kickapoo is one of the many thin, persistent bands of limestone of the Kansas Coal Measures. These bands outcrop in a northeast-sonthwest direction and apparently extend entirely across the state. The Kickapoo is stated to have been traced for a distance of two hundred miles, and its thickness varies from four to fifteen feet. At the nodule locality the thickness does not exceed four feet, and while there seems to be a slight thickening eastward, the amount is apparently not significant. As a rule the limestone is not well exposed, since the thick, overlying Lawrence shale weathers very readily and keeps it covered. Its position, however, can easily be located by the terrace which it has determined.

Beginning at the surface, the section at the quarry is as follows:

1. Shale, oxidized or gray, to the grass roots	3 to 5	feet
2. Limonite nodule layer	13 inc	ehes
3. Gray and blue shale		"
4. Brown and yellow shaly sandstone. This layer		
is somewhat calcareous and quite soft	2	"
5. Brown and yellow sandy fossiliferous shale		"
6. Nodule layer. Gray and grayish gray shale	1/2	"
7. Kickapoo limestone. Gray and blue limestone,	Ĩ	
oölitic near the top	4 feet	

The same sequence is present at Blue Mound, about five miles east of Lawrence. There are, however, fewer nodules, and they are also smaller, and vertebrate remains, while present, are of little value. The limonite nodules also occur and are like those of the little quarry. About fourteen miles south of Lawrence, near Baldwin, the same sequence, in so far as it relates to the Kickapoo, the limonite nodule layer and the other shale, likewise obtains. At this locality a single nodule like those which contain the vertebrates at Lawrence, was found. It was about one-half inch in diameter and contained nothing. The same sequence was found near the village of Vinland, about ten miles south of Lawrence, but no vertebrate nodules appear to be present. At this locality there is a thin bed of coal a few feet above the limonite nodule band. Traced northeastward, the sequence is the same near the village of Tonganoxie and three nodules were found in the thin shale just above the limestone. None, however, contained anything.

Description of the Nodules.—The nodules are generally of a gray color, with a granular surface, similar to that which they would have, were they made of lime and sand. In shape they vary from spherical to oblong, and are generally of regular proportions; but some are quite irregular. A few are slender elongate. The spherical shape is the most common, but the oblong ones carry the better fossils. They appear to have silica as their chief component, but a considerable percentage of lime is also present.

Some of the oblong nodules are as much as two inches in length, while a few of the round ones are not more than onehalf an inch long. The diameters of the average nodules vary from three-fourths to one and one-fourth inches. The outside usually affords no indication of the contents; but a few have been collected with the fossils protruding, one having a piece of petrified wood projecting for fully one-half inch. That the shape to a large extent was determined by the inclosed bone is indicated by the fact that slender nodules contain long bones, while skulls are usually inclosed in those which are oblong.

About one foot above the vertebrate zone is another layer in which the nodules have an elongated, lenticular shape, and are composed of impure limonite. They vary in length from one to four inches, are frequently hollow, and contain no fossils.

Abundance of Nodules.—In order to determine the abundance and distribution of the nodules, a space with an area of fifty-six square feet was cleared and the nodules carefully collected. From this space were obtained two hundred and thirty-five, sixty of which contained vertebrate remains. The nodules are unequally distributed, and appear to be most abundant in the depressions of the limestone. From one square foot as many as a dozen have been collected, while from another area of equal size not one has been obtained. Unequal distribution of fossils also occurs, the greatest number of those having any value having been collected in one part of the outerop.

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Fossil Content of the Nodules and Inclosing Shales.—The fossils of the nodules are chiefly vertebrates. Those collected consist of skulls, bones, and spines of fishes, a crustacean (Palaeocaris, probably new), one specimen of Nautilus cf. planovolvis, and eight pieces of wood, one of which shows a great development of the medullary rays and another the vascular bundles. There are no leaves, such as occur so abundantly at the Mazon Creek locality, while invertebrates are rare in the nodules, although quite common in the inclosing shales. It was at first thought that some of the remains were amphibian, but this view appears to be erroneous. About eight hundred nodules have been broken open, and from these more than one hundred and fifty vertebrate fossils of value have been obtained. Many of the nodules carry what are thought to be coprolites, some of them contain unidentifiable fragments of bone, and a still greater number are apparently These figures show that the locality is far more fosbarren. siliferous than that of Mazon Creek, where Doctor Moodie estimates that there is one vertebrate fossil to every thousand nodules.\*

The vertebrates were submitted to Doctor Moodie, and his identifications are as follows: — tooth of Cladodus, teeth of Cochliodonts, two teeth of Diplodus, spine of Ctenacanthus, dermal tubercles of fishes, fish coprolites, and eighteen skulls of small fishes, whose systematic position has not been determined. Three of the skulls contain remarkably well-preserved casts of the brain—a feature of preservation which Doctor Moodie states, "is unique in the history of vertebrate paleontology." †

The fossils of the inclosing shales are of a totally different character. There are no vertebrates, nor any wood. The invertebrates are not uniformly distributed, but are in patches. They consist of small forms, forms with a more or less spherical shape, or forms with air chambers. All are of marine origin. Those which have been identified are Axophyllum rude (?) (rare), Meekellu striatocostata (r), Orbiculoidea nitida (r), Productus nebraskensis (r), Pugnax utah (common), Bellerophon stevensanus (r), Trepospira sphærulata (r), Kautilus planovolvis (r), Orthoceras sp., crinoid stems, and several additional species of unidentifiable gastropods and pelecypods.

In the brown shale above the nodule bed, there are also fossils and nodules, the latter of lenticular shape, brown in color, generally hollow, and altogether without fossils. The biologic facies must have been quite different, since the fauna is mollus-

\* Moodie, this Journal, vol. xxxiv, p. 279, 1912.

+ Moodie, personal communication.

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can. No brachiopods appear to be present. The fossils which have been identified are Aviculopecten occidentalis, Astartella sp., Edmondia cf. nebraskensis, E. sp., Macrodon tenuistriatus, M. sp., Nucula bellistriata, N. cf. beyrichia, N. ventricosa, Bellerophon cf. crassus, Euphemus carbonarius, Trepospira sphærulata, Metacoceras sangamonense, Phillipsia major, and quite a number of additional pelecypods which have not been determined.

The underlying Kickapoo limestone contains sixty-two species, eighteen of which are brachiopods, while no fossils have been reported from the Lawrence outcrops of the overlying Lawrence shale, and, except for *Prestwichia danæ*, none have been discovered elsewhere. In this respect they resemble the Bandera, LeRoy (fossil insects excepted), and Tecumseh shales, while several others of the Kansas shale zones contain only a few species.

Conditions of Deposition.—The Kansas Coal Measures consist of a series of alternations of more or less barren shales and thin fossiliferous limestones, of which many of the latter can be traced as escarpments or terraces from the northern side of the state to the southern, and, in addition, several of them have been traced into Nebraska, Missouri and Oklahoma. The shale zones are generally not highly calcareous, and most of them locally contain thin bands of coal, or highly carbonaceous shale, a thin bed of the former outcropping on the campus of the State University. The limestones are of marine origin, and such is also true of many of the shales, but it is certainly equally true that some of the latter are to be considered as deposits of freshwater origin. The absence of thick zones of coarse sandstone permits the inference that the land was not of great relief, and was probably characterized by sluggish, meandering streams which spread layers of mud over their flood plains and deltas. During times of relative stability the delta extended into the sea, which the typical marine deposits indicate was at no time of great depth. The shore is probably to be conceived as a wide mud flat with small shore lakes and swamps, over which the tide swept for greater or less distances. Intermittent submergence would from time to time bring portions of the mud beneath the sea and initiate the deposition of limestone, thus giving rise to an interfingering of marine and continental deposits—a type of sedimentary structure characteristic of delta deposits which have been laid down in shallow seas.\*

The Kickapoo limestone represents an incursion of the sea, while the Lawrence shale indicates the possible driving back

\* Barrell, Jour. Geol., vol. xlv, p. 354, 1906.

of the marine waters and the deposition of mud under nonmarine conditions. It is inferred that the beds immediately succeeding Kickapoo limestone deposition record the struggle for supremacy of the two rival deposits. The almost coexistent marine organisms and thin coal beds indicate the critical line between land and water and probably the tidal zone.

A peculiar fact in connection with the fossils of the nodule bed is that the nodules contain almost wholly vertebrates, while none have been found in the inclosing shales. This could readily be explained on the assumption that the nodules were pebbles and transported to the invertebrates—an assumption, however, which is disproved by the fact that the nodules show no evidence of ever having undergone transportation.

As has been noted above, the invertebrates in the shales are either small, spherical, or contain air chambers. Shells of this character are readily transported for long distances by currents of little velocity, the cephalopods and small shells being floated and the large spherical ones rolled. Hence it may be that the invertebrates were transported to the nodules.

Many modern shores are characterized by lakes and swamps in which live animals and plants that are quite different from those of the adjacent shore. Many of the lakes are fresh, while others are salty. Into the latter the sea effects an entrance twice daily, while at some time or other many of the freshwater lakes are likely to be reached by waves and tides of unusual height. Into the lakes in this way are brought empty shells which are irregularly distributed over the bottom, thus producing the co-occurrence of animals of different habitats. Elsewhere the senior author has shown that into the modern peat deposits of Anticosti Island such typical marine animals as echinoderms are carried by the waves.\*

It is possible that a similar state of affairs obtained at the time of the deposition of the nodule bed. After the death of the fishes, their decaying bodies would have precipitated the matter composing the nodules. The empty shells, however, would have been incapable of doing this. It would frequently have been the case that a few shells would have retained small amounts of organic matter and hence been able to become the centers of nodules. In this way, the irregular distribution of the invertebrates in the shales and their great scarcity in the nodules admit of ready explanation.

The fossiliferous bed just above the nodule layer probably indicates a slight ingression of the sea. The fossils are uniformly distributed and quite different from those below. The animals appear to have lived where their shells are found.

\* Twenhofel, this Journal, vol. xxx, p. 67, 1910.

#### W. M. Bradley-New Silver-Tellurium Mineral. 163

Zonal Assignment of the Nodule Bed.—Whether the Lawrence shales shall still continue to be regarded as unfossiliferous will depend on the disposition made of the beds described above. They record the beginning of the end of marine sedimentation and are followed by non-marine deposits. Lithically they belong to the Lawrence shales. Faunally they are related to the Kickapoo limestone; but since lithology is the chief basis for the division of the Pennsylvanian of Kansas it would seem that their reference to the shale formation would be the more logical, and such an assignment is made.

University of Kansas, June, 1914.

# ART. XV.—Empressite, a New Silver-Tellurium Mineral from Colorado; by W. M. BRADLEY.

Some years ago, what appeared to be a new mineral was found in the Empress-Josephine Mine in the Kerber Creek District of Colorado by Professor R. D. George of the University of Colorado. No analyses were made at that time, but qualitative tests were obtained which showed the presence of silver and tellurium. Several small specimens were recently sent to the writer for investigation. They were all massive in structure, careful inquiries having failed to locate any material showing crystal faces. The mineral occurs in very fine granular and compact masses associated with galena and native tellurium. It is metallic in luster, and gives a gravish black to black streak. The fracture is finely conchoidal to uneven, and upon such surfaces the color is a pale bronze. The mineral is brittle to friable, and has a hardness between 3 and 3.5. The specific gravity was determined as 7.510. In the oxidizing flame on charcoal it fuses at 1 giving a heavy white coating of tellurium dioxide and a black globule, which if placed in the reducing flame gives on cooling white dendritic points of silver on its surface. Prolonged heating in the oxidizing flame gives a globule of silver. In the open tube a faint white sublimate of tellurium dioxide is formed which if strongly ignited fuses to colorless globules. The mineral is readily soluble in hot dilute nitric acid.

The specimen selected for analysis was examined under a microscope and was found to contain several very minute seams of non-metallic mineral matter which was practically all removed by crushing the specimen to very fine grains and then picking out by the aid of a lens any fragments which showed adhering white material. The method of analysis may be briefly stated as follows: After dissolving the mineral in nitric acid and filtering off traces of insoluble matter the silver was precipitated and weighed as silver chloride. Tellurium was essentially determined by precipitating it in the metallic state by sulphurous acid. Traces of tellurium contained in the filtrate were recovered by precipitating it as tellurium sulphide, the resulting precipitate being dissolved by a solution of bromine in dilute hydrochloric acid and the tellurium finally precipitated and weighed as TeO<sub>2</sub> according to the method of Browning and Flint.\*

The results of the analyses follow:

	I	II	Average	Ratios	
Insoluble	•38	•39	•39		
Ag	45.16	45.17	45.17	•418	1.00
Te	54.62	54.89	54.75	$\cdot 429)$	1.03
Fe	•30	·15	·22	·003 ∫	1 00
	100.46	100.60	100.53		

From the analysis it will be seen that the mineral gives a ratio of practically Ag: Te::1:1, which fact points strongly to the conclusion that the formula AgTe represents a new mineral species. The name empressite has been given to it by Professor George on account of the fact that it was found in this particular mine. While the above ratio does not give a formula that is in harmony with the generally accepted views relating to valence, nevertheless if considered from a metallographic standpoint it will be seen to be but one of many compounds which show irregularities if attempts are made to interpret them by means of valence. A table of such compounds may be found in Desch's Metallography.<sup>+</sup> Some typical examples are as follows:

#### Silver-Aluminum Series.

#### Ag<sub>3</sub>Al Ag<sub>2</sub>Al

#### Aluminum-Gold Series.

Al<sub>2</sub>Au AlAu AlAu<sub>2</sub> Al<sub>2</sub>Au<sub>5</sub>

\*This Journal, xxviii, 112, 1909.

<sup>†</sup>Longmans, Green & Co., London and New York; second edition. Appendix, pp. 399-418.

### W. M. Bradley-New Silver-Tellurium Mineral. 165

It is generally recognized that the formulæ of inter-metallic compounds cannot be rationalized on the basis of our common ideas of valence. The silver-tellurium system has been worked out by the customary thermal-micrographic method. Guertler\* in his handbook on metallography reviews the work of various authors, principally Pellini and Quercigh, and concludes that there are two compounds in the series, namely, Ag, Te, which is identical with the isometric hessite, and a compound of questionable character, viz. AgTe or Ag.Te. Abnormalities in the equilibrium relations interfere with the exact determination of this formula. Guertler, however, regards AgTe as the more probable one. This compound is formed by reaction between Ag. Te and the liquid at 444°. It undergoes polymorphic transformation at 412°. There is no intercrystalline solubility throughout the entire series, or in other words no solid solution. The natural mineral empressite, which corresponds very closely to the atomic ratio Ag: Te, exhibits a structure wholly in conformity with the conclusions stated above. Upon metallographic examination of a polished section it was found to be a structurally homogeneous substance, showing large irregular light and dark polygonal grains with no interstitial matter. It thus appears to be a definite compound with the formula AgTe.

In conclusion the author wishes to express his thanks to Professor George, who so kindly furnished the material that made this investigation possible, and also his indebtedness to Professor C. H. Mathewson of the Sheffield Scientific School, who made the metallographic examination.

Mineralogical Laboratory of the Sheffield Scientific School of Yale University, New Haven, Conn., June 3, 1914.

\* Vol. I, Part II, 924-926.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXVIII, No. 224.—August, 1914.

# ART. XVI.—A New Volumetric Method for the Determination of Sulphurous Acid; by George S. JAMIESON.

Most of the methods for the determination of sulphurous acid, either free or combined, have been based upon iodometric processes. The difficulties formerly encountered in the iodometric analysis of these substances have been overcome by the modification of Giles and Shearer,\* which consists in adding the sulphurous acid or sulphite to a measured excess of N/10iodine solution and titrating the unaltered iodine with N/10sodium thiosulphate solution.

The method to be described is based upon the titration of sulphurous acid with potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid and a small volume of an immiscible solvent such as chloroform. This general method of titration is the well known one of L. W. Andrews,<sup>+</sup> but as far as is known it has not been applied previously to the titration of sulphurous acid. The method is especially adapted for use with solutions, although it is possible to titrate sulphites without previous solution as shown beyond. It has the advantage over the iodometric method in requiring only a single very stable volumetric solution instead of two solutions which cannot be preserved for a long time unchanged.

In order to test the method, a solution containing 3.567 grams of normal potassium iodate in a 1000<sup>cc</sup> was prepared. According to the equation of the expected reaction

## $KIO_3 + 2H_2SO_3 + 2HCl = 2H_2SO_4 + ICl + KCl + H_2O$

the equivalent of this solution is  $1^{cc} = .002135g$ . of SO<sub>a</sub>.

The potassium iodate solution was standardized with pure resublimed iodine under the same conditions as described beyond for the titration of sulphurous acid.

No.	Iodine taken	KIO₃ used	Wt. of I for 1 <sup>cc</sup>
Ι	·4261	50.22 cc	·00845
II	$\cdot 2024$	23.90	.00847
verage			.00846

Since the reaction in the case of the iodine is represented by the equation

#### $4I + KIO_{s} + 6HCl = KCl + 5ICl + 3H_{s}O$

the strength of the potassium iodate solution was  $1^{\circ\circ} = 0.02135$ g. SO<sub>2</sub>. The titrations were carried out in a glass stoppered bottle of 250<sup>cc</sup> capacity in the presence of a cooled

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\*J. Soc. Chem. Ind., iii, 197, and iv, 303. † Journ. Amer. Chem. Soc., xxv, 756, 1903. ‡ Stronger solutions can be used to advantage when comparatively large amounts of sulphurous acid are to be titrated.

mixture of 30° of concentrated hydrochloric acid, 20° of water, and 6<sup>cc</sup> of chloroform. During the first part of the titration, the iodate is added rapidly while shaking the bottle so as to give the contents a circular motion, until the iodine which gradually appears and increases to a maximum amount has largely disappeared from the solution. Then the stopper is inserted and the solution is thoroughly shaken. The titration is continued with very thorough shaking of the closed bottle after each addition of potassium iodate solution until the end point, which is the disappearance of the violet color of the chloroform, is obtained.

The following table contains the results of titrating measured quantities (5-20<sup>cc</sup>) of sulphur dioxide solutions which had recently been titrated by the Giles-Shearer method :

No.	SO₂ taken	KIO₃ used	$\mathrm{SO}_2$ found	Error
1	.0224	10.23	.0225	+.0001
2	.0290	13.70	.0292	+.0005
3	·0290	13.72	·0293	+.0003
4	.0315	14.85	.0317	+.0002
5	.0317	14.95	.0318	+.0001
6	.0471	22.20	.0473	+.0002
7	.0628	29.70	·0634	+.0006
8*	·1146	22.80	·1145	0001
9	·1699	33.80	$\cdot 1697$	0002
10	.0426	8.20	.0427	+.0001
11	$\cdot 1362$	27.10	·1360	0002

These results show a very satisfactory agreement among themselves and with the actual amounts present.

The result sobtained by titrating measured quantities  $(6-15^{cc})$ of a sodium bisulphite solution are as follows :

No.	SO <sub>2</sub> taken	KIO₃ used	$\mathrm{SO}_2$ found	Error
1	.0495	23.40	·0499	+.0004
2	.0492	23.20	.0495	+.0003
3	.0492	23.12	·0494	+.0002
4	.0328	15.40	·0329.	+.0001
5	.0336	15.70	·0335	0001
6	.0224	10.20	.0224	.0000

It is important to cool the hydrochloric acid solution to  $15^{\circ}$ -18° C. before adding the sulphite solution. If it is desired to titrate much larger amounts of sulphite, it is recommended that the sulphite solution should be added to a titration bottle which contains 10-15<sup>cc</sup> of iodine monochloride<sup>+</sup> solution in addition to the usual amounts of hydrochloric acid, etc.

SO<sub>2</sub>.  $\dagger$  To prepare this solution, dissolve 10 grams of potassium iodide and 6.44 grams of potassium iodate in 75<sup>cc</sup> of water, add 75<sup>cc</sup> of concentrated hydro-

<sup>\*</sup> Titrations 8-11 were made with a potassium iodate solution  $1^{cc} = 005020$  g.

The iodine monochloride reacts with the sulphite and prevents any loss of sulphur dioxide. The liberated iodine is titrated with potassium iodate solution in the usual manner. The use of iodine monochloride does not change the sulphur dioxide equivalent of the potassium iodate solution.

Several experiments were made by adding weighed amounts of calcium sulphite to hydrochloric acid solutions which contained iodine monochloride as described above, and after thorough shaking, the liberated iodine was titrated.

No.	Wt. of CaSO <sub>3</sub>	$\mathrm{KIO}_3$ used	$SO_2$ found	$SO_2$ present
1	·0890	19.92 <sup>cc</sup>	47.86%	47.98%*
2	·0553	12.45	48.06	66
3	.0878	19.70	47.90	- 66
4	.0751	16.90	48.04	66

Weighed portions of sodium bisulphite were titrated in the same manner as the calcium sulphite.

No.	Wt. of HNaSO₃	KIO₃ used	$SO_2$ found	$SO_2$ present
1	0.0972	26·35°°	57.88%	58.01%
2	$\cdot 1271$	34.56	58.04	"
3	·1392	37.85	58.05	"
4	$\cdot 1372$	37.25	57.96	"

It is recommended that the sulphite should be weighed in a short specimen tube and after dropping it into the titration bottle, the stopper should be inserted quickly so as to avoid any loss of sulphur dioxide.

Furthermore it should be observed that the strength of the hydrochloric acid in which the titration is made is of much importance. If more than  $20^{\circ\circ}$  of a solution is to be titrated or if a large volume of the potassium iodate solution is required, sufficient hydrochloric acid should be added to give the proper strength, which is 15 to 20% actual acid as previously stated.

Sheffield Chemical Laboratory, Yale University, New Haven, Conn., May 11, 1914.

chloric acid, then add a globule of chloroform, in a glass stoppered bottle, and adjust exactly to a faint iodine color by shaking and adding dilute potassium iodide or potassium iodate, as the solution may require. \* Average of 2 determinations by the Giles-Shearer method.

# L. Page—Relativity and the Ether.

## ART. XVII.—Relativity and the Ether; by LEIGH PAGE.

THE object of this paper is to discuss the properties of a type of ether which is consistent with the Principle of Relativity, and to show that all the phenomena of electrodynamics, —those relating to accelerated charges as well as those involving charges moving with constant velocity,—are an exact consequence of the postulate of the relativity of all systems which are moving with constant velocities. Also an expression will be derived for the electromagnetic mass of an electron whose tield is not quasi-stationary, as in the case of Abraham's, Bucherer's and Lorentz's electrons.

Let K and K' denote two systems moving with constant velocities, the velocity of the second relative to the first being  $\mathbf{v}$ . Let XYZ be a set of orthogonal right handed axes fixed in K and so oriented that K' is moving relative to K in the direction of the Z axis. Let X'Y'Z' be a set of axes fixed in K' and mutually parallel to XYZ. Unprimed letters denote quantities as measured in K and primed letters the same quantities as measured in K'. The Principle of Relativity demands that the velocity of a light wave proceeding in any direction shall be the same whether measured by an observer in K or by one in K'. The mathematical expression of this condition is contained in the familiar Lorentz-Einstein group of homogeneous linear transformations.\*

 $t' = \frac{t - \beta_c^{z}}{\sqrt{1 - \beta^{z}}} \qquad t = \frac{t' + \beta_c^{z'}}{\sqrt{1 - \beta^{z}}}$   $x' = x \qquad x = x' \qquad (1)$   $y' = y \qquad y = y'$   $z' = \frac{z - vt}{\sqrt{1 - \beta^{z}}} \qquad z = \frac{z' + vt'}{\sqrt{1 - \beta^{z}}}$ 

where c = velocity of light, and  $\beta = \frac{v}{c}$ . By differentiation the usual transformations for velocity and acceleration can, be obtained.

$$\frac{V_{x}'}{V_{x}} = \frac{V_{y}'}{V_{y}} = \frac{\sqrt{1 - \frac{V'^{2}}{1 - \frac{V'^{2}}{c^{2}}}}}{\sqrt{1 - \frac{V'^{2}}{c^{2}}}} = \frac{1 + \beta \frac{V_{z}'}{c}}{\sqrt{1 - \beta^{2}}} = \frac{\sqrt{1 - \beta^{2}}}{1 - \beta \frac{V_{z}}{c}}$$

$$V_{z}' = \frac{V_{z} - v}{1 - \beta \frac{V_{z}}{c}}$$

$$V_{z} = \frac{V_{z}' + v}{1 + \beta \frac{V_{z}}{c}}$$
(2)

\* Einstein, Annalen der Physik, xvii, 891, 1905.

where  $\mathbf{V}$  is the velocity of the particle considered; and

$$\frac{f_x'}{\left(1 - \frac{V'^2}{c^2}\right)^{\frac{3}{2}}} = \frac{f_x + \beta \left[\frac{V_x}{c}f_z - \frac{V_z}{c}f_x\right]}{\left(1 - \frac{V^2}{c^2}\right)^{\frac{3}{2}}\sqrt{1 - \beta^2}}$$

(3)

and a similar expression for  $f_{y}'$ 

$$\frac{J_{z}^{t'}}{\left(1-\frac{V'^{2}}{c^{2}}\right)^{\frac{3}{2}}} \equiv \frac{J_{z}^{t}}{\left(1-\frac{V'^{2}}{c^{2}}\right)^{\frac{3}{2}}}$$

where  $\mathbf{f}$  is the acceleration of the particle considered.

To be in accordance with the Principle of Relativity, the ether must have one of two possible characteristics: either (a) it must be absolutely homogeneous, or (b) all non-homogeneities must be moving in straight lines with the velocity of light. For, since it would be impossible, ideally as well as actually, to locate the same point in a homogeneous continuum at two successive instants, it would be impossible to measure the velocity of any material object relative to such a continuum. Hence the existence of a perfectly homogeneous ether would be in complete accord with the Principle of Relativity.

To explain interactions between material particles, however, it is necessary to assume the existence of non-homogeneities in the ether. So we must make use of the second characteristic which we may ascribe to the ether without contradicting the Principle of Relativity:—the property of transmitting all nonhomogeneities in straight lines with the velocity of light. Since this velocity is an invariant of the Lorentz-Einstein transformation, the existence of non-homogeneities travelling through the ether with the velocity of light would not provide a means of measuring the velocity of a material particle relative to the ether. Consequently the Principle of Relativity would be in no way violated by the assumption of the existence of such an ether.

The character of these non-homogeneities, which, for brevity, we may call strains,\* will determine the state of the ether at every point and instant. We will suppose that this strain can be completely represented by a single-valued vector function of position in space, **E**. This vector **E** must have the following properties: (a) at any point the product of the volume element  $d\tau$  and the divergence of **E** must be proportional to the charge present in  $d\tau$ ; (b) the charge must be an invariant for the

\*The word "strain" is used in a perfectly general sense, and is not intended to imply any relative displacement of discrete particles.

Lorentz-Einstein transformation. Hence the divergence of  $\mathbf{E}$  will be zero in ether devoid of matter, and every charged particle will be a continuously emitting source of strains. One other assumption, which is suggested by symmetry, is necessary. To an observer relative to whom the charged particle is, for the instant, at rest, the strains must be emitted uniformly in all directions.

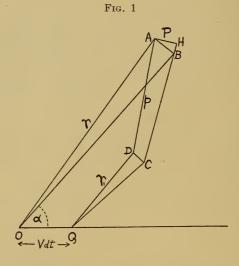
The most convenient way to represent these strains geometrically will be by means of tubes of strain spreading out from each charged particle. While we may consider these tubes. which are analogous to "tubes of force," to have a crosssection which increases as one proceeds outwards from the charged particle in such a manner that they fill all space, yet we must endow them with some property that will enable us to determine the direction of the strain (which in general will be different from its direction of motion) at each point in space. E will have the direction of the tube at the point and instant considered, and will be proportional in magnitude to the number of tubes per unit cross-section. We will choose our units so as to make this factor of proportionality, as well as that between the divergence of **E** and the density of charge, equal to unity. This amounts to the adoption of Lorentz's units of charge and electric force. Any point on a tube of strain will move with the velocity of light in a straight line of length l, drawn

from the position of the particle at a time  $\frac{l}{c}$  earlier, to the

point in question. To an observer relative to whom the particle is at rest at the instant considered, the tubes of strain in its immediate vicinity will appear to diverge from the particle in such a way that equal solid angles will contain equal numbers of tubes of strain. If a number of particles are producing strains in the ether, the resultant strain at any point will be the vector sum of the strains due to the individual particles.

Before proceeding to a consideration of the strains due to a moving charge, let us consider the simple case of a charge which is permanently at rest relative to the observer. According to former theories, the charge would be surrounded by a uniformly diverging field of stationary strains, whereas, according to the theory developed here, the charge would be a continuously emitting source of strains which move outward through the ether with the velocity of light. Since, however, the direction of motion would be parallel to the strains themselves, the number of tubes of strain per unit cross-section at any point in the field would be constant, and the same as in former theories of the ether. A little consideration will show that the emission of strains does not necessarily involve an emission of energy. In fact, in the simple case under discussion, it is obvious that the energy density at any point in space, if it varies with the square of the strain, would remain constant, and that the total energy of the field would be finite.

In the following mathematical treatment Gibb's vector notation will be used. If **i**, **J**, **k** are three unit vectors parallel respectively to the X J Z axes, the vector operator  $\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z}$  will be denoted by  $\nabla$ . **P** · **Q** denotes the scalar product of the two vectors **P** and **Q**, **P** × **Q** the vector product of these two vectors.  $\nabla \cdot \mathbf{P}$  is the divergence of **P**,  $\nabla \times \mathbf{P}$  the curl or rotation of **P**, **Q** ·  $\nabla \mathbf{P}$  the derivative of **P** in the direction of **Q** multiplied by the magnitude of **Q**, etc. To distinguish vectors from scalars, Gothic type will be used for the former. Thus **c** is the vector whose magnitude is *c*.



# The Effects of Matter on Ether.

(a) Effect of a Charged Particle.

A charge at O (fig. 1) has a velocity **V** in the direction **OO** and an acceleration **f** (not shown in the figure) in any direction. This charge may represent an electron, if the electron is considered to be a point-charge, or an element of an electron if the electron is supposed to occupy a finite portion of space. In the time dt the charge will have moved to Q. Let  $\mathbf{r} = \mathbf{OA}$ ,  $\mathbf{r}_{,} = \mathbf{OD}, \mathbf{p} = \mathbf{DA}$ , where  $\mathbf{DA}$  and  $\mathbf{CB}$  are the bounding elements of a tube of strain at P at a time  $\frac{\overline{OA}}{c}$  later than the time at  $\overline{OA}$ 

which the charge was at O. Then if  $t = \frac{\overline{OA}}{c}$ 

$$\mathbf{r} = \mathbf{c}t$$
  

$$\mathbf{r}_{1} = (\mathbf{c} + d\mathbf{c})(t - dt)$$
  

$$\mathbf{p} = \mathbf{r} - \mathbf{r}_{1} - \mathbf{V}dt$$
  

$$= (\mathbf{c} - \mathbf{V})dt - td\mathbf{c} \qquad (4)$$

where **p** has the direction of the tube of strain at the point P. On account of our choice of units the total number of tubes of strain diverging from the particle will be equal to the charge e on the particle. If the electron is a point-charge e will be finite, while if the electron occupies a finite portion of space ewill be an infinitesimal of the same order as the volume  $d\tau$  of the particle under consideration.

If K' is the system of the charged particle at the instant the strain under consideration leaves the charge,  $\mathbf{V} = \mathbf{v}$  and it follows from (2) that

$$\sin a' da' = \sin a da \frac{(1-\beta^2)}{(1-\beta\cos a)^2}$$

where a is the angle between the vectors  $\mathbf{V}$  and  $\mathbf{c}$ . Hence

$$\mathbf{E} = \frac{e}{4\pi r^2} \frac{(1-\beta^2)}{(1-\beta\cos\alpha)^2} \frac{\mathbf{p}}{p\cos B\widehat{A}H}$$

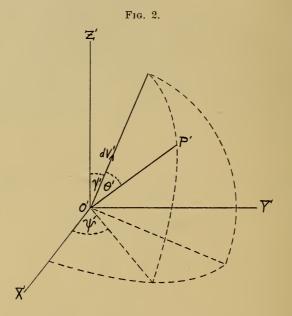
$$= \frac{e}{4\pi r^2} \frac{(1-\beta^2)}{\left(1-\frac{\mathbf{c}\cdot\mathbf{V}}{c^2}\right)^2} \frac{\mathbf{p}}{\mathbf{p}\cdot\mathbf{r}}$$
(5)

gives the strain in the ether at the point P at a time  $\frac{r}{c}$  later than the time when the charged particle occupied the position O. **E** is given in terms of the distance  $\mathbf{r} = \overline{\mathbf{OP}}$ , the velocity  $\mathbf{V}$ of the charge at the instant when it was at O, and the vector  $\mathbf{p}$ . Equation (4) gives  $\mathbf{p}$  in terms of  $\frac{\partial \mathbf{c}}{\partial t}$ , which will be shown to be a function of the velocity  $\mathbf{V}$  and the acceleration  $\mathbf{f}$  of the charge at the instant when it was at O. Then it will be possible to express  $\mathbf{E}$  in terms of the known quantities  $\mathbf{r}$ ,  $\mathbf{V}$  and  $\mathbf{f}$ .

We wish to evaluate  $\frac{\partial \mathbf{c}}{\partial t}$  at the point P (fig. 2) for the particular tube of strain which originated at O at a time earlier

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equal to  $\frac{OP}{c}$ . Consider three systems, K, K' and K''. K is the system for which **E** is to be determined, and relative to which the charge has a velocity **V** and an acceleration **f** at the time  $\frac{\overline{OP}}{c}$  earlier than that for which the value of **E** at P is desired. K' is the system of the charged particle when at O. Without loss of generality we can choose axes so that **V** is par-



allel to the Z and Z' axes, and **f** lies in the YZ or Y'Z' plane. Hence  $\mathbf{V} = \mathbf{v}$ . K'' is the system of the charged particle at a time dt after the particle has left O. K'' will have some velocity  $d\mathbf{V}'$  relative to K', where  $d\mathbf{V}'$  must evidently lie in the Y'Z' plane.  $\gamma'$  is the angle between  $d\mathbf{V}'$  and  $\overline{\mathbf{0'Z'}}$ ,  $\theta'$  that between  $d\mathbf{V}'$  and  $\overline{\mathbf{0'Z'}}$ ,  $\theta'$  that between  $d\mathbf{V}'$  and  $\overline{\mathbf{0'Z'}}$ , and the plane determined by  $d\mathbf{V}'$  and  $\overline{\mathbf{0'P'}}$ .

As usual we shall denote the components of  $d\mathbf{V}$  by  $dV_y$  and  $dV_z$ , and those of **c** by  $c_x$ ,  $c_y$ ,  $c_z$ . The following relations may be derived from equations (1) and (2):

$$dV' = \frac{dV_z\sqrt{1 + (1 - \beta^2)\left(\frac{dV_y}{dV_z}\right)^2}}{(1 - \beta^2)}$$

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 $\tan \gamma' = \sqrt{1-\beta^2} \, \frac{d V_y}{d V_z}$ 

If l', m', n' are the direction cosines of c'

$$l' = \sin \theta' \cos \psi'$$
  

$$m' = \sin \theta' \sin \psi' \cos \gamma' + \cos \theta' \sin \gamma'$$
  

$$n' = -\sin \theta' \sin \psi' \sin \gamma' + \cos \theta' \cos \gamma'$$

and

$$c_{x} = cl = \frac{cl' \sqrt{1 - \beta^{2}}}{1 + \beta n'}$$

$$c_{y} = cm = \frac{cm^{2} \sqrt{1 - \beta^{2}}}{1 + \beta n'}$$

$$c_{z} = cn = \frac{c(n' + \beta)}{1 + \beta n'}$$

Hence

$$dc_{x} = cdl = \frac{c\sqrt{1 - \beta^{2}}[dl' + \beta(n'dl' - l'dn')]}{(1 + \beta n')^{2}}$$
$$dc_{y} = cdm = \frac{c\sqrt{1 - \beta^{2}}[dm' + \beta(n'dm' - m'dn')]}{(1 + \beta n')^{2}}$$
$$dc_{z} = cdn = \frac{c(1 - \beta^{2})dn'}{(1 + \beta n')^{2}}$$

Since the angle between any particular tube of strain in the immediate vicinity of the charged particle and the direction of  $d\mathbf{V}'$  must have the same value to an observer in K'' when the charge is in K'' as this angle has to an observer in K' when the charge is in K', and since both these angles must lie in the same plane,

$$d\theta' = -\frac{\sin \theta' \frac{dV_z}{c}\sqrt{1 + (1 - \beta^2) \left(\frac{dV_y}{dV_z}\right)^2}}{(1 - \beta^2)}$$

$$d\psi' = 0$$
Hence

$$dl' = \frac{-\sin\theta'\cos\theta'\cos\psi'\frac{dV_z}{c}\sqrt{1+(1-\beta^2)\left(\frac{dV_y}{dV_z}\right)^2}}{(1-\beta^2)}$$

$$\frac{(\sin\theta'\sin\gamma'-\cos\theta'\sin\psi'\cos\gamma')\sin\theta'\frac{dV_z}{c}\sqrt{1+(1-\beta^2)\left(\frac{dV_y}{dV_z}\right)^2}}{(1-\beta^2)}$$

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 $\frac{(\sin\theta'\cos\gamma' + \cos\theta'\sin\psi'\sin\gamma')\sin\theta'\frac{dV_z}{c}\sqrt{1 + (1 - \beta^2)\left(\frac{dV_y}{dV_z}\right)^2}}{(1 - \beta^2)}$ 

Substituting these values in the expressions for  $dc_x$ ,  $dc_y$  and  $dc_z$ , and reducing, we obtain the following vector equation;

$$d\mathbf{c} = -\frac{\left[d\mathbf{V} \times (\mathbf{c} - \mathbf{V})\right] \times \mathbf{c}}{c^2(1 - \beta^2)}$$
(6)

Hence, from (4), since  $t = \frac{r}{c}$  where  $r = \overline{OP}$ ,

$$\mathbf{p} = \left\{ \left( \mathbf{c} - \mathbf{V} \right) + \frac{r \left[ \mathbf{f} \times (\mathbf{c} - \mathbf{V}) \right] \times \mathbf{c}}{c^{s} (1 - \beta^{2})} \right\} dt$$
$$\mathbf{p} \cdot \mathbf{r} = \left( c^{2} - \mathbf{V} \cdot \mathbf{c} \right)^{-r} dt$$

c

Therefore

$$\mathbf{E} = \frac{e \left(1 - \beta^{2}\right)}{4\pi r^{2} c} \left\{ \left(\mathbf{c} - \mathbf{V}\right) + \frac{r \left[\mathbf{f} \times (\mathbf{c} - \mathbf{V})\right] \times \mathbf{c}}{c^{3} (1 - \beta^{2})} \right\}$$
(7)

$$= \frac{e\left(1-\beta^{2}\right)}{4\pi r^{3}\left(1-\frac{\mathbf{r}\cdot\mathbf{V}}{rc}\right)^{3}} \left\{ \left(\mathbf{r}-\frac{r}{c} \mathbf{V}\right) + \frac{\left[\mathbf{f}\times\left(\mathbf{r}-\frac{r}{c} \mathbf{V}\right)\right]\times\mathbf{r}}{c^{2}\left(1-\beta^{2}\right)}\right\}$$

If  $\mathbf{E}_{\mathbf{v}}$  is the value of  $\mathbf{E}$  for a charged particle moving with constant velocity  $\mathbf{V}$ , (7) can be put in the form

$$\mathbf{E} = \mathbf{E}_{\mathbf{v}} + \frac{(\mathbf{f} \times \mathbf{E}_{\mathbf{v}}) \times \mathbf{r}}{c^2 (1 - \beta^2)}$$
(8)

This perfectly general expression gives the ether strain at P due to a charged particle at O moving with any velocity  $\mathbf{V}$  and acceleration  $\mathbf{f}$ . However  $\mathbf{E}$  at P is not determined by this expression for the time when the charge is at O, but for a time later equal to the time taken by light to travel from O to P. (7) and (8) are identical with the expressions that have been derived from Lorentz's retarded potentials.\* It is to be noted, however, that the preceding derivation is based on nothing more than the assumption of the existence of an ether which is in accordance with the Principle of Relativity—i. e. one that transmits all non-homogeneities in straight lines with the velocity of light—, and the assumption that every charged particle is a center of uniformly diverging tubes of strain.

\* Compare G. A. Schott, Electromagnetic Radiation, p. 23.

Two types of field are of especial interest on account of their simplicity. If the charged particle has been moving with constant velocity for an infinite time, (7) gives the familiar expression

$$\mathbf{E} = \frac{e}{4\pi r^{3}} \frac{(1-\beta^{2})\mathbf{r}}{(1-\beta^{3}\sin^{2}a)^{\frac{3}{2}}}$$
(9)

where **E** is the ether strain at P at the *same* instant as that at which the charge is at O, **r** being the vector  $\overline{\mathbf{OP}}$  and a being the angle between **r** and **V**. The tubes of strain are straight lines diverging from the charged particle.

The second case of interest is the field of a charged particle which for an infinite time has had a constant acceleration  $\phi$ relative to its own system and which has zero velocity relative to the observer in K at the instant considered. This is the type of motion a charged particle would assume in a uniform field. For this case (7) reduces to

$$\mathbf{E} = \frac{e}{4\pi r^3} \frac{\left(1 + \frac{\mathbf{\phi} \cdot \mathbf{r}}{2c^2}\right)\mathbf{r} + \frac{1}{2c^2}\left(\mathbf{\phi} \times \mathbf{r}\right) \times \mathbf{r}}{\left(1 + \frac{\mathbf{\phi} \cdot \mathbf{r}}{c^2} + \frac{\mathbf{\phi}^2 r^2}{4c^4}\right)^{\frac{3}{2}}}$$

$$e^{\left[\left(1 + \frac{\mathbf{\phi} \cdot \mathbf{r}}{c^2}\right)\mathbf{r} - \frac{r^2}{2c^2}\mathbf{\phi}\right]}$$
(10)

$$= \frac{e}{4\pi r^3} \frac{\left(1 + \frac{\mathbf{\Phi} \cdot \mathbf{r}}{c^2}\right) \mathbf{r} - \frac{r^2}{2c^2} \mathbf{\Phi}}{\left(1 + \frac{\mathbf{\Phi} \cdot \mathbf{r}}{c^2} + \frac{\mathbf{\Phi}^2 r^2}{4c^4}\right)^{\frac{3}{2}}}$$

where **E** is the ether strain at P at the *same* instant as that at which the charge is at rest at O, and **r** is the vector  $\overline{\mathbf{OP}}$ . The tubes of strain are circles having their centers in a plane perpendicular to  $\phi$  at a distance from the charged particle equal to  $-\frac{c^2}{\phi^2}\phi$ . To an observer in motion relative to the charge the ether strain can be obtained from (10) by means of the transformation equations (16) subsequently derived. This field,\* on account of its importance, will be discussed more in detail later.

## (b) Equations of the Ether Strain.

First we shall derive the equations of the ether strain due to a single charged particle. Then, since the total ether strain is the vector sum of the strains due to all the particles whose fields extend to the point in question, the general equations will follow at once.

\*Compare G. A. Schott, Electromagnetic Radiation, p. 63 et seq.

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Consider a point P fixed in the system K. Let dl be an infinitesimal line drawn from P in the direction of E, and let  $c_1$  be the component of c in the same direction. Now **E** is a vector function of position in space, which has everywhere the direction of the tubes of strain and is equal in magnitude to Hence  $\frac{\partial \mathbf{E}}{\partial t} dt$  at the number of tubes per unit cross-section. P can readily be shown to be made up of three terms, namely:  $-\mathbf{c} \cdot \vec{\nabla} \mathbf{E} \, dt$ , the change in **E** due to the fact that the tubes of strain at a point  $-\mathbf{c}dt$  from P will reach P in the time dt;  $\begin{bmatrix} -\mathbf{E} \nabla \cdot \mathbf{c} + \mathbf{E} & \frac{\partial c_1}{\partial \bar{l}} \end{bmatrix} dt$ , the change in **E** due to the fact that the direction of c changes from point to point, and consequently the density of the tubes of strain will change in the time dt;  $\begin{bmatrix} \mathbf{E} \cdot \nabla \mathbf{c} - \mathbf{E} \frac{\partial c_1}{\partial t} \end{bmatrix} dt$ , the change in **E** due to the twisting of the tubes of strain in the time dt. Therefore,  $\frac{\partial \mathbf{E}}{\partial t} = -\mathbf{c} \cdot \nabla \mathbf{E} - \mathbf{E} \nabla \cdot \mathbf{c} + \mathbf{E} \cdot \nabla \mathbf{c}$ Therefore, at any point outside the charged particle,  $\frac{\partial \mathbf{E}}{\partial t} = \nabla \times (\mathbf{c} \times \mathbf{E})$ (11)since  $\nabla \cdot \mathbf{E} = 0$ We shall now turn our attention to the determination of  $\frac{\partial}{\partial t}$  (c × E) It can easily be shown that  $\frac{\partial \mathbf{c}}{\partial t} = -\mathbf{c} \cdot \nabla \mathbf{c}$ Hence, making use of this result and (11) $\frac{\partial}{\partial t} (\mathbf{c} \times \mathbf{E}) = -\mathbf{c} \cdot \nabla (\mathbf{c} \times \mathbf{E}) - (\mathbf{c} \times \mathbf{E}) \nabla \cdot \mathbf{c} - (\mathbf{E} \cdot \nabla \mathbf{c}) \times \mathbf{c}$  $= -c^2 \nabla \times \mathbf{E} + \nabla \times (\mathbf{c} \cdot \mathbf{E} \mathbf{c}) - (\mathbf{E} \cdot \nabla \mathbf{c}) \times \mathbf{c}$  $-(\mathbf{c} \times \mathbf{E}) \cdot \nabla \mathbf{c} + \mathbf{c} \nabla \cdot (\mathbf{c} \times \mathbf{E})$ But the most general type of field is that given by equations (7). For this field it can readily be shown that

 $\nabla \cdot (\mathbf{c} \times \mathbf{E}) = 0 \tag{12}$ 

and

$$\mathbf{C} \times (\mathbf{c} \cdot \mathbf{E} \, \mathbf{c}) = (\mathbf{E} \cdot \nabla \, \mathbf{c}) \times \mathbf{c} + (\mathbf{c} \times \mathbf{E}) \cdot \nabla \, \mathbf{c}$$

Hence

$$\frac{\partial}{\partial t} (\mathbf{c} \times \mathbf{E}) = -c^2 \nabla \times \mathbf{E}$$
(13)

So the ether strain due to a single charged particle is determined, for a point outside the particle, by the equations

$$\nabla \cdot (\mathbf{c} \times \mathbf{E}) = 0$$
  
$$\frac{\partial}{\partial t} = \nabla \times (\mathbf{c} \times \mathbf{E})$$
  
$$\frac{\partial}{\partial t} (\mathbf{c} \times \mathbf{E}) = -c^2 \nabla \times \mathbf{E}$$

in which the two vectors, **E** and **c** × **E**, appear. Consider now the resultant ether strain due to all the particles whose fields extend to the point under consideration. If by **E** we denote this resultant strain, and by **H** the sum of the vectors  $\frac{1}{c}$  (**c**×**E**) due to the individual particles, the preceding equations take the form

$$\nabla \cdot \mathbf{H} = 0$$
  

$$\dot{\mathbf{E}} = c \nabla \times \mathbf{H}$$
(14)  

$$\dot{\mathbf{H}} = -c \nabla \times \mathbf{E}$$

for any point devoid of matter.

If matter is present at the point under consideration, we can resolve **E** into two components, one of which represents the strain due to the matter at P. Then it is easily shown that . the first and third of the above equations remain unchanged, while the expression for  $\dot{\mathbf{E}}$  contains the additional term  $-\mathbf{V} \bigtriangledown \cdot \mathbf{E}$ .

So, in general,

$$\nabla \cdot \mathbf{H} = 0$$

$$\nabla \times \mathbf{H} = \frac{1}{c} \left( \dot{\mathbf{E}} + \mathbf{V} \nabla \cdot \mathbf{E} \right)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \dot{\mathbf{H}}$$
(15)

Hence we have derived the field equations of electrodynamics from nothing more than the assumption of the existence of an ether which is in accordance with the Principle of Relativity, and the assumption that a charged particle is the center of uniformly diverging tubes of strain.

# (c) Transformation Equations.

The strain in the ether at a point P in K, in so far as it is due to a single charged particle, is defined by **E** and **c** at that point. It is desired to find **E**' in K' at the same point and instant. As usual axes will be so oriented that K' has the velocity **v** relative to K in the positive Z direction. Let x, y, zbe the coördinates of P, and x+dx, y+dy, z+dz the coördinates of a point very close to P on the same tube of strain. Then from (1) and (2) it follows that

$$dx' = dx + \frac{\beta \frac{c_x}{c} dz}{1 - \beta \cos a}$$
$$dy' = dy + \frac{\beta \frac{c_y}{c} dz}{1 - \beta \cos a}$$
$$dz' = \frac{\sqrt{1 - \beta^2}}{1 - \beta \cos a} dz$$

where a is the angle between c and v. Hence

$$E_{x}' = \frac{E_{x} + \frac{1}{c^{2}} \left[ \mathbf{v} \times (\mathbf{c} \times \mathbf{E}) \right]_{x}}{\sqrt{1 - \beta^{2}}}$$
$$E_{y}' = \frac{E_{y} + \frac{1}{c^{4}} \left[ \mathbf{v} \times (\mathbf{c} \times \mathbf{E}) \right]_{y}}{\sqrt{1 - \beta^{2}}}$$
$$E_{z}' = E_{z}$$

give the strain  $\mathbf{E}'$  in K' in terms of  $\mathbf{E}$  and  $\mathbf{c}$  in K at the same point and instant, and the relative velocity  $\mathbf{v}$  of the two systems. Consider now the resultant ether strain due to all particles whose fields extend to the point in question. If we make the same substitutions as before,

$$E_{x}' = \frac{E_{x} + \frac{1}{c} \left[ \mathbf{v} \times \mathbf{H} \right]_{x}}{\sqrt{1 - \beta^{2}}}$$

$$E_{y}' = \frac{E_{y} + \frac{1}{c} \left[ \mathbf{v} \times \mathbf{H} \right]_{y}}{\sqrt{1 - \beta^{2}}}$$
(16)

### The Effects of Ether on Matter.

In the discussion of the effects of matter on ether we have been led, with a considerable degree of certainty, to exact expressions for the ether strain even in the case of the most general type of motion. The discussion of the effects of ether on matter presents greater difficulty. Following the usual convention, we shall define the force  $\mathbf{F}$  on a charged particle as the product of the charge e of the particle and the ether strain in the vicinity of the charge as measured in the charge's system. For an electron of finite volume F will consist of two parts, (a) the force F, due to the ether strains set up by charges outside the electron, (b) the force  $\mathbf{F}_{2}$  due to the ether strains produced by the electron itself.  $\mathbf{F}_{1}$  is certainly proportional to  $-\mathbf{f}$ . If unbalanced forces are excluded

But

$$\mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2 = 0$$

But Therefore  $\mathbf{F}_2 = -m_0 \mathbf{f}$ 

$$\mathbf{F}_{1} = m_{0}\mathbf{f}$$

where  $m_0$  may be a function of f and its derivatives, as well as of the dimensions of the charged body under consideration.

Suppose the charge is at rest, at the instant considered, in system K'. Then  $\mathbf{V} = \mathbf{v}$  and from (3)

$$f'_{x} = \frac{f_{x}}{(1-\beta^{2})}$$
$$f'_{y} = \frac{f_{y}}{(1-\beta^{2})}$$
$$f'_{z} = \frac{f'_{z}}{(1-\beta^{2})^{\frac{3}{2}}}$$

Combining these transformations for f with those for E given in equations (16), we obtain (as e is an invariant)

$$m_{o} = \frac{eE_{x}'}{f_{x}'} = \frac{e\left\{E_{x} + \frac{1}{c}\left[\mathbf{V}\times\mathbf{H}\right]_{x}\right\}}{f_{x}}\sqrt{1-\beta^{2}}$$

and a similar equation for  $\frac{eE_{y}'}{f_{y}'}$ ,

 $m_{o} = \frac{eE_{z}'}{f_{z}'} = \frac{eE_{z}}{f_{z}} (1-\beta^{2})^{\frac{3}{2}}$ 

Hence the charge acts, to an observer in K, as if it were subject to a force

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$$\mathbf{F}_{i} = e \left\{ \mathbf{E} + \frac{1}{c} \left[ \mathbf{V} \times \mathbf{H} \right] \right\}$$
(17)

and had a longitudinal mass  $\frac{m_o}{(1-\beta^2)^{\frac{3}{2}}}$  and a transverse mass  $m_o$ 

 $\sqrt{1-\beta^2}$ 

# The Mass of an Electron which has had a Constant Acceleration Relative to its own System for an Infinite Time.

Let  $\phi$  be the constant acceleration of a point relative to its own system. Orient axes so that the acceleration of the point relative to system K is in the positive Z direction, and fix time and space origins so that t=0 and z=0 when the point is at rest relative to K. Let **f** be the acceleration and **v** the velocity of the point relative to K at the time t. Then (1), (2), (3) give at once:

$$f = \phi \left(1 - \beta^2\right)^{\frac{3}{2}} \tag{18}$$
$$\phi t$$

$$B = \frac{c}{\sqrt{1 + \frac{\phi^2 t^2}{2}}}$$
(19)

$$z = \frac{c^{2}}{\phi} \left\{ \sqrt{1 + \frac{\phi^{2}t^{2}}{c^{2}}} - 1 \right\} = \frac{c^{2}}{\phi} \left\{ \frac{1}{\sqrt{1 - \beta^{2}}} - 1 \right\}$$
(20)

Instead of a point consider an infinitesimal straight line  $\overline{OP}$  parallel to the Z axis. The end O has the acceleration  $\phi$ ; we desire to find the acceleration and velocity of the end P at any instant. Consider an infinite number of systems moving in the Z direction relative to K. Then, since  $\overline{OP}$  has had a constant acceleration relative to its own system for an infinite time, the postulate of the relativity of all systems moving with constant velocities demands that the length  $\overline{OP}$  as measured by an observer in K when O is at rest in K shall be the same as the length  $\overline{OP}$  as measured by an observer in any other system when O is at rest in that system. Call this constant length  $d\lambda$ . Let dl be the length  $\overline{OP}$  as measured in K at any time. Then from (1)  $dl = d\lambda \sqrt{1-\beta^2}$  to second order of small quantities.

Now when  $\dot{O}$  is at rest in K, P may have a velocity  $d\mu$ and acceleration  $\phi + d\phi$  in the Z direction.  $d\mu$  will have to be a constant velocity relative to O's system and  $\phi + d\phi$  a constant acceleration relative to O's system for the same reason that  $d\lambda$  is a constant length relative to O's system.

Hence at any time t (20) gives

$$\overline{OP} = d\lambda + \frac{c^2 d\phi}{\phi^2} \left[ 1 - \frac{1}{\sqrt{1 + \frac{\phi^2 t^2}{c^2}}} \right] + \frac{t d\mu}{\sqrt{1 + \frac{\phi^2 t^2}{c^2}}}$$
$$= d\lambda + \frac{c^2 d\phi}{\phi^2} \left[ 1 - \sqrt{1 - \beta^2} \right] + \beta \frac{c d\mu}{\phi}$$

But at any time t

$$\overline{OP} = dl = d\lambda \sqrt{1 - \beta^2}$$

Hence

$$(1 - \sqrt{1 - \beta^2}) \left( d\lambda + \frac{c^2 d\phi}{\phi^2} \right) + \beta \, \frac{c d\mu}{\phi} = 0$$

This equation must be true for all values of  $\beta$ , hence

$$d\mu = 0 \tag{21}$$

$$d\phi = -\frac{\phi^2 d\lambda}{c^2} \tag{22}$$

Integrating (22) for the instant when O is at rest in K we get

$$\phi = \frac{\phi_0}{1 + \frac{z\phi_0}{c^2}} \tag{23}$$

where  $\phi_0$  is  $\phi$  at O.

When  $z = -\frac{c^2}{\phi_0}$ ,  $\phi = \infty$  and v = c.

Next consider an infinitesimal straight line  $\overline{OQ}$  perpendicular to the Z axis. At any time t

$$z_{q} = \frac{c^{2}}{\phi} \left[ \sqrt{1 + \frac{\phi^{2}t^{2}}{c^{2}}} - 1 \right] + \frac{c^{2}d\phi}{\phi^{2}} \left[ 1 - \frac{1}{\sqrt{1 + \frac{\phi^{2}t^{2}}{c^{3}}}} \right] + \sqrt{\frac{td\mu}{1 + \frac{\phi^{2}t^{2}}{c^{2}}}}$$
$$z_{o} = \frac{c^{2}}{\phi} \left[ \sqrt{1 + \frac{\phi^{2}t^{2}}{c^{2}}} - 1 \right]$$

Reasoning in the same way as before, we see that  $\phi + d\phi$ and  $d\mu$  must be constant, and that  $z_q = z_o$  for any value of t. Hence

$$\begin{aligned} d\mu &= 0 \\ d\phi &= 0 \end{aligned} \tag{24}$$

Suppose O to be a charged particle. Then (21) to (25) show that when O is at rest in K every point in O's field will be at rest in K. Hence at every point, **c** must be parallel to **E** and  $\mathbf{c} \times \mathbf{E}$  must be zero. (25) shows that all points in a plane perpendicular to the Z axis must have the same acceleration, and (23) gives this acceleration as a function of z. Since  $\phi$  becomes infinite for  $z = -\frac{c^2}{\phi_0}$  the field comes to an abrupt end at the plane  $z = -\frac{c^2}{\phi_0}$ . In fact it can easily be shown that a light wave travelling in the -z direction must have left the charged particle at a time  $t = -\infty$  in order to have reached any point on the plane  $z = -\frac{c^2}{\phi_0}$  at the time t = 0. As we proceed in the +z direction the acceleration of the field at the instant t = 0 becomes less and less, vanishing at infinity.

Since **c** and **E** have the same direction at any point at the time t = 0, it follows that the tubes of strain are circles of the form

$$\left(\rho - h\right)^2 + \left(z + \frac{c^2}{\phi_o}\right)^2 = h^2 + \frac{c^4}{\phi_o^2}$$

$$x + ky = 0$$
(26)

where  $\rho = \sqrt{x^2 + y^2}$ , and h and k are the parameters. These circles pass through O and have their centers in the plane  $z = -\frac{c^2}{\phi_0}$ .

The equipotential surfaces are spheres of the form

$$x^{*} + y^{*} + \left[z - \left(b - \frac{c^{*}}{\phi_{\circ}}\right)\right]^{*} = b^{*} - \frac{c^{*}}{\phi_{\circ}^{*}}$$
(27)

where b is the parameter.

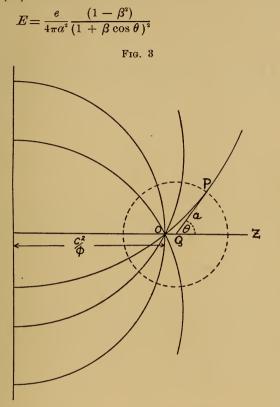
Making use of the fact that in the immediate vicinity of the charged particle equal solid angles must contain equal numbers of tubes of strain, we get the previously derived equations (10) for the strain at any point at the time t = 0.

Let the dotted circle (fig. 3) be an equipotential surface, with center at Q and radius  $\overline{QP} = a$ . Then from (27)

$$a = \sqrt{b^2 - \frac{c^4}{\phi^2}}$$

$$\overline{QQ} = -\frac{c^2}{\phi} + \sqrt{\frac{c^4}{\phi^2} + a^2} = b - \frac{c^2}{\phi}$$

From (10) the ether strain at P is



where  $\theta$  is the angle between  $\overline{QP}$  and the Z axis, and  $c\beta$  is the velocity of the center of strain O at a time  $t = -\frac{a}{c}$ , i. e.

$$\beta = \frac{\frac{\phi_{o}a}{c^{2}}}{\sqrt{1 + \frac{\phi_{o}^{2}a^{2}}{c^{4}}}}$$

In order that there shall be no ether strain inside this equipotential surface, and in order that the ether strain outside shall be that given by (10), it is necessary that there should be a surface distribution of charge given by

$$\sigma = \frac{e}{4\pi a^2} \frac{(1-\beta^2)}{(1+\beta\cos\theta)^2}$$

Hence the resultant force  $\mathbf{F}_2$  on the electron due to its own field is

$$\mathbf{F}_2 = -\frac{e^2 \mathbf{\phi}_0}{6\pi c^2 a} \sqrt{1 + \frac{\mathbf{\phi}_0^2 a^2}{c^4}}$$

If  $\phi$  is the acceleration of that plane perpendicular to the Z axis which cuts the electron into two parts having equal charges,

$$\phi = \phi_{\circ} \sqrt{1 + \frac{\phi_{\circ}^2 a^2}{c^4}}$$

Hence

$$\mathbf{F}_{2} = - \frac{e^{2}}{6\pi c^{2}a} \mathbf{\phi}$$
<sup>(28)</sup>

justifying the assumption made in discussing the effects of ether on matter. The "Ruhmasse"  $m_{\circ}$  is found to be a function only of the charge e and radius a of the electron;

$$m_{\rm o} = \frac{e^2}{6\pi c^2 a} \tag{29}$$

which is exactly the same expression as that for the mass of the quasi-stationary Lorentz electron. However it is to be noted that the force on the electron due to its own field is *not* the product of the mass of the electron by the acceleration of its geometrical center, but the product of the mass by the acceleration of that plane, perpendicular to the direction of acceleration, which cuts the electron into two parts having equal charges.

It can easily be shown that when the electron is in motion relative to K the tubes of strain will be circles with the same centers but larger radii. If t denotes the time measured from the instant when the electron is at rest in K, either earlier or later, the radius of that tube of strain defined by the parameter

h in (26) will be  $\sqrt{h^2 + \frac{c^4}{\phi_0^2} + c^2 t^2}$ . If t is earlier than the instant when the electron is at rest in K, the field will be limited by the plane  $z = ct - \frac{c^2}{\phi_0}$ ; if later, by the plane  $z = -ct - \frac{c^2}{\phi_0}$ . According to (16) both the apparent force on the electron due to the outside field, and the retarding force due to the electron's own field, will remain constant. The acceleration f at any time will be given by (18), where  $c\beta$  is the velocity at the instant considered of that plane, perpendicular to

186

the direction of acceleration, which cuts the electron into two parts having equal charges. The apparent mass, at the same instant, will be  $\frac{m_o}{(1-\beta^2)^{\frac{3}{2}}}$  where  $\beta$  has the same meaning

as above.

In conclusion, it is to be noted that the above method of finding the retarding force due to the electron's own field does not explain, any more than Lorentz's original treatment of the subject did, why the mutual repulsion of the parts of the electron does not cause it to explode.\*

#### Summary.

The electrodynamic equations have been shown to be the kinematical consequences of three fundamental assumptions, to wit:

(a) An ether exists which transmits strains in accordance with the postulate of the relativity of all systems moving with constant velocities;

(b) A charged particle is the center of uniformly diverging tubes of strain;

(c) The mechanical force on a charged particle is equal to the product of the charge on the particle and the ether strain in its immediate vicinity as measured in the charge's system. Thus the number of assumptions underlying the theory of electrodynamics has been reduced to half the number contained in Lorentz's electrodynamic equations.

The field due to an electron which is moving under the influence of a uniform external field has been investigated by a new method, and an exact expression for the mass of such an electron derived.

Sloane Physical Laboratory of Yale University, New Haven, Conn., June 17, 1914.

\*See H. T. Wolff, Ann. d. Physik, xxxvi, p. 1066, 1911, and G. A. Schott, Electromagnetic Radiation, p. 262 et seq.

# SCIENTIFIC INTELLIGENCE.

#### MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. La Méthode Universelle de Fedoroff; by W. W. NIKITIN; translated from the Russian by LOUIS DUPARC and VÉRA DE DERVIES. 2 vols. 516 pp., 113 text figs. and atlas of 8 pls. Paris and Liége, 1914 (Librairie Polytechnique, Ch. Béranger, Éditeur).--This book, as its subtitle indicates, is a systematic description of the procedure of operations necessary to make a determination of the optical constants of minerals. It embodies the original and well-known methods devised by Federov for use with his universal stage for the microscope. These have been described from time to time in the various journals, but this is the first-time that a complete discussion of them has appeared in any language except Russian.

The book includes an Introduction which discusses the general laws of the optics of minerals and then in the succeeding chapters treats of the following subjects : the fundamental problems of mineral optics together with the various graphic methods in use to record their results ; the special apparatus used; determination of the character of the optical ellipsoid; determination of the character of the optical ellipsoid; determinnation of the indices of refraction in thin sections; description of the order of procedure to determine the elements of the ellipsoid of elasticity of biaxial and uniaxial minerals; determination of the birefringence of biaxial and uniaxial minerals and the order of procedure used; determination of the birefringence, optical angle and angle of extinction in the cases where direct observation is not possible.

The book is well and amply illustrated and should form a valuable addition to the mineralogists' working library. W. E. F.

2. Les Hypothèses Cosmogoniques Modernes; par ALEX. VÉRONNET. Pp. 171. Paris, 1914 (Librairie Scientifique A. Hermann et Fils).—In this volume the author gives a review of the hypotheses of Kant and LaPlace with some of the later modifications, followed by his own speculations, which show a fine disregard of evidence. He assigns 2,000,000 years since the temperature at the earth's poles passed below the boiling point. In one or two million years more he predicts that the temperature of even the equator will sink to zero. J. B.

3. La Forme de la Terre et sa Constitution Interne; par ALEX. VÉRONNET. Pp. 32. Paris, 1914 (Librairie Scientifique A. Hermann et Fils).—This pamphlet reviews the advance of knowledge regarding the form of the earth from the time of the ancients. There is little or nothing which is new in it. J. B.

4. Monograph of the Shallow-water Starfishes of the North Pacific Coast, from the Arctic Ocean to California; by A. E. VERRILL.—In the notice of this work, as printed on p. 107 of the July number, the following corrections should have been made: Line 14, for Asterridæ, read Asteriidæ; line 24, for that region, read those regions.

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#### SCIENTIFIC INTELLIGENCE.

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## [FOURTH SERIES.]

# ART. XVIII.—Geology of Bermuda Island; the Igneous Platform; by L. V. PIRSSON.

Introductory.—A brief preliminary paper by the writer and Dr. T. Wayland Vaughan,\* of the United States Geological Survey, stated that a deep boring had been recently made in Bermuda Island, which, after passing through the lime carbonate deposits, was continued for a long distance in volcanic rocks.

The object of the paper was merely to give notice of the investigation and of our being at work in this field. The study of the volcanic rocks, and that part of the general geology of the island connected with them, has been undertaken by the writer, and the results of this work are embodied in the present paper. The investigation of the lime carbonate deposits and their bearing on the later geologic history of the island, especially on its coral reef problems, is being carried out by Doctor Vaughan, assisted by Doctor Jos. A. Cushman, of the United States Geological Survey, who has made a special study of the Foraminifera contained in the samples, and the results of their part of the work will be given at a later date.

Origin of the Boring.—The manner in which this deep boring was put down in Bermuda Island has been stated in the preliminary paper, but for convenience may be briefly recapitulated here. It was undertaken by the owners of the Princess Hotel, a large modern house which attracts many visitors, especially from the eastern American cities, in the winter months. The managers have found the problem of maintaining a supply of fresh water adequate to the needs of such an establishment at times difficult, since in Bermuda the chief dependence is on rainfall stored in cisterns. In some manner the owners were persuaded that it might be worth while to risk the capital nec-

#### \*This Journal, xxxvi, p. 70, 1913.

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 225.—Sept., 1914. 14 essary to undertake a deep boring in hopes of obtaining an additional supply. This hope was, of course, not realized, only salt water being met with in the course of the drilling. After carrying the bore-hole down to 1,413 feet, it was abandoned while in solid lava. The writer, through the courtesy of one of the managers of the hotel, Mr. F. L. Howe, while making a brief visit in Bermuda in April, 1912, had the opportunity of inspecting this well when it had attained a depth of about 800 feet, and of seeing the material which was then being brought up. Later he was presented with a complete set of specimens illustrating the geologic section made by the well, accompanied by a plan of the well drawn to scale and many valuable notes. Owing to Mr. Howe's interest in the scientific data which the well might afford, careful records were kept and samples taken as the work progressed. One set of these, which came into possession of the United States National Museum through the American Consul at Hamilton, Bermuda, Mr. W. Maxwell Greene, he has also had the opportunity of freely using, through the courtesy of Doctor Richard Rathbun, assistant secretary in charge. In addition, Professor R. A. Daly, of Harvard University, has kindly permitted the use of some thin sections of material obtained by him. To these gentlemen, and especially to Mr. Howe, we desire to express our obligations and thanks in this place.

Situation and Nature of the Boring.—The site of the well is in Southampton parish on the slope of a hill about a mile west of the lighthouse on Gibbs' Hill. Why this particular spot was selected the writer has been unable to learn, but it was probably due to some appearance in the topography which led the projectors to believe that this was the most favorable spot. It is 135 feet above sea-level. Unfortunately, for scientific purposes, the boring was not made with a diamond drill by which a solid core is obtained, but by one of a churn drill type, in which the drill is raised and dropped, the work being done by a steam engine and suitable machinery. This reduces the rock to a powder, whose fineness depends, in a measure, on the nature of the material encountered. Down to 785 feet, until solid lava was reached, the well throughout the depth of soft material was cased; an outer casing of 8 inches diameter extending down to 695 feet, while through this was passed an inner casing down to 785 feet with a diameter of  $6\frac{5}{8}$  inches. The caliber of the uncased part in the firm lava is 6 inches down to 1,080 feet; below this to the bottom, 1,413 feet, it is  $4\frac{1}{5}$  inches. Since the casing, however, was placed, very naturally, only in the zone of soft rock, the material obtained in this way, though containing pebbles and fragments, was also decomposed, and, therefore, as will be seen in the petrologic portion of this paper, ill fitted for petrographic study. From

### the Igneous Platform.

the uncased part in firm lava the samples are all powders, varying from a medium to a very fine sand in size of grain.

As the boring progressed below sea-level no fresh water was encountered, but at various levels salt water came into the well. According to the notes furnished by Mr. Howe, this occurred several times between 785 and 1,000 feet, and again between 1325 and 1385 feet. The significance of this will be discussed later.

#### List and Nature of the Samples.

The samples of the material met in the course of drilling the well, according to the labels and description, are indicated as representing the nature of the rock between specified points. The distance between these points is given in the accompanying table. Possibly each sample was taken at a certain time and at a definite point, but it may have been so selected as to give an average between points. In general, their homo-geneous appearance indicates that if the latter is the case they are fairly representative, in most of them, of the stretch of rock between the given points, though in the case of the firm lavas below 700 feet, which, as will be seen, show a rather monotonous regularity in their appearance, the petrographic study has proved in several cases that two rocks of somewhat different nature are mingled in the same sample. In all, 48 samples comprise the collection, and the stretches which they represent and their general character is briefly shown in the appended table.

List	of	Samples	of	Bermuda	Well.
0.04	S	ft mbits	D	annan da 1	in a na

NO.	1,	61 1	Feet.	Soft	white	Bermuda	lime-ro	ck.	
66	2,	110	66	"	"	66	66		
"	3,	241	"	66	66	66	66		
"	4.					66	66		
66	5,	265	66	"	66	66	66		
"		286	"	66	66	66	66		
66	7					66	66		
"	8,	341	"	66	66	"	_66		
"						wish brow	vn, clay	-like, po	owder.
"		393-		" "		nish crum			
"		480-		"	Light	brown,	compac		
					wit	th calcite 1	balls.		
"	12,	485-	505	66		n fragn emble dec			within,
"	13,	505-	518	66	Brow	n fragn emble dec	nents,	gray	within,
"	14,	<b>5</b> 18-	544	44		n, earthy :			
"		544-		66	Brow	n, earthy, nts ; calci	with s	mall gra	ay frag-
"	16,	550-	554	"	Brow	n, earthy, nts.			ay frag-

	1	9	2	L.	V.	P	irsson–	-Geology	of	Bermuda	Island	:
--	---	---	---	----	----	---	---------	----------	----	---------	--------	---

No.	17,	554- 573	Feet.	Brown, earthy, with soft gray frag- ments.
"	18,	573- 574	"	Soft, blackish gray fragments, filled with small calcite balls.
66	19,	574- 578	"	Brown, earthy fragments, filled with
	20,	578- 583	"	small calcite balls. Brown, earthy fragments, filled with
"	21,	583- 645	"	small calcite balls. Blackish gray particles, soft, mixed
44	22,	645- 665	"	with much white calcite. Lead gray particles, compact, soft, in-
"	23,	665- 695	"	cluding white calcite. Fragments of a very dense lead-gray lava, soft and brown in places on
"	24,	695- 708	"	the surface. Lead-gray dense lava, some brownish ;
66	05	500 514	66	amygdaloidal.
	25,	708- 714		Dense blackish-gray lava.
	26,	714-716		
	27,	716-738		Compact lead-gray lava.
66	28,	738- 744	66	· · · · · · · · · · · · · · · · · · ·
	29,	744- 815		· · · · · · · · · · · · · · · · · · ·
"	30,	815- 835	66	
	31,	835- 860	"	Dense black lava, somewhat amygda- loidal.
"	32,	860 - 920	66	Compact lead-gray lava.
66	33,	920 - 975	" "	
66	34,	975 - 995	"	"
66	35,	995 - 1002	"	،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،،
64	36,	1002 - 1022	66	Dense black lava, amygdaloidal.
66	37,	1022 - 1045	" "	Compact lead-gray lava.
"	38,	1045-1075	"	Dense black lava, very amygdaloidal, some gray rounded grains.
"	39.	1075-1110	46	Compact lead-gray lava.
46		1110-1140	"	Dense black lava, somewhat amygda-
66			66	loidal (analyzed).
	· · · ·	1140-1200		Compact lead-gray lava.
	42,	1200-1255		Dense blackish-gray lava, somewhat amygdaloidal.
66	43,	1255-1280	"	Compact blackish-gray lava, slightly amvdaloidal.
"	44,	1280-1325	"	Very dense blackish-gray lava, slightly amvgdaloidal.
"	45,	1325–1360	"	Very dense blackish-gray lava, slightly amygdaloidal.
" "	46,	1360-1385	"	Very dense blackish-gray lava, slightly
"	47,	1385-1400	"	amygdaloidal. Very dense blackish-gray lava, slightly
٤,	48,	1400-1413	"	amygdaloidal. Very dense blackish-gray lava, slightly
		Bottom of	well	amygdaloidal.

Bottom of well.

## the Igneous Platform.

F	'n	G	1	L	

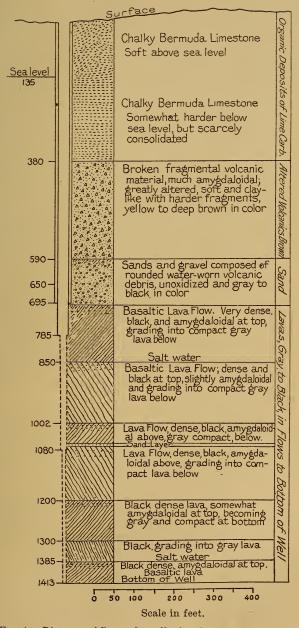


FIG. 1. Diagram of Bermuda well, showing geologic section.

The various facts which are embodied in the foregoing table, together with those covering the dimensions of the boring, may be graphically shown in the accompanying figure (fig. 1). From this it is easy to see that the boring has penetrated three zones of essentially different materials, the natures of which are indicated on the side of the diagram, as follows: first, the soft chalky Bermuda limestones; second, a layer of soft oxidized volcanic matter, yellow to brown in color; and third, firm compact lavas, dark gray in color, which persist to the bottom of the well. Each of these three zones has been found to have particular features of its own, which when subjected to study have proved to be of interest in throwing light on the geologic history of the island. That of the first, the chalky limestones, has yielded information concerning the work of organic life and the more recent phases of that history. The study of the oxidized and unoxidized layers of volcanics, with the conclusions to be drawn from them, will be given in the following part of this paper, and there is appended the results of a petrographic investigation, carried so far as the nature of the material permitted.

#### Zone of Oxidized Material.

This extends from where the Bermuda limestone ends down to about 600 feet below the surface. Its general color is a leather brown varying from a pale buff-yellow to dark brown. In some cases the inner portion of fragments is a brownishgray to lead-gray. In the sample taken at 573–574 feet the color is quite different, a dark blackish-gray; on either side of this thin layer the regular brown color obtains and its significance will be discussed later.

All the samples consist of a mixture of sand or earthy powder, mingled with fragments, which in some cases are as large as hickory nuts. The material is soft; in some cases it can be readily rubbed between the fingers, in others it is not so friable but can be easily cut or scraped with the finger-nail; the hardest pieces can be readily cut with a knife.

The series begins with a very fine-textured material of a buff color, which is in altered lava; some small white specks in it may be decomposed phenocrysts. This is succeeded from 393-485 feet by fragmental material which is very evidently a decomposed amygdaloid. The larger pieces still retain the amygdaloidal structure and are filled with amygdules the size of fine shot; mingled with the debris of this are many larger separated amygdules of calcite. From 485-518 feet the material is different; the amygdaloidal structure is wanting, the fragments are of a fine dense texture, and are evidently a highly altered, very compact lava. While they are outwardly brown, they are within of a lead-gray; sometimes of a deep Indian-red, the color of ferric oxide. Some of them show occasional angular inclusions of a soft whitish clay, apparently from their shape altered phenocrysts. Some of these fragments are rounded, ovoid to sub-angular, and appear distinctly like water-worn pebbles. They are about the size of a hazel nut. That the rounded form is a natural one is shown by the fact that the pebbles have a thin outer coating, or crust, of brown colored substance; when this is broken into, as remarked above, they are lead-gray within. This would indicate that the pebble had altered after it had received its shape.

The material from 518–573 feet, both the fragments and fine debris, is a rich earth-brown, and resembles indeed clots of dried earth ; some of it is full of harder, more compact pieces, whose shape and nature indicate small pebbles of decomposed lava, while others, which are filled with rather regularly-spaced calcite spheroids the size of shot, are evidently pieces of altered amygdaloid. The brown earth acts as a cement in holding the crumbly fragments together.

The thin layer, 573–574 feet, is the blackish one mentioned above; it is quite clearly an altered amygdaloid. The dark, compact mass is filled with whitish to pale brown calcite balls, varying in size from fine shot to peas. Its significance is discussed beyond.

From 574 to 583 the brown earthy material recurs filled with calcite ovoids, and hence a broken down and altered amygdaloid. It is more amygdaloidal than any of the preceding samples.

#### Zone of Unoxidized Material.

At 583 feet a change occurs, the samples are no longer brown and weathered, but blackish to dark or medium gray in color, and it is clear that, whatever opinion may be held as to the cause of this difference, they have been subjected to a different set of conditions from those which affected the foregoing material. There is one slight exception to this rule, as noted below.

The sample taken between 583 and 645 feet is evidently a broken-up amygdaloid; it consists of a mixture in nearly equal parts of whitish calcite spheroids the size of fine to coarse shot, and small particles of a compact gray lava of the same size. There are also a number of brown and reddish altered fragments in it. Although it might be assumed that the crushing of the amygdaloid was done by the drill, it is believed that the latter merely penetrated a layer of amygdaloidal material previously reduced to a coarse sandy consistency by some other agency. The evidence for this consists in the fact that the particles of dense lava do not show the sharp angular forms and splintery fracture surfaces which would be seen in the latter case, but are distinctly dull of surface, rounded to sub-angular, and with the pitted, dimpled texture caused by repeated impacts, and characteristic of water-worn material. It has, in other words, the aspect of a beach sand composed of volcanic material laid down in the sea before surficial oxidizing agencies had had an opportunity to act, to any great extent, upon it.

Sample 22, from 645 to 665 feet, is quite similar, save that the amygdaloidal character is nearly wanting, and the particles are nearly all lava. In 23, from 665 to 695 feet, the material consists of a few large fragments up to one and-a-half inches long; evidently in part angular chips from some larger piece: these are brownish and partly oxidized on the surface of cracks. Other pieces of a lead-gray color are not oxidized, and are rounded to sub-angular and with pebbly surfaces. They appear water-worn.

Number 24, from 695 to 708 feet, consists of two things : gray to brown water-worn, rounded pebbles and sand of more or less altered lava and whitish amygdules, mingled with sharp angular splintery chips, often showing somewhat conchoidal fracture surfaces, of a dense hard, grayish-black lava. It is evident that in this short stretch the drill passed through the sands and gravels recorded above and encountered for the first time solid lava in place. This is shown also by the fact that at this point, as may be seen by reference to the diagram, fig. 1, it was found unnecessary to use any longer a casing for the well, as the hole was now in solid rock. The bottom of the fragmental deposited material may then be set at approximately 700 feet.

From here to the bottom of the well the material is practically of a uniform and monotonous nature, finely-comminuted rock, such as would be obtained by pounding a dense compact lava in a mortar. The tiny fragments are sharply angular with splintery shapes and surfaces. The only variations that can be seen among them is that some are darker in color, almost black, others lead-gray, and the black samples are in the finer powder, owing to the greater compactness and hardness of the rock. They also contain in several instances, as shown on the diagram, more or less amygdaloidal material, consisting of small calcite balls the size of fine shot. This combination of greater compactness of texture and the amygdaloidal condition is taken to indicate the upper surface of lava flows successively penetrated.

The one exception to this general uniformity of the samples,

from 25 to 48 inclusive, is seen in number 38, which, in addition to consisting of the tiny, angular chips characteristic of a triturated rock, contains also grains which are distinctly rounded as by water; and such grains are of a different color and appearance, being light gray to brown, and distinctly oxidized. It is assumed, therefore, that in this stretch from 1,045-1,075feet a bed of sand was encountered, showing deposits which had been worn upon a beach.

#### Geological Conclusions.

The most striking general feature of the series of samples of volcanic material below the limestones, which end at 250 feet below sea-level, is the thoroughly and deeply oxidized condition of those above 600 feet in depth, compared with the little or entirely unoxidized nature of those below this point. Thev are all of them far below the present sea-level, so that they appear to be subject to similar conditions so far as their present situation is concerned. Nor can we find an explanation in the idea that this difference may be due to structure of some kind; that the oxidized material represents originally fragmental volcanics, while the unoxidized is from solid lava flows, because in number 18 we find a thin layer of unoxidized fragmental material lying in the midst of the oxidized zone, and below 600 feet we first pass through a considerable layer of unoxidized fragmental sandy deposit before striking the solid lava. This makes it evident that the material of the oxidized zone has, at some former period in its history, been subjected to conditions quite different from those now obtaining, and which have affected the lower zone. The brown color and earthy appearance at once suggest the work of the atmosphere, and the contrast between the two that the lower zone, having been always below sea-level, its rocks have been protected from weathering, and have been subjected only to such action as seawater is able to exert. This action, so far as the writer has been able to discover, has not been definitely studied. There seems to be general agreement, however, that rocks which are protected by sea-water from the atmosphere will not suffer oxidation and may even remain unchanged. More than half a century ago J. D. Dana\* observed the protective effect of sea-water in preventing the oxidation of basalt on the south coast of Australia. He says "it is a general and important fact that a rock which alters rapidly when exposed to the united action of air and water, is wholly unchanged when immersed in water, or exposed to a constant wetting by the surf." In commenting on this, Merrill<sup>+</sup> says: "While no exception can

\* Reports of the Wilkes Exploring Expedition, Geology, p. 514. † G. P. Merrill, Rocks, Rock-Weathering, and Soils, p. 239.

be taken to the conclusion regarding those rocks wholly immersed, the question naturally arises in one's mind if the absence of decomposition products in those rocks constantly wetted by the surf and in many stream beds may not be due, in part at least, to erosion, as noted above."

Thus if the rocks are entirely immersed, in Merrill's opinion, oxidation will be prevented.

As will be shown later under the petrographic description of the Bermuda lava, this basalt when wholly immersed in seawater does not remain unchanged, but the alteration is a very different one from the ordinary decay and oxidation of weathering.

Joly\* tried the action of both fresh and salt water on basalt, but his experiments had the object of ascertaining its relative solubility in the two fluids. He does not mention any results of oxidation, and one must conclude that no notable effect of this kind occurred.

Chamberlin, t in mentioning this subject, says: "In the main, the ocean waters protect the sediments from weathering and similar changes, except as organic matter buried with them induces change."

The reports of the Challenger Expedition offer contributory though not direct evidence pointing to the same conclusion. In those parts of the ocean near the lands where red clays occur they are regarded as products of land waste, while, as Chamberlin remarks, # "the blue muds indicate lack of oxidation, or perhaps deoxidation."

The red clay on the floors of the abyssal ocean basins would appear to be an exception, but opinion regarding the origin of this deposit is still unsettled, some holding it chiefly as the remains of hard parts of organisms, while others, who have most studied it, believe it to be chiefly of volcanic origin. It has also been suggested that it may be largely eolian dust. In the latter case, as a product of land waste it would be oxidized, and it is to be noted that if of volcanic origin it may also have been oxidized before settling into the sea-water. It may also be suggested that it may be partly cosmic dust in origin and in some part metallic in character. Particles of metallic iron might be oxidized passing through the atmosphere, or become so later by reacting with water, and give the red coloration. The chemistry of the sea is an extremely large and complex

subject, and it is more than probable that the processes taking

‡Loc. cit., p. 363.

<sup>\*</sup> J. Joly : Some Experiments on Denudation by Solution in Fresh and Salt Water. Proc. Roy. Irish Acad., xxiv, Sec. A., pp. 21-23, 1902.

<sup>+</sup> Chamberlin and Salisbury, Geology, vol. i, p, 360, 1904.

place in one part of it may be very different from those in another part. As the researches of Dittmars and others have shown, the gases of the air are dissolved in sea-water and it contains oxygen in considerable quantity, even to considerable depths. At first thought this might appear to give sea-water a capacity for oxidation, but in considering the matter the effect of organic life must be taken into account. Thus Buchanan\* has shown that in the seas about Scotland in the bottom deposits sulphur and sulphides are being formed, and this process reduces the oxidized products of land waste to blue muds. Various other instances might be cited to show that at the bottom in shallower waters, where life abounds, reduction, not oxidation, is taking place. In some waters, as in those of the Black Sea, a considerable amount of hydrogen sulphide is found in solution, which has been ascribed to the action of bacterial life. It seems, therefore, most probable, if not certain, that in shallow waters along coasts at the bottom there would be not only no oxidation of buried lavas and sediments, but a tendency to a reducing action. That deposited sediments are not always reduced shows merely that the deposit is too rapid and the action too feeble to convert them.

If it be admitted, as suggested above, that the oxidized material represents the product of land waste, then the conclusion follows that Bermuda was once an island, composed of volcanic rocks rising above the level of the sea, which has been entirely cut away by the erosive action of the waves. Under this conception everything disclosed by the boring falls logically into place. At the bottom and up to 700 feet lie the original lava flows which built up the cone, unoxidized because the rocks have been protected by the sea from the work of the atmosphere. Above them comes a relatively thin band of deposit, perhaps 75 feet thick, consisting of water-worn, but also unoxidized or but little oxidized debris of volcanic rock, sands, and gravels. This is what we should naturally expect, for this represents the first attack of the waves upon the upward growing volcano, or the early material eroded by them from the new land. Some of the particles of the deposit may practically have never been exposed to the action of the atmosphere, while others were affected by it only a short period of time before being carried out from the beach and deposited under water.

As time advances, however, there must come a change. The lighter, more porous, less firm upper portion of the lava flows, indicated by the amygdaloidal structures, and which

\* British Assoc., 1881, p. 584.

were also probably covered with more or less loose debris which would be first attacked by the waves and fed to them by the drainage, would give place to more solid, resistant lavas, and with increasing progress to thicker and thicker masses. The rate of erosion would then be, comparatively, greatly retarded, and the action of the atmosphere would have time to make itself felt upon the material of the land surface before it was eroded by the waves and buried under the sea. Consequently, we should expect the deposit from then on to exhibit the oxidation characteristic of land waste, which is, in fact, the chief feature of the samples from 590 feet up to 380 feet, where the limestones begin.

In the history, however, thus briefly sketched two episodes occurred, which are of interest in this connection and should not be forgotten. It relates to samples numbered 38 and 18. Number 38 is from a depth of 1,045 to 1,075 feet, and, while much of it is splintery rock broken by the drill, it also contains a large proportion of neatly-rounded water-worn grains of lava, some of which are more or less weathered, together with small specks of red oxidation products of iron ore. This must represent one of the earlier stages of the emergence of the growing volcano above the sea and the attack upon it by the waves. As in the higher level at 700 feet, mentioned above, there was no serious or deep weathering before the material was washed out and deposited on the lower slopes of the volcanic mass beneath the water. This was then covered by fresh outflows of lava as the formation of the cone continued.

In a similar manner the thin layer of number 18, 573-574 feet, which consists of unoxidized blackish material in the midst of the weathered land-waste, indicates a renewal of volcanic activity and the wearing and washing down of this new volcanic product. It may, therefore, represent the last outbreak that occurred before the volcano became extinct.

Tuffs and Breccias.—An important feature of the discussion of the Bermuda volcano is the question whether it was wholly a lava cone or a mingling of flows with tuffs and breccias. This problem, obviously, cannot be definitely answered. So far as the evidence goes no tuffs or breccias, it is thought, are indicated. Certainly from 700 feet down the samples with one exception appear to be merely those of crushed, solid rock. If the boring had been made by a diamond drill with the production of a solid core it would be of course much easier to determine whether tuffs and breccias were present, through the section given us by the well. The pounding up of the rocks by the churn drill makes it much more difficult. It seems fairly safe to say, however, as mentioned above, that none are present from 700 feet down. It is also thought that the samples from this point up are composed wholly of the oxidized waste of lavas similar to those lower The reason for this belief is that where these samples down. contain fragments which are obviously not chips broken by the drill but are, so to speak, automorphic, as many of them are, such fragments do not appear like lapilli. They are very prevalently fragments of an amygdaloid or of solid lava, often smoothly rounded, as if by beach rolling, as described above. Amygdaloid may occur among breccias, but it is certainly much more characteristic of the upper part of lava flows. No pieces having an empty vesicular structure have been observed. Judging from these facts, it is thought that the balance of evidence points to the absence of the products of explosive volcanic activity. Moreover, the very basic, basaltic nature of most of the lavas, which is shown later under their petrographic description, agrees with this idea, for the magmas which furnish such rocks are usually very fluid and their discharge, as is well known, is far less apt to be attended with explosive phenomena than more siliceous felsic ones.

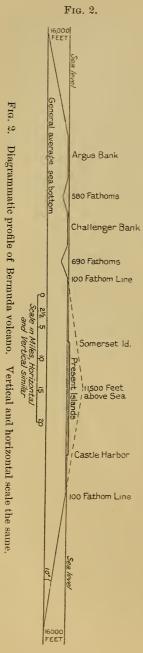
If it be true, then, that the Bermuda volcano is mainly or wholly a lava cone as indicated, this would have an important bearing on the topographic form of the original island, from the fact that lava cones are relatively rather flat with low angles of slope, compared with tuff and breccia cones, which are steep and high.

Form and size of the Bermuda Volcano.-Bermuda Island has been thought to be situated upon the apex of a volcanic mountain mass, and Verrill\* has made some suggestions as to its size, slopes, and probable history, but until the present boring was undertaken, there have been no direct facts which would prove this. Other than the statements and suggestions of Verrill, so far as the writer is aware, there has been no attempt made to consider its form and size in this connection. It would seem of interest to do this to obtain some data for comparison with other volcanic masses of a similar nature and situation.

Alexander Agassiz<sup>†</sup> has given a partial profile of Bermuda running in a northeast and southwest direction and slightly bent, so that it passes through the greatest length of the island and then through the Argus and Challenger Banks to the southwest. In this profile the vertical scale is much exag-

\* Bermuda Islands, Pt. IV, Geology and Paleontology, Trans. Conn. Acad. Arts and Sci., vol. xii, 1907, p. 55. † Visit to the Bermudas in March, 1894, Bull. Mus. Comp. Zool., vol. xxvi,

No. 2, 1895.



The writer has redrawn this gerated. profile from the Bermuda chart, making the vertical and horizontal scales the same in order to show the mass in its true proportions. It has also been completed by carrying the slopes down to the ocean floor, for which a mean depth of about 16,000 feet has been assumed. The resultant profile is shown in fig. 2. All minor irregularities of course disappear when so small a scale is used. It is not pretended that this profile has more than approximate accuracy, but it serves its purpose here quite as well in considering the main features of the old volcano as a more correct one drawn on a larger scale. In fig. 3 is given a rough sketch map which shows the general form of the volcanic mass. This indicates that on the sea floor the base extends in a northeast and southwest direction some 90 miles as an elongate ridge, whose greatest breadth may be some 25-30 miles. At the sea-level it has been cut away to a platform, which at the 100 fathom line has a length of about 32 miles and a width of 16 miles. Southwest from it are the Argus and Challenger Banks, which are rudely circular in shape, about 5-6 miles in diameter, about the same distance from each other, and about 4 miles from the main platform. From the depth of the valleys which separate them from the main mass and from each other it seems clear that they represent subordinate volcanic cones which have also been cut away The constructed by action of the sea. profile gives for the main outer slopes angles of 12 degrees. The soundings on the Bermuda chart, which give data for the slopes, are as follows, measured in nautical miles (6080 feet) from the 100 fathom line in each case:

S.S.W.	Argus	Bank	8	miles	1870	fathoms	= 12	•
S.E.	ũ	"	13	"	2250	66	= 9	0
N.W.	Challenger	"	5.	5"	2175	66	= 23	0
S.E.	"	66	11	"	1820	"	= 10	0
S.E.	Main	"	6	66	1240	"	= 11	0
N.E.	66	66	6	"	1260	"	= 12	0
N.W.	"	66	4	66	1370	"	= 18	0

FIG.	3.
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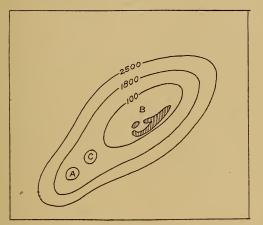


FIG. 3. Sketch map of the Bermuda volcanic mass. A, Argus Bank; C, Challenger Bank; B, Bermuda Bank, on which the present islands are shown. Numbers are depths in fathoms.

The only point where information is wanting is the west slope of the Argus Bank. On the southwest, south, southeast, east, northeast, and north sides of the mass the slope is from 10-12 degrees; the northwest slope is steeper, reaching its maximum of 23 degrees off the Challenger Bank. The soundings also show variations of slope in places, but these are minor irregularities which need not be considered here. On the north side the main mountain falls off 1,250 fathoms in 6 miles, a slope of 14 degrees; the Argus Bank 1,270 fathoms in 10 miles, a slope of 9 degrees. The low angles shown are indicative of a cone built chiefly of basaltic lavas rather than of felsic breccias and tuffs, and this accords with the results of the boring and with the slopes and petrographic character of other great extrusive piles in mid-ocean, such as Hawaii and Samoa. It is not intended by this to deny the possibility that breccias and tuffs may make up a considerable portion of the mass; the steeper angles of slope of the smaller Argus and Challenger volcanoes in places indicate that they may be largely constructed of fragmental material; only that, taking everything into consideration, it seems most probable that the mass as a whole is composed chiefly of basaltic lavas.

If we assume that the main platform represents the truncated top of a single volcanic peak and continue the profile upward by the dotted lines shown in figure 2, then this peak would have risen 11,500 feet above the present sea-level, or about 26,000 feet above its base on the sea floor. This compares with Hawaii, whose peaks reach a height of 30,000 feet above the ocean bottom, and Samoa, 25,000 feet. It is quite as probable, however, that this platform was cut through several coalescing volcanic cones and in this case the height would not have been so great.

The definite alignment of the Bermuda volcanoes is similar to that observed in numbers of volcanic island groups in the Pacific and suggests their situation upon a great fissure or fault-line in the lithosphere. If the whole Bermuda mass is composed entirely of volcanic material, as seems probable from its isolated position, it represents an extrusion of at least, roughly, 2,500 cubic miles of igneous magma, and it is, therefore, one of the larger volcanic occurrences of the world.

The debris of the land that has been cut away by atmospheric erosion and the work of the sea must have been in considerable part distributed over the flanks of the volcano. The coarsest particles of it would lie nearest to the shore and thus highest up. This is indicated by the character of the material found in the boring, which seems to have been largely gravel and coarse sand, judging by the size of the grains and pebbles. This of course would tend to broaden somewhat the submarine platform and increase its size, but it has not been a very considerable factor in this direction, for the depth of the whole deposit is only about 300 feet and the point where the boring was made is one where it might reasonably be assumed to be as thick as anywhere over the platform. Compared with the bulk of the mass such a deposit would be a mere skin over its truncated top and flanks. This assumption, if correct, would tend to suggest that the former land was composed rather of several lower, smaller cones than the huge one indicated in the profile.

The present depth of water over the different banks and the extent to which the bore penetrates before passing through the limestones into water-worn debris seems to indicate a change in water level of perhaps 200 feet since the time when the waves were attacking the coast line of the former island. This point will be considered more fully by Doctor Vaughan.

It has been considered, in drawing the section, that where amygdaloidal lava was encountered, this would indicate the upper surface of a flow. According to this, seven flows are shown with a total thickness of 700 feet. The average thickness would be of course 100 feet for each flow, which is not excessive, but one would be 150 feet. There were probably more flows than this, some of which were not amygdaloidal at the top and which could not, therefore, be differentiated in the crushed rock of the samples; and this is indicated by petrographic variations within single samples. In general it is noted that the lava of the upper part of a flow is denser and darker, giving way to lighter colored, lead-gray, less compact material below.

Mr. Howe's notes show that in two places, after the lava in place was penetrated, salt water entered the well. These places, as the section shows, are at points between lava flows and thus a natural place in which to expect it. For along such surfaces of contact and especially on account of the porous, vesicular, broken nature of the upper part of the lower flow, the water would be able to penetrate rather than through the solid middle portion of a flow.

Geological Age of the Volcano.-The identification of the foraminifera from the Bermuda well by Doctor Cushman and the study of the calcareous deposits by Doctor Vaughan have led the latter, in a communication which he has kindly sent me in advance of his own publications, to assign the Eocene, or lower Oligocene, as the time when they began to accumulate on the submerged volcanic basement. The submergence progressed until the basement, in, probably, Miocene time, was entirely blanketed by calcareous deposits 100 feet thick. He feels, therefore, that it appears safe to assign an Eocene, or pre-Eocene, age to the Bermudian volcanic activity. The great size of the extrusive mass has been previously described and to accumulate this huge pile a period of time, long perhaps even from the geologic standpoint, must have been required and another long interval to cut away completely the island masses and reduce them to the platforms that now exist. Verrill\* suggests that the volcano was completed or formed during the Triassic or at its close and correlates it with the igneous outflows which characterized this period along the North American coast. It may indeed date from this time, but it should be observed that the diabases of the Triassic are a feature of the border of an entirely different earth-segment from the one on which the Bermuda volcano is situated, one which has had a very different geologic history, and that they made their appearance while the region was undergoing tectonic movements of which we have no knowledge in the Bermuda area. We have indeed no direct way of knowing the period in which volcanic activity has begun in the case of sub-

\* Op. cit. p. 53.

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 225.—Sept., 1914. 15 marine volcanoes. Provided that one believes in the permanence of the deep ocean basins, it is clear that volcanoes situated on their floors, after they had been cut down to sea-level, if they once projected above it, would be protected from further erosion and would remain indefinitely as protuberant masses.

Coral Island Platforms.—It appears to the writer that what has been learned regarding the history of the Bermuda volcano has an important bearing on the question of the way in which the platforms on which coral islands, barrier reefs and atolls are situated, have been formed. There is of course nothing new in the idea that these may be volcanic in origin, only in Bermuda we have once more a positive demonstration of the fact. We have also seen that, provided the volcanic masses are of sufficient antiquity, they may, even though of great size, have been reduced to sea-level; furnishing platforms of wide extent. As mentioned above, such masses reduced to sea-level would continue to project from the ocean abysses indefinitely and many of them may be of great geologic age. There is nothing in the mere size of any of the atolls of the Pacific which would preclude their being placed on the stumps of former volcanic masses; it is not intended to assert by this that the foundation in every case is necessarily a volcanic one. If such masses have once been brought down to sea-level and continue to exist and that level changes within limits from time to time by warpings in different places of the sea floor, or by an accumulation of ice on the lands and its melting, as suggested by Daly,\* then conditions of shallow water over them may be established suitable for their colonization by those organisms concerned in the production of the so-called coral reefs, which may be formed under the conditions postulated by Vaughan.

This paper will be followed by one dealing with the petrography of the igneous rocks.

Sheffield Scientific School of Yale University, New Haven, Conn., April, 1914.

> \* This Journal, vol. xxx, p. 297, 1910. † Jour. Wash. Acad. Sci., vol. iv, p. 26, 1914.

# ART. XIX.—The Ternary System: Diopside—Forsterite— Silica; by N. L. BOWEN.

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GENERAL SUMMARY

#### INTRODUCTION.

THE system dealt with in the present paper is a part of the more general ternary system CaO-MgO-SiO<sub>2</sub>, and is that part which is probably of greatest interest to the petrologist, since,

among the solid phases, there are representatives of the important rock-forming mineral groups, the pyroxenes and the olivines.

The compound diopside,  $CaMgSi_2O_e$ , was studied formerly at this laboratory<sup>\*</sup> in an investigation of the system  $CaSiO_g$ -MgSiO<sub>s</sub>. This system was treated as binary, but recent work<sup>†</sup> has shown that the compound MgSiO<sub>s</sub> is unstable at its melting point and can itself be treated only as part of a two-component system. It is necessary, therefore, to treat the system  $CaSiO_s$ -MgSiO<sub>s</sub>, or at least the portion of it CaMgSi<sub>2</sub>O<sub>e</sub>-MgSiO<sub>s</sub>, as a part of the ternary system CaMgSi<sub>2</sub>O<sub>e</sub>-Mg<sub>2</sub>SiO<sub>4</sub>-SiO<sub>2</sub>. The present paper, which deals with this ternary system, is, therefore, essentially a revision of former work on CaMgSi<sub>2</sub>O<sub>e</sub> and MgSiO<sub>3</sub>, in which it has been found necessary to study completely the field of the ternary system.

#### METHOD OF WORKING.

The mixtures used were made up from specially purified silica, calcium carbonate, and magnesia obtained by igniting the carbonate to constant weight. Equilibrium was studied by the method of quenching, which consists in holding a small charge of known composition at a measured temperature for a period of time and then chilling instantly to room temperature. The charge is then examined under the microscope and the phases present are determined.

The phases found represent equilibrium at the furnace temperature for inert bodies like the silicates, unless there exists a readily reversible inversion in a solid phase, in which case the low temperature form may be found under the microscope whereas the high temperature form existed in the furnace. In such cases the solid phase nearly always gives evidence of having passed through this inversion.

The furnace used was a platinum resistance furnace and the temperature was measured by means of a Pt: Pt-Rh thermoelement which was calibrated by quenching charges of pure artificial minerals of known melting-point.

One point, however, namely the melting-point of the compound forsterite, was determined by observing directly the phenomenon of melting in an iridium furnace, the temperature being measured optically. This method of determining the temperature at which a mixture becomes visibly fluent is satisfactory for fixing the melting temperature of a compound or a eutectic when these form thin liquids, but cannot be relied

\* Allen, White, Wright and Larsen : Diopside and Its Relation to Calcium and Magnesium Metasilicates, this Journal (4), xxvii, 1, 1909.

+ Bowen and Andersen, this Journal (4), xxxvii, 487, 1914.

upon in determining points on the liquidus intermediate between a eutectic and a compound. Some investigators<sup>\*</sup> have, however, used this method on these intermediate compositions, although a little consideration would make it clear that such compositions will soften either at the eutectic point or at some temperature intermediate between the eutectic and the liquidus point, but always well below the liquidus.

#### THE BINARY SYSTEMS.

The results obtained in the three binary systems will first be presented.

#### The System Mg<sub>2</sub>SiO<sub>4</sub>-SiO<sub>2</sub>.

The system  $Mg_{2}SiO_{4}$ -SiO<sub>2</sub> has been described in a former publication which deals with the system MgO-SiO<sub>2</sub>.<sup>+</sup> The equilibrium diagram is given in fig. 1. The principal feature of this system is the fact that the compound  $MgSiO_{4}$  (clinoenstatite) is unstable at its melting-point, breaking up at 1557° into liquid and forsterite. The details of the system are given in the paper referred to.

#### The System CaMgSi<sub>2</sub>O<sub>6</sub>-SiO<sub>2</sub>.

The system, diopside-silica, shows the simple eutectic relation (fig. 2). Diopside melts at 1391°. The eutectic between diopside and tridymite is at 1362° and at the composition, diopside 84 per cent, silica 16 per cent.

The quenching experiments by which the figure was determined are tabulated below (Table I).

The liquidus for silica was determined up to 1580°, approximately the limit of safety with the platinum resistance furnace. Though the quenching experiments do not definitely prove its existence, a break on the silica liquidus is shown at 1470°, corresponding to the inversion point tridymite-cristobalite found by Fenner.

Lime-Magnesian Amphibole.—In one of the mixtures containing diopside 85 per cent and silica 15 per cent; which was melted and quickly cooled, crystals were found which, in general appearance, were very similar to the amphibole obtained when MgSiO<sub>s</sub> is quickly cooled. The crystals have, however, considerably higher refractive indices than the magnesian amphibole and probably are a lime-magnesian amphibole. The exact composition cannot be decided upon, inasmuch as the material was obtained only in the viscous mixture containing excess silica. It is probable that the viscosity of the mixture and the quick cooling condition the formation of this amphi-

\* Deleano, V. S., Zs. anorg. Chemie, lxxxiv, 401, 1914.

+ Bowen and Andersen, this Journal (4), xxxvii, 487.

bole, as has been found to be true of the pure magnesian amphibole.\*

The refractive indices are  $\gamma = 1.638 \pm .003$ ,  $a = 1.620 \pm .003$ . Optical character +, 2V about 45°. Occasional markings suggesting the amphibole cleavage of 120° were observed.

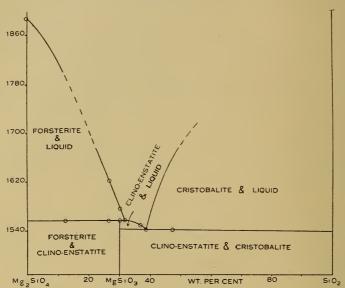


FIG. 1.

TABLE I.

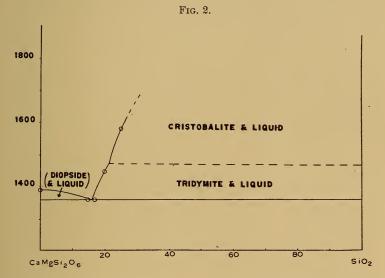
Composit Diopside	tion SiO₃	Initial condition	Tempera- ture	Time	Result
90	10	crystalline	1360	1 hr.	all crystalline
"	66	۰، ۲	1365	1 hr.	glass and diopside
"	"	66	1375	1 hr.	glass and diopside
66	66	66	1380	1 hr.	glass only
85	15	"	1360	1 hr.	all crystalline
66	66	<b>66</b>	1364	1 hr.	glass and diopside
83	17	"	1364	1 hr.	glass and tridymite
80	20	66	1448	2 hrs.	
66	"	66	1453	$\frac{1}{4}$ hr.	glass only
75	25	"	1577	2 hrs.	glass and cristobalite
66	"	66	1583		glass only

# The System CaMgSi<sub>2</sub>O<sub>6</sub>-Mg<sub>2</sub>SiO<sub>4</sub>.

The system diopside-forsterite also shows the eutectic relation (fig. 3). The eutectic point, at the composition forsterite 12 per cent, diopside 88 per cent, is only about  $4^{\circ}-5^{\circ}$  lower than

\* Allen, Wright and Clement : Minerals of the Composition  $\rm MgSiO_3,$  this Journal (4), xxii, 434, 1906.

the melting-point of diopside. There is no appreciable solid When the mixture diopside 95 per cent, forsterite 5 solution. per cent is crystallized both forsterite and diopside appear in the product. The very slight lowering of the melting-point is, therefore, not due to solid solution of forsterite in the diopside. An explanation is offered towards the end of this paper under the heading, "Freezing-point Lowering in Silicate Melts."



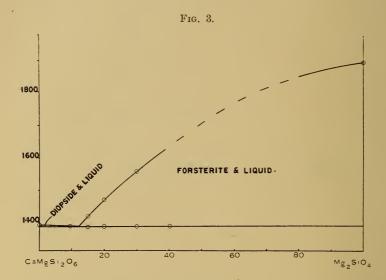
The liquidus for forsterite was not determined above  $1552^{\circ}$ and the upper part is, therefore, shown as a dotted curve extending to the melting-point of forsterite. The quenching experiments on the system are tabulated below.

		• !	TABLE II.		
	oosition Forsterite	Initial condition	Tempera- ture	Time	Result
90	10	crystalline	1386°	$\frac{1}{2}$ hr.	no change
66	66	" "	1389°	$\frac{\tilde{1}}{2}$ hr.	glass and diopside
85	15	""	1389°	$\frac{1}{2}$ hr.	glass, forsterite and diopside
"	"	"	$1391^{\circ}$	∄hr.	glass and forsterite
"	"	"	$1412^{\circ}$	$\frac{1}{2}$ hr.	glass and forsterite
"	" "	"	$1415^{\circ}$	$\frac{1}{2}$ hr.	glass only
80	20	"	1448°	į <sup>±</sup> hr.	glass and forsterite
"	"	"	$1453^{\circ}$	į̃hr.	glass only
70	30	66	$1550^{\circ}$	$\frac{1}{2}$ hr.	glass and forsterite
"	"	"	1554°	$\frac{\tilde{1}}{2}$ hr.	glass only
60	40	"	1600°	$\frac{\tilde{1}}{2}$ hr.	glass and forsterite

#### THE TERNARY SYSTEM.

#### Preliminary Statement.

The problem in the ternary system is the location of the fusion surface for each of the solid phases. Considering composition alone, the solution of the problem consists in the delimiting of the *fields* for the various solid phases. The *field* for solid phase A is such that it includes all the points representing the composition of all the liquids which can exist



in equilibrium with solid A. Considering temperature alone, the solution of the problem consists in finding the temperature at which crystallization begins (or melting is complete) in each mixture.

The method of quenching is particularly useful in the solution of the problem. If a mixture of known composition is held at various temperatures and the temperature is determined at which the last crystals, say A, disappear (dissolve in the liquid), then it is known that the composition dealt with lies in the field of A and the temperature of the fusion surface for that composition is also determined. (The crystals which disappear last on heating are also those which appear first on cooling and are called the *primary phase*.) If a mixture of a different composition is taken and the primary phase is found to be B, then it is known that the *boundary curve* between the fields of A and B lies between these two compositions. By taking intermediate mixtures, a point on the boundary curve is fixed between as narrow limits as possible. Another series

of mixtures fixes another point on the boundary curve and so the whole curve may be located. The same work fixes the temperature of a number of points on the boundary curve. It is apparent from the foregoing that all liquids lying on the boundary curve between the fields of A and B are in equilibrium with A and B.

The results are best expressed graphically by means of a solid figure in which composition is plotted horizontally, on triangular coördinates, and temperature vertically. For representation on a plane surface, composition is plotted on triangular coördinates and temperature is indicated by means of *isotherms*.

In the three binary systems there are a total of five solid phases,—diopside, cristobalite, tridymite, clino-enstatite and forsterite. The expectation is, therefore, that in the ternary diagram each would have its field, i. e. that there would probably be five fields, six boundary curves, and three ternary invariant points.\* The equilibrium diagram would then have the general form shown in fig. 4.

An equilibrium diagram analogous to fig. 4 would be the result if there were no solid solution or only limited solid solution between any of the solid phases. In the actual case, however, the equilibrium diagram is very different, for clinoenstatite and diopside form an unbroken series of solid solutions, monoclinic pyroxenes. The result is that clinoenstatite, diopside and all the intermediate pyroxenes have but one field in common, and there are, therefore, only three boundary curves and only one ternary invariant point; viz. that corresponding with the equilibrium,—cristobalite, tridymite, pyroxene, and liquid (fig. 5).

It is now necessary to tabulate the quenching experiments which gave the results outlined above. The composition of any point in the triangle can, of course, be expressed in terms of the three components at its corners, but the composition is more readily visualized if the triangle is considered divided into two parts by the pyroxene conjugation-line and the composition of a point in the one part expressed as pyroxene of a certain composition + silica and, in the other part, as pyroxene + forsterite. In the tables this latter method will be followed. The abbreviation En will be used to indicate the composition MgSiO<sub>3</sub> and Di to indicate CaMgSi<sub>2</sub>O<sub>6</sub>. The abbreviations are not intended to imply anything concerning the state of crystallization of the mixture. Thus an uncrystallized mixture (glass) of composition CaMgSi<sub>2</sub>O<sub>6</sub> 60 per cent, MgSiO, 40 per cent would be indicated Di 60 En 40.

\*Such points are, of course, invariant only when the system is considered as a condensed system.

		Downer	ing curve,	r or ster tt	e-1 growe	one.
	Compositio	n	Initial	Tempera	-	
	Pyroxene	$\mathrm{SiO}_2$	condition	ture	$\operatorname{Time}$	Result
90	(En 81 Di 19)	10	crystalline	$1510^{\circ}$	1 hr.	glass only
	· · · · · ·	10	· · ·	1516	1 hr.	glass and pyroxene
95	(En 81 Di 19)	5	66	1520	1  hr.	glass and pyroxene
	<i>c c</i>	66	، ،	1524	1 hr.	glass only
97	(En 81 Di 19)	3	66	1525	1 hr.	glass, pyroxene and forsterite
	66	66	" "	1529	1 hr.	glass only
95	(En 63 Di 37)	5	" "	1486	1  hr.	glass only
00	(En 00 D1 01)		66	1482	1 hr.	glass and pyroxene
97	(En 63 Di 37)	3	66	1485	1 hr. '	glass, pyroxene and
۰.	(24 00 21 01)	Ŭ		1100		forsterite
	" "	" "	4.4	1490	1 hr.	glass only
97	(En 44 Di 56)	3	4.4	1430	1 hr.	glass and pyroxene
	· /	6.6	66	1435	1 hr.	glass only
98	(En 44 Di 56)	$^{2}$	6.6	1432	1 hr.	glass, pyroxene and
	•					forsterite
	(En 25 Di 75)	0	٠.	1410	1  hr.	glass and forsterite
98	(En 25 Di 75)	<b>2</b>	٠٠	1407	1 hr.	glass and pyroxene
	66	66	٤٥	1410	1 hr.	glass only
100	(En 20 Di 80)	0	66	1390	1 hr.	glass and pyroxene
	<i>" "</i>	" "	66	1392	1 hr.	glass only
	Pyroxene	Mg <sub>2</sub> SiO	4			
98	(En 17 Di 83)		44	1390	$1 \ hr.$	glass and pyroxene
96	(En 17 Di 83)	4	66	1392	1 hr.	glass and forsterite

# TABLE III.Boundary Curve, Forsterite-Pyroxene.

# Boundary Curve, Pyroxene-Silica.

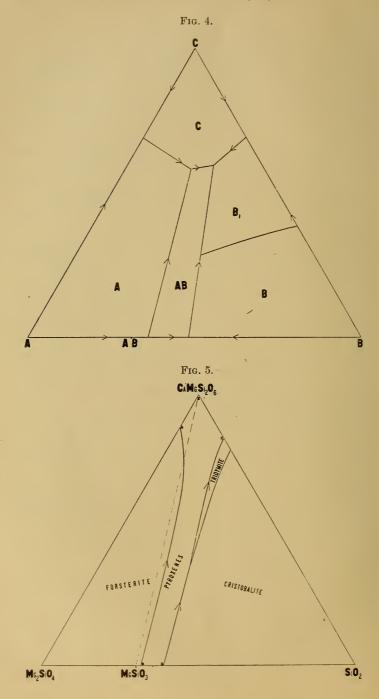
	Pyroxene	$SiO_2$				
85	(En 81 Di 19)	15	crystalline	$1516^{\circ}$	2 hrs.	glass and cristo- balite
	"	13	<i>" "</i>	1516	2  hrs.	glass and pyroxene
85	(En 63 Di 37)	15	66	1483	2 hrs.	glass, pyroxene and cristobalite
	"	66	66	1487	2  hrs.	all glass
85	(En 44 Di 56)	15	٤ ٢	1436	2 hrs.	glass, tridymite and cristobalite
	" "	÷ (	" "	1429	2 hrs.	glass, tridymite and pyroxene
87	(En 44 Di 56)	13	66	1431	2  hrs.	glass and pyroxene
85	(En 25 Di 75)	15	66	1400	2 hrs.	glass and tridymite
		66	66	1390	2 hrs.	glass and tridymite
	6 6		66	1380	2  hrs.	glass, tridymite and pyroxene
87	(En 25 Di 75)	13	66	1380	2 hrs.	glass, tridymite and pyroxene
	6.6	۶ ۵	" "	1384	2  hrs.	glass only
85	(En 17 Di 83)	15	" (	1370	2 hrs.	glass and rare tridymite
	" "	66	66	1368	2  hrs.	glass, tridymite and pyroxene
85	(En 7 Di 93)	15	<i></i>	1368	2  hrs.	glass and tridymite
	"	6.6	<i>c i</i>	1366	2 hrs.	glass, tridymite and pyroxene

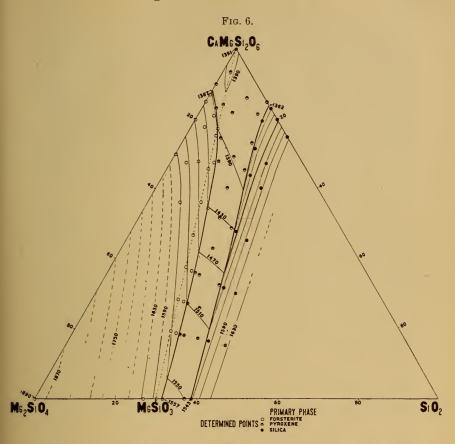
Diopside—Forsterite—Silica.

# TABLE III (continued).

Points on Silica Surface.

					5	
	Compositio		Initial	Temper-		
	Pyroxene	$SiO_2$	$\operatorname{condition}$	ature	Time	$\mathbf{Result}$
80	En 81 Di 19)	20	crystalline	$1610^{\circ}$	1 hr.	glass and cristo-
	í.		-			balite
	66	66	66	1620	1 hr.	glass only
80	(En 63 Di 37)	20	"	1587	1 hr.	glass and cristo-
						balite
	"	66	66	1593	1 hr.	glass only
80	(En 44 Di 56)	20	66	1556	1 hr.	glass and cristo-
						balite
~ ~		"	66	1562	1 hr.	glass only
80	(En 25 Di 75)	20		1538	1  hr.	glass and cristo-
	"	66	66	1 ~ 10	4.1	balite
00			"	1543	1 hr.	glass only
80	(En 17 Di 83)	20	••	1502	1 hr.	glass and cristo-
		"	4.6	1500	1 1	balite
				1507	1 hr.	glass only
		Р	oints on Pyr	roxene Si	ırface.	
0.0	(TT. 70 T): 00)					
92	(En 72 Di 28)	8	crystalline	1504° ·		glass and pyroxene
00	(En 59 D: 47)		44	1508	1 hr.	glass only
92	(En 53 Di 47)	8	66	$\frac{1461}{1457}$	1 hr.	glass only
0.9	(En 11 D; 56)		66	$1437 \\ 1427$	1 hr.	glass and pyroxene
92	(En 44 Di 56)	8	"	$1427 \\ 1432$	1 hr.	glass and pyroxene
92	(Fn 95 D; 65)	8	66	$140.2 \\ 140.7 \\ 140.7 \\ 140.7 \\ 140.7 \\ 140.7 \\ 140.7 \\ 140.2 \\ 140.$	1  hr.	glass only
92	(En 35 Di 65)	6	64	1413	1 hr. 1 hr.	glass and pyroxene
92	(En 25 Di 75)	8	66	1390	1  hr.	glass only glass only
02	(EII 20 D1 70)		66	1386	1 hr.	glass and pyroxene
92	(En 7 Di 93)	8	66	1377	1  hr.	glass and pyroxene
0~	(111 * 11 00)		4.6	1382	1 hr.	glass only
				10010	1	grass only
		F	oints on Fo	sterite Sı	ırface.	
100	(En 81 Di 19)		crystalline	$1550^{\circ}$	$\frac{1}{2}$ hr.	glass and forsterite
			č 6 6	1554	$\frac{1}{2}$ hr. $\frac{1}{2}$ hr. $\frac{1}{2}$ hr. $\frac{1}{2}$ hr.	glass only
100	(En 72 Di 28)		66	1534	1% hr.	glass only
	· · · · · · · · · · · · · · · · · · ·		66	1530	$\frac{1}{2}$ hr.	glass and forsterite
100	(En 63 Di 37)		6.6	1512		glass and forsterite
	6 G G G G G G G G G G G G G G G G G G G		66	1516	$\frac{1}{2}$ hr.	glass only
100	(En 53 Di 47)		6.6	1490	$\frac{1}{2}$ hr. $\frac{1}{2}$ hr.	glass and forsterite
	" "		٠.	1494	$\frac{1}{2}$ hr,	glass only
100	(En 44 Di 56)		66	1459	$\frac{1}{2}$ hr.	glass and forsterite
- 0.0	" "		66 66	1464	1⁄2 hr. 1⁄2 hr.	glass only
100	(En 35 Di 65)		66 66	1428	$\frac{1}{2}$ hr.	glass and forsterite
				1432	$\frac{1}{2}$ hr.	glass only
100	(En 25 Di 75)			1393	$\frac{1}{2}$ hr. $\frac{1}{2}$ hr.	glass and forsterite
				1397	$\frac{1}{2}$ hr.	glass only
P	yroxene Fo	rsterit	е			
80	(En 33 Di 67)	20	66	1550	1/2 hr.	glass and forsterite
		66	66	1555	$\frac{1}{2}$ hr. $\frac{1}{2}$ hr.	glass only
90	(En 25 Di 75)	10	"	1468	I/a hr	glass and forsterite
		66	٤،	1472	$\frac{1}{2}$ hr.	glass only
80	(En 17 Di 83)	20	6.6	1518	$\frac{1}{2}$ hr.	glass and forsterite
	66	"	"	1523	$\frac{1}{2}$ hr.	glass only
89	(En 13 Di 87)	11	<i></i>	1430	$\frac{1}{2}$ hr. $\frac{1}{2}$ hr. $\frac{1}{2}$ hr. $\frac{1}{2}$ hr. $\frac{1}{2}$ hr. $\frac{1}{2}$ hr.	glass and forsterite
0.0	(T) 10 D1 01		66 66	1434	$\frac{1}{2}$ hr.	glass only
92	(En 13 Di 87)	.8	"	1407	$\frac{7}{2}$ m.	glass and forsterite
				1412	$\frac{1}{2}$ hr.	glass only .





General Character of the Fusion Surfaces.

In fig. 5 the boundary curves are drawn in accordance with the results stated in Table III. In fig. 6 the determined points are indicated and the isostherms drawn as far as they are fixed by these points. All points on the pyroxene surface are determinable by the quenching method. In the forsterite field and in the silica field only points below 1625° (usually below 1580°) were determined. The pyroxene surface is one of relatively gentle gradient, falling from the more magnesian mixtures towards the more calcic. The forsterite surface mounts steeply towards forsterite (melting-point 1890°). The silica surface mounts still more steeply, in its determinable part, towards silica.

## The Melting Point of Cristobalite.

In the paper on the system MgO-SiO,\* it was stated that indications were found that the liquidus of cristobalite is very steep close to the entectic, clino-enstatite-cristobalite. The statement was made in this tentative form because it was considered possible that equilibrium had not been obtained in these rather siliceous mixtures. Later work has, however, shown that equilibrium between liquid and solid is readily attained in these mixtures and that points on the cristobalite liquidus can be fixed with precision. The points found in the diopside-silica system, in the clino-enstatite-silica system and several intermediate points in the ternary system all agree in showing that the silica surface is very steep.

It is true that a lessening of the gradient is shown at the higher attainable temperatures (note spacing of the isotherms as fixed by determined points fig. 6) so that the silica surface may not mount as high as the steep gradient at lower temperatures would suggest. Nevertheless it is clear that the indicated melting point of cristobalite must be higher than 1625°, the value found by Fenner,† higher than 1685° even, the value found by Endell and Rieke.<sup>±</sup>

The mixture MgSiO, 75 per cent, SiO, 25 per cent held at 1625° for one hour gives glass and considerable cristobalite, an amount which would require a raising of the temperature 40°- $50^{\circ}$  to effect its solution. This estimate  $(40^{\circ}-50^{\circ})$  may be made with considerable assurance on the basis of much experience with quenchings of mixtures in the silica field. Even at the composition 25 per cent SiO<sub>2</sub>, then, the liquidus is well above 1625°. I do not know how to reconcile these determinations with the evidences of melting found in cristobalite by Fenner at 1625° and by Endell and Rieke at 1685° unless it is as Dr. Fenner has suggested to me, that cristobalite has a variable molecular constitution and a similarly variable melting-point according to the conditions under which it is formed, a peculiarity which he has shown to be true of its low-temperature inversion. In the various mixtures used in the present work, in which the cristobalite is crystallized simply by cooling the molten mixture, there is no evidence of variability. All the points on the silica surface are entirely consistent with each other, a fact which probably indicates that true equilibrium is obtained between the various molecules which make up the solid phase, cristobalite.

\* Bowen and Andersen, this Journal (4), xxxvii, 487, 1914.

<sup>&</sup>lt;sup>†</sup>Fenner, C. N., The Stability Relations of the Silica Minerals, this Journal, (4), xxxvi, 381, 1913.
<sup>‡</sup> K. Endell and R. Rieke, Zs. anorg. Chem., lxxix, 239-259, 1912.

#### Diopside—Forsterite—Silica.

The fact that equilibrium is readily obtained between solid and liquid in these melts, and that the high temperature of the points found is not due merely to a sluggishness in the solution of cristobalite, was shown in a manner which is illustrated by the following example. The completely crystallized mixture diopside 75 per cent,  $SiO_2$  25 per cent was held at 1575° for periods varying from 15 minutes up to 5 hrs. In each case the resultant product was glass and a very little cristobalite. On the other hand the same mixture, again completely crystalline, was held at 1585° for only 15 minutes and the product

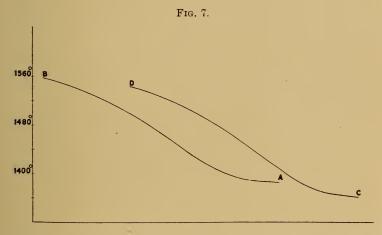


FIG. 7. Vertical sections along boundary curves. AB forsterite-pyroxene, CD pyroxene-silica.

is pure glass without cristobalite. This same method of checking the temperatures of the silica surface was applied to all the points except those above  $1600^{\circ}$ . It is not advisable to hold the furnace at these higher temperatures for a period of 5 hrs., but since it has been shown above that a period of 15 minutes is sufficient to obtain equilibrium, holding the mixture for one hour, as was done for example with the mixture MgSiO<sub>3</sub> 75 per cent, SiO<sub>2</sub> 25 per cent at  $1625^{\circ}$ , provides an ample margin of safety to insure equilibrium.

It may therefore be repeated that the results point consistently to a melting-point of cristobalite much higher than 1625°. Cristobalite formed by other methods and consisting of various molecules in *metastable* equilibrium in the single solid phase may, however, show a beginning of melting at the lower temperatures found by Fenner and by Endell and Rieke.

#### General Character of the Boundary Curves.

The composition diagram, with isotherms, is a scheme for representing both composition and temperature on a plane surface (in plan). It is a projection, on the plane of the base, of the solid figure showing the fusion surfaces. Now a vertical section of the solid figure shows the temperature relations somewhat more clearly than do the isotherms, just as a vertical section along a given direction in a mapped area shows the relief more strikingly than does a contoured map. Fig. 7 has therefore been drawn to show the temperatures along the boundary curves. It represents vertical sections of the solid figure along the boundary curves. Composition is, of course, not indicated and is known only by referring the curves to their position on the composition diagram.

The figure shows that the boundary curve, forsteritepyroxene, falls continuously, becomes gradually flatter as it approaches the point where it cuts the pyroxene conjugation line and thenceforth is nearly flat.

The boundary curve pyroxene-silica is, strictly speaking, composed of two boundary curves, pyroxene-cristobalite and pyroxene-tridymite. The difficulty of getting silica to assume the equilibrium form in the neighborhood of the inversion point tridymite-cristobalite  $(1470^{\circ})$  is very great and in quenchings near this temperature both forms were usually found. Any sudden change of direction which this boundary curve may have at the inversion temperature is, therefore, not discoverable experimentally. The two curves may, for convenience, be considered as the one boundary curve pyroxenesilica.

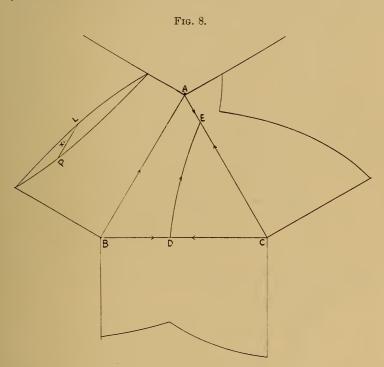
The pyroxene-silica boundary falls continuously from the eutectic, clino-enstatite-silica to the eutectic diopside-silica. It becomes considerably flattened at the lower temperatures, but there is clearly a continuous fall, without a minimum.

Such boundary curves can be interpreted only in terms of complete solid solution between diopside and clino-enstatite, a fact which is confirmed by other evidence presented later.

#### Brief Theoretical Discussion of Solid Solution in Ternary Systems.

The relations in the present system are somewhat complex and, so far as the writer is aware, a system showing the same general relations has not been investigated nor has such a system received theoretical treatment. Before proceeding further with the discussion of the equilibrium diagram it would, therefore, be well to discuss some theoretical cases of solid solution in ternary systems which have been treated by Schreinemakers.\* No attempt is made to discuss all possible cases. Attention is confined to systems which lead up to that under investigation.

One simple case is shown in fig. 8. Here the two components A and B form a complete series of solid solutions and each forms a eutectic with C. These relations, in the binary systems, are shown in the diagrams erected on the sides of the



triangle. As will be noted, the arrows indicate, in the ternary diagram, the direction of *falling* temperature, a method maintained throughout the present paper.

All liquids of composition represented by a point in the area ABDE may exist in equilibrium with a solid solution A + B. All liquids in the area DEC may exist in equilibrium with C and all liquids lying along the curve DE may exist in equilibrium with both solid C, and a solid solution A + B.

Fig. 9 shows the relations at any temperature T<sup>o</sup>. LNM is the isotherm for temperature T<sup>o</sup>. The phases present for various compositions at this temperature are as follows:

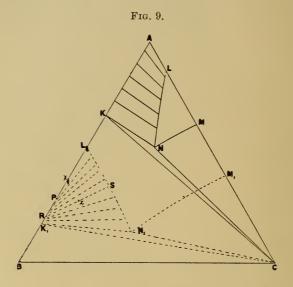
\*Zs. phys. Chem., l, 169; li, 547.

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 225.—Sept., 1914. 16 area LNM all liquid

ALKN liquid L to N and solid solution A to K. MNC liquid M to N and solid C.

KNC liquid N, solid solution K, and solid C.

KCB solid C and solid solution K to B.



At a higher temperature  $T_1^{\circ}$  for which  $L_1N_1M_1$  is the isotherm the relations are indicated by the dotted lines:

area  $AL_1N_1M_1$  all liquid

liquid  $N_1$  to  $L_1$  and solid solution  $P-K_1$ liquid  $M_1$  to  $N_1$  and solid C liquid  $N_1$ , solid solution  $K_1$  and solid C  $\mathbf{L}_{\mathbf{N}}\mathbf{K}_{\mathbf{N}}$ 

 $\mathbf{M}_{1}\mathbf{N}_{1}\mathbf{C}$  $\mathbf{K}_{1}\mathbf{N}_{1}\mathbf{C}$ 

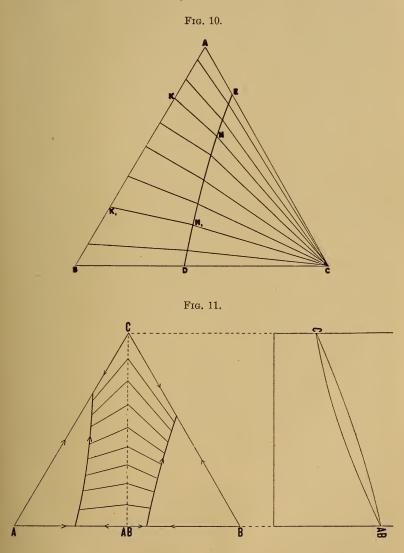
K CB solid C and solid solution K, to B.

The lines crossing the fields ALNK for the temperature T°, and L,K,N, for the temperature T,° join the composition of a liquid with that of the solid solution which is in equilibrium with it. Thus at  $T_1^{\circ}$  a mixture of total composition x consists of solid solution R and liquid S, and a mixture of total composition x, consists of liquid L, and solid solution P, a relation which is shown in the binary system in fig. 8.

The lines KN, K<sub>1</sub>N<sub>1</sub>, RS, etc., might be referred to as *solid*phase-indicating lines since they indicate the composition of the solid-phase which is in equilibrium with various liquids. KN and K, N, are special cases of solid-phase-indicating lines since they are also the boundaries of the three-phase field. It will be necessary to refer to lines of this type in general terms later and the name *three-phase-boundaries* will be used.

## Diopside—Forsterite—Silica.

Since the points N and  $N_1$  represent the composition of liquids in equilibrium with two solid phases they evidently would lie on the boundary curve DE of fig. 8. From each



point along the boundary curve lines corresponding with NK and  $N_1K_1$  and with NC and  $N_1C$  may be drawn. A set of these lines is shown in fig. 10. They are the three-phase-boundaries for various temperatures and indicate the composi-

tion of the solid phases which can exist in equilibrium with liquids represented by the various points along DE.

The three-phase-boundaries NC, N<sub>i</sub>C, etc., are simply lines radiating from the composition of the pure solid C and require no special discussion. The three-phase-boundaries NK, N<sub>i</sub>K<sub>i</sub>, etc., crossing the solid solution field, have a specific direction determined by the properties of the system. Their usefulness in discussing the crystallization of a mixture will appear later.

Figure 11 illustrates the case of a ternary system in which the components A and B form a stable compound AB and this compound gives a complete series of solid solutions with the third component C. In this case two systems of the type of fig. 8 are combined; each half C-A-AB and C-B-AB may be treated separately and C-AB is a simple binary system of the type shown in the side figure. The three-phase-boundaries would then be of the type indicated in the figure (fig. 11).

After discussing these simpler systems the case of a com-pound unstable at its melting point, as in the system under investigation, may now be proceeded with. In fig. 12 is shown a theoretical case similar to the system under investigation. We cannot in this case divide the system into two ternary systems, and the system C-AB cannot be treated as a binary system. A solid solution of any composition between C and K behaves on melting as a true binary mixture and its behavior is expressed by the binary partial-diagram of the side figure (a). A solid solution of any composition between K and L behaves on melting as a true binary mixture until the temperature of the isotherm passing through the point K is reached and its behavior is again expressed by the side diagram up to this temperature, but with further rise of temperature the component A begins to separate and the mixture no longer behaves as a binary mixture. With solid solutions between L and AB liquid begins to form and the component A begins to separate simultaneously at a temperature higher than that of the point K, the behavior throughout the melting being that of a ternary mixture. The three-phase-boundaries of this system are of the type shown in fig. 12: NP, MP, N, P, M, P, etc.

There may, also, be a minimum on the solid-solution line between K and C as shown in fig. 12 (b). Accompanying this there may be (or may not be) a minimum on one or both of the boundary curves. The system investigated falls under the type of fig. 12 (b). There is a very flat ill-defined minimum close to diopside. On the boundary curves, as we have seen, there are no minima.

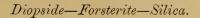
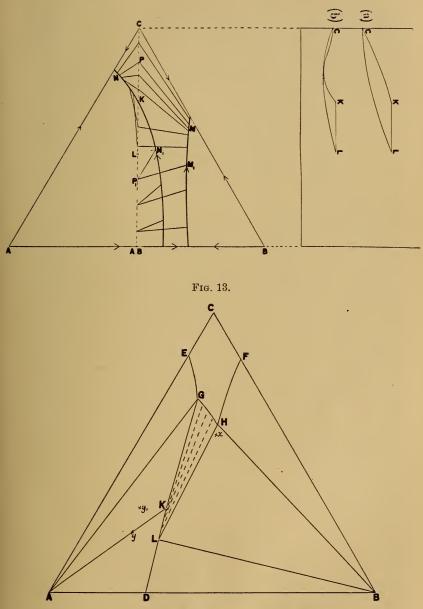


FIG. 12.



1400°

Methods of Determination of the Three-Phase-Boundaries.

The Composition Method.—After discussing theoretical systems of various types, we shall now return to the system under investigation and point out the methods used in determining the three-phase-boundaries.

Figure 12 indicates the relations at 1400°. The phases present for various compositions at equilibrium are as follows :

Ļ	ECFHG	all liquid
	EGA	liquid E to G and forsterite
	GKA	liquid G, pyroxene K and forsterite
	KAD	forsterite and pyroxene K to D
	LDB	tridymite and pyroxene L to D
	LHB	liquid H, pyroxene L and tridymite
	$\operatorname{HBF}$	liquid H to F and tridymite
	KLHG	liquid G to H and pyroxene K to L.

The lines GK and HL are evidently three-phase-boundaries. In order to determine this figure experimentally it is necessary to know the position of the isotherm EGHF for 1400° especially of the points G and H which lie on the two boundary curves of fig. 6. The temperature of all points along the boundary curves has already been experimentally determined (fig. 6). It is now necessary only to determine the points K The point L can be fixed by taking any mixture in and L. the triangle CBD, that is, any mixture of pyroxene and silica and holding it at 1400°. If it is all liquid, or if it consists of liquid and only one solid phase, another composition must be tried until one is found which at 1400° consists of liquid and the solid phases pyroxene and tridymite. If the composition of the pyroxene can now be determined, the point L is thereby determined. The pyroxene cannot be separated and analyzed, but its composition can be determined fairly closely by optical methods and the point L approximately fixed. In the actual procedure it is never necessary to try a number of mixtures as it might appear to be from the above discussion. If a mixture corresponding to a point (x) on (or very close to) the boundary curve at a temperature slightly higher than 1400° is used, the desired result, viz., two solid phases and liquid, will necessarily be obtained.

In a similar manner the point K can be determined. A mixture which at  $1400^{\circ}$  will give forsterite and pyroxene is held at  $1400^{\circ}$  and the composition of the pyroxene (point K) determined optically. By working at other temperatures the three-phase-boundaries (lines corresponding with GK and HL) for various temperatures can be approximately fixed by this method of determining the composition of the pyroxene in a three-phase mixture (the composition method).

area

The Temperature Method.—The three-phase-boundaries can be determined by another method which gives more accurate results. Any composition along the line AK (fig. 13) shows the two solid phases pyroxene and forsterite at 1400°. If the temperature is raised a very little, liquid begins to form. This fact may be used to determine the figure corresponding to fig. 13 for any temperature. Thus if a mixture of composition y is held at various temperatures and the temperature of beginning of melting determined, this will be found to be 1400°. If a mixture of composition  $y_1$  is taken it is found to begin to melt at a somewhat lower temperature. If, then,  $Ay_1$  is produced to meet the pyroxene line CD at  $K_1$  and the point  $G_1$  on the isotherm for this lower temperature is joined with the point  $K_1$ , the line  $K_1G_1$  will be the three-phase-boundary for this temperature.

It is easy to see that the three-phase-boundaries LH and  $L_1H_1$  can be determined in a similar manner, namely, by finding the temperatures at which various mixtures of pyroxene and silica begin to melt. This method (the temperature method) is more accurate than the composition method and was the one followed. The results were confirmed by the composition method in some instances during the course of some experiments in which pyroxenes of various compositions were prepared, for optical purposes, by holding a mixture at a temperature at which it gave pyroxene and glass. (Table IX.)

The figure used in the discussion (fig. 13) is the experimentally determined figure for  $1400^{\circ}$ , determined by the temperature method. It shows that the pyroxenes (K to L) are very much richer in magnesia than the liquids with which they are in equilibrium (G to H). As will appear later, this is uniformly true in the present system except in compositions very close to diopside.

The three-phase-boundaries for several other temperatures were determined by this method of finding the temperature of beginning of melting for various mixtures. The procedure is to hold the completely crystallized mixture at successively higher temperatures until the temperature is attained at which the first trace of glass is found in the quenched product. The results are given in Table IV. The information given in Table IV is expressed graphically in figs. 14 and 15, i. e. the three-phase-boundaries are drawn. Only those drawn in full lines have been experimentally determined. It was not possible to fix them accurately for the lower temperatures because over a considerable range of composition these lower-melting mixtures show practically the same temperature of beginning of melting. Dotted lines are given to show the general direction which the undetermined lines must take.

#### TABLE IV.

Temperature of Beginning of Melting.

Composition	*	
. Pyroxene	$\overline{\mathrm{SiO}_2}$	Temperature
$100(Di_{s_3}En_{17})$	0	$1390 \pm 4$
$100(Di_{75}En_{25})$	0	$1390 \pm 4$
$100(Di_{56} En_{44})$	0	$1390 \pm 4$
$100(\text{Di}_{37} \text{En}_{63})$	0	$1395 \pm 4$
$100(Di_{19} En_{81})$	0	$1416 \pm 4$
$100(\mathrm{Di}_{9.5}^{*}\mathrm{En}_{90.5}^{*})$	0	$1450 \pm 4$
$95(\text{Di}_{75}\text{En}_{25})$	5	$1365 \pm 4$
95(Di <sub>56</sub> En <sub>44</sub> )	5	$1375 \pm 4$
$95(\text{Di}_{19} \text{En}_{81})$	5	$1400 \pm 4$



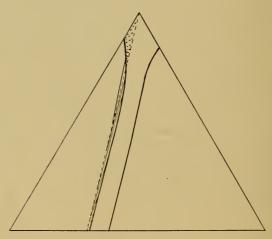


FIG. 14. Showing three-phase-boundaries for the phases pyroxene, forsterite and liquid (true scale).

Fig. 16 is analogous to fig. 13 and shows the relations at various isotherms.

The points a and b of fig. 16 for 1390° correspond with the points L and K of the theoretical case fig. 12 (b).

# The Course of Crystallization in Typical Mixtures.

We are now in a position to discuss, with the aid of the three-phase-boundaries, the crystallization of typical mixtures.

<sup>\*</sup> The material was in each case subjected to preliminary treatment which consisted in converting the mixture to glass and then crystallizing the glass at about 1300°. The reason for this treatment will appear later.

Crystallization when perfect equilibrium obtains will first be considered.

In the case of two substances which form a eutectic, the crystallization of any mixture can be fully described when the two freezing-point curves have been experimentally determined; or, if the two substances form a complete series of solid solutions like the plagioclase feldspars, the crystallization of

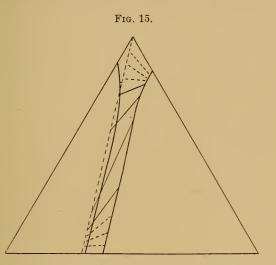
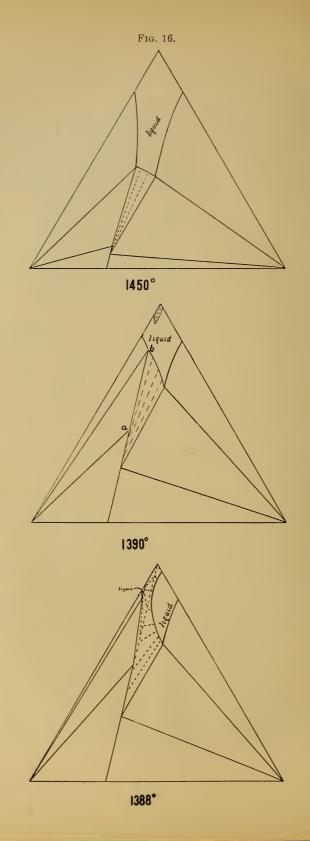


FIG. 15. Showing three-phase-boundaries for the phases pyroxene, silica and liquid (true scale).

any mixture can be described if solidus and liquidus have been experimentally determined. So in the present system the experimental determination of boundary curves, isotherms and three-phase-boundaries makes possible a discussion of the crystallization of any mixture. Such a discussion is not theoretical, but is based directly on the experimental results. It is true that with a charge of a given composition the exact course of crystallization, necessary when complete equilibrium obtains, can not in some cases be experimentally realized because the charge can not be cooled slowly enough, but, by making quenching experiments at various temperatures, any desired stage of the process can be experimentally realized. The discussion of crystallization when perfect equilibrium is attained is important because a very close approach to this behavior would be furnished by a large body of material when very slowly cooled and kept thoroughly mixed.

In order to make it possible to follow the geometrical relations it is necessary to distort the figure somewhat as has been

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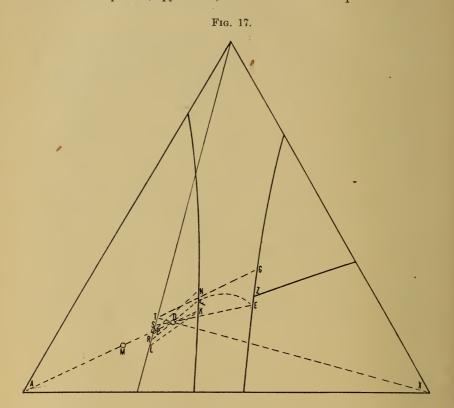


done in fig. 17. The space between the boundary curve, forsterite-pyroxene, and the pyroxene conjugation line, has been widened, relatively, and the three-phase-boundaries, LK, RF, etc., have been made to cross this space less obliquely than they should if drawn to true scale. A glance at figs. 14 and 15 will convince one that the geometrical relations could not be followed if the boundary curves and the three-phase-boundaries were drawn in their proper relative positions. The distorted figure illustrates the principles involved equally well, besides facilitating the discussion.

Crystallization with Perfect Equilibrium between Liquid and Solid Phases.-If a liquid of composition M (fig. 17) is allowed to cool, forsterite begins to crystallize at the temperature of the isotherm through the point M and continues to crystallize until the temperature of the point K on the boundary curve is reached. In the meantime the composition of the liquid has changed from M to K along the straight line AMK. Since liquid K is saturated with pyroxene that phase then begins to crystallize, and since we now pass into a threephase-area the composition of the pyroxene can be found by drawing the three-phase-boundary through the point K, i. e., KL, and L represents the composition of the pyroxene. When the temperature is further lowered pyroxene continues to crystallize and forsterite begins to redissolve. The composition of the liquid now changes along the boundary curve and the composition of the pyroxene in the act of crystallization, as well as that of the pyroxene which has already separated (if there is perfect equilibrium), changes toward S. When the temperature of the point N is reached, the liquid finally disappears and the whole consists of pyroxene of composition P and forsterite, NP being the three-phase-boundary for the temperature of the point N. The proportion of pyroxene to forsterite is as MA: MP.

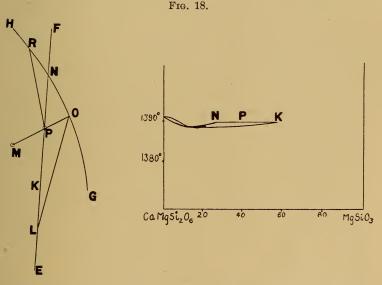
If the composition of the original liquid had been that of the pyroxene P, forsterite would crystallize first as before, and the whole course of crystallization would be precisely as given above. At the temperature of the point N, in this case, the last of the liquid and the last of the forsterite are used up simultaneously and the whole consists simply of pyroxene of composition P.

If the composition of the original liquid was that of the point D, forsterite would crystallize first as before and crystallization would follow the same course as in the two preceding cases until the temperature of the point F is reached. At this temperature the last of the forsterite has dissolved and the mixture consists of liquid of composition F and pyroxene of composition R, FR being the three-phase-boundary through the point D. The composition of the liquid now leaves the boundary curve and crosses the pyroxene field on the curve FE, pyroxene continuing to crystallize and changing in composition towards S. When the temperature of the point E is reached cristobalite begins to crystallize. At this temperature the liquid has the composition E and pyroxene the composition S, SE being the three-phase-boundary through the point D for the three phases, pyroxene, cristobalite and liquid. With



further lowering of temperature the composition of the liquid changes along the boundary curve from E towards Z, cristobalite and pyroxene continue to crystallize and the pyroxene changes in composition towards T. At the temperature of the point Z cristobalite changes to tridymite, if perfect equilibrium is attained, and with further lowering of temperature tridymite and pyroxene continue to crystallize. When the temperature of the point G is reached the liquid finally disappears; the last minute quantity has the composition G, and the pyroxene has the composition T, GT being a three-phase-boundary. The whole now consists of pyroxene of composition T and tridymite in the proportion, pyroxene : tridymite = DX : DT.

It is apparent from the foregoing discussion that all mixtures of forsterite with the pyroxene P become completely crystalline at the temperature of the point N, or, vice versa, begin to melt at the temperature of the point N. The threephase-boundary PN can, therefore, be determined by taking any mixture of forsterite with pyroxene of composition P, or pyroxene P itself, and determining the temperature of beginning of melting. It will be recalled that this was the method used in determining the three-phase-boundaries.



Similarly any mixture of tridymite with the pyroxene T, but not pyroxene T itself, begins to melt at the temperature of the point G and the first minute quantity of liquid formed has the composition G.

In fig. 18 the behavior is represented of mixtures whose composition lies closer to the point at which the boundarycurve, forsterite-pyroxene, cuts the pyroxene conjugation line. FE is a portion of the conjugation line and GNH a portion of the boundary curve. If a liquid of composition M is crystallized, forsterite first separates and the composition of the liquid changes toward O. At the temperature of the point O, pyroxene of composition L begins to crystallize, OL being the three-phase-boundary for the temperature of the point O. The composition of the liquid now follows the boundary curve, forsterite gradually redissolves and pyroxene changes in composition. When the liquid has the composition N the pyroxene has the composition K. When the temperature of the point R is reached, the liquid finally disappears, the vanishing amount having the composition R, and the pyroxene having the composition P, RP being the three-phase-boundary for the temperature of the point R. The whole then consists of forsterite and pyroxene P.

If the original mixture had the composition P, forsterite would separate first, as before; at O, pyroxene L would begin to separate and forsterite to redissolve, the whole behavior being the same as that of composition M, until the temperature of the point N is reached. At this temperature the re-solution of forsterite is complete and the whole consists of pyroxene K and liquid N, which is also of pyroxene composition. Thenceforth the melt behaves as a binary mixture and its behavior is expressed in the simple binary diagram of fig. 18, in which the points N, P and K correspond with the points so lettered in the ternary figure and of which no further explanation is necessary. All the rearrangement between liquid and solid which is necessary in order to get crystallization strictly according to the binary diagram of fig. 18 is, of course, in practice impossible on account of the very small temperature interval involved. What really happens is the crystallization of the liquid N in toto to pyroxene of composition N.

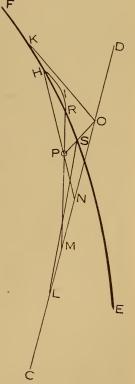
The behavior of liquid of composition P is typical of that of all liquids of pyroxene composition between N and K. The behavior of liquids of composition between K and pure MgSiO<sub>3</sub> is given in the discussion of the liquid P of fig. 17. All liquids between N and pure diopside behave as binary mixtures and the binary diagram of fig. 18 expresses their behavior completely.

The existence of both the solidus and liquidus shown in fig. 18 is, of course, not experimentally determinable on account of the extremely small intervals involved. All that has been shown is the existence of a very flat minimum, whose exact position cannot be located. The occurrence of the minimum was proved as follows: A charge of a given composition close to diopside was compared with diopside by quenching the two together from the same temperature. The charges were separated only by platinum foil  $\cdot 02^{mm}$  thick, so that there was no possibility of a difference of temperature. In this manner it was shown that the composition, diopside 82 per cent, MgSiO<sub>2</sub> 18 per cent, and also the mixture 77 per cent diopside give only glass at a temperature slightly lower than that at which the diopside gives only glass. Of these two mixtures the 82 per cent mixture is completely molten at a temperature slightly lower than the 77 per cent mixture. These observations show that there is a minimum in the neighborhood of the 82 per cent mixture, though it is not more than  $2^{\circ}-3^{\circ}$  lower than the melting-point of diopside. The occurrence of the minimum is entirely consistent with all the relations found in the system.

The Precipitation, Complete Solution and Reprecipitation of Forsterite.—There is a small area, close to the point of intersection of the boundary curve and conjugation line, every point of which lies at the intersection of two three-phaseboundaries. The point P of fig. 19 represents one of these. The crystallization of a liquid of com-

position P takes place in the following manner: Forsterite first crystallizes out and the liquid changes in composition towards S. At the temperature of the point S pyroxene of composition L begins to crystallize out. When the temperature is lowered the composition of the liquid follows the boundary curve, forsterite begins to dissolve and the pyroxene to change in composition. When the temperature of the point R is reached, the liquid has the composition R, forsterite has completely redissolved and the pyroxene has the composition M, RM being the three-phase-boundary for the temperature of the point R. The composition of the liquid now leaves the boundary curve and follows the general course RIH lying entirely in the pyroxene field. During the temperature interval between R and H, the mixture consists entirely of pyroxene crystals and liquid, without crystals of forsterite. At the temperature of the point H the pyroxene has the composition N and reprecipitation of forsterite begins, HN being the three-phase-boundary for the temperature of the point H. With further lowering of temperature crystallization of both pyroxene and forsterite

FIG. 19.



continues, the liquid changing in composition along the boundary-curve towards K, and the composition of the pyroxene changing towards O. When the temperature of the point K is reached the liquid finally disappears, the last vanishing quantity having the composition K. The whole then consists of pyroxene O and forsterite (OP produced passes through the composition of forsterite).

In the actual system under investigation the temperature interval between the points S and K is only  $2^{\circ}-3^{\circ}$  and the behavior above described cannot be experimentally realized, and, therefore, has no practical importance in the present system. The necessity of such a behavior is, however, important as a general fact in systems of like character inasmuch as it illustrates the possibility of the precipitation, complete solution and reappearance of a crystalline phase as the normal result of cooling.

Crystallization without Interaction between the Liquid and the Solid Phases Already Separated.—The crystallization of any mixture of a system such as the present may be considered to take place in a manner somewhat different from that outlined for the case of perfect equilibrium. It may be considered that when a crystal has separated it is never redissolved and that when a mix-crystal separates its composition does not thereafter suffer any change. The crystals which are separating at any instant are at equilibrium with the liquid but those that have already separated may not be.

When crystallization takes place in this manner a liquid of composition M, P or D of fig. 17 would behave as follows: Forsterite would crystallize out first and the composition of the liquid would change to K. At the temperature of the point K pyroxene of composition L would begin to separate. In the case of complete equilibrium the re-solution of forsterite would now begin and the liquid would change along the boundary curve. In the case we are now considering, liquid and forsterite do not interact and the composition of the liquid crosses the pyroxene field and meets the boundary curve pyroxenetridymite at a point lower than E, say G.\* In the meantime the composition of the pyroxene separating has changed from L to T and there exist in the mixture, pyroxene crystals of all compositions varying from L to T. When the temperature is that of the point G and the composition of liquid is G, tridymite begins to crystallize and the composition of the liquid changes along the boundary curve pyroxene-tridymite. Meantime the composition of the pyroxene separating changes from T towards pure diopside and final crystallization takes place only when the temperature is that of the eutectic diopside-tridymite, when the remaining infinitesimal amount of liquid has the composi-

\* The exact curve which indicates the change in the composition of the liquid is, unlike FE, such that the tangent to it at any point passes through the composition of the pyroxene in equilibrium with liquid of the composition and at the temperature represented by the point.

tion of this eutectic and the crystalline phases separating are tridymite and pure diopside.

It will be recalled that we started with any of the mixtures M, P or D. Any of these mixtures would, then, if crystallized in this manner, consist of forsterite, tridymite, and pyroxene varying in composition from L to pure diopside. The actual amount of pyroxene approaching L in composition would be relatively large; the amount approaching diopside, relatively very small; the amount of pure diopside infinitesimal.

# Importance of Distinguishing between the Two Types of Crystallization.

It is of great practical importance in working out such a system to bear in mind the distinction between crystallization of these two types. Crystallization of the first type, viz.: that in which there is perfect equilibrium between the liquid and the solid phases, is favored by very slow cooling during which plenty of time is allowed for interaction between the liquid and the solid phases which have already separated from it. Crystallization of the second type is favored by quick cooling during which the liquid is in equilibrium at any instant only with the solid phases separating at that instant. It is very doubtful if, in practice, the period of cooling could ever be sufficiently prolonged to realize crystallization of the first type. Crystallization of the second type is often, however, very closely approached, if not actually realized, by heating a charge of 20 to 50 grams to the liquid state and then removing it from the furnace and allowing it to cool to room temperature. This is, of course, true only of those mixtures which crystallize readily, that is, those rich in pyroxenes or forsterite; the silica rich mixtures may not crystallize at all with such treatment.

If, then, a mixture of composition P (fig. 17) is heated till completely liquid and then allowed to cool, crystallization taking place freely, the result will be forsterite, tridymite and pyroxene varying from L to diopside.\* The mixture P should, however, consist, when completely crystalline, simply of homogeneous pyroxene of composition P. The heterogeneous material prepared by rapid crystallization is not at equilibrium though it will persist indefinitely—and should not be used to investigate equilibrium whether by the method of quenching or by the method of noting the heat effect of any change recorded by the thermoelement in running a heating curve. The initial mate-

\* In the actual case, owing to undercooling, the composition of the pyroxene varies between somewhat narrower limits. The essential point is that the pyroxene is of variable composition.

Am. Jour. Sci.-Fourth Series, Vol. XXXVIII, No. 225.-Sept., 1914. 17 rial in any such experiment should itself be at equilibrium. If it is desired, for example, to determine the temperature of beginning of melting of a mixture of composition P, the heterogeneous material prepared by rapid crystallization will be found to begin to melt at the temperature of the eutectic between diopside and tridymite. On the other hand, if the homogeneous pyroxene P is the initial material, melting will not be observed until the temperature of the point N (fig. 17) is reached. Now the behavior of the heterogeneous material can be interpreted after the true equilibrium has been studied throughout the system but the converse is not true, that is, equilibrium in the system can not be determined from the behavior of this heterogeneous material.

It has already been stated that any mixture, say the mixture P, can not in practice be cooled slowly enough to ensure perfect equilibrium between the liquid and the solid phases, and a homogeneous pyroxene P cannot therefore be prepared by slow cooling. Since it is necessary to prepare the homogeneous pyroxene of composition P not only in order to obtain material to use in studying equilibrium, but also to prove the very existence of this pyroxene, some other method of making it must be resorted to. The method is simple and consists in quenching a small charge of composition P, from the liquid state, thereby obtaining a glass, and then crystallizing the glass at a temperature below that of the point N. Similarly the mixture M must be crystallized from glass at a temperature below N, if a mixture to be used in studying equilibrium is desired.

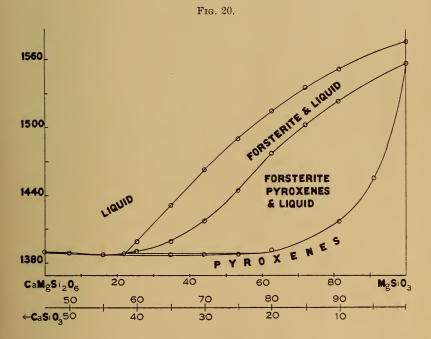
It was in this manner that all the pyroxenes between diopside and clino-enstatite were prepared and the fact of complete solid solution between the two compounds, already indicated by the shape of the fusion surfaces, was thereby demonstrated beyond doubt. The heterogeneous preparations prepared by crystallization during cooling from the liquid state create an entirely false impression as to the extent of solid solution, when examined under the microscope, unless the manner of crystallizing already described is previously suspected. The preparation contains both pyroxene close to clino-enstatite and pyroxene close to diopside and the natural conclusion is that there is only limited solid solution close to each compound.

Confirmation of the above statements concerning the mode of crystallization of the cooling liquid comes from the work of Zinke on the diopside-clino-enstatite series.\* The mixtures were crystallized by cooling their melts, and Zinke noted, besides diopside and clino-enstatite, pyroxene of small (and variable) optic axial angle. The small optic axial angle is,

\*G. Zinke, Neues Jahrb. Min., 1911, II, p. 132-

as will be shown in the optical part of this paper, characteristic of pyroxenes of intermediate composition. There is no doubt, then, that Zinke obtained intermediate pyroxene of varying composition as we have stated should be obtained with the procedure followed.

It is obvious from the foregoing discussion that in describing any experiment performed on a mixture belonging to such a system it is necessary to state the initial condition of the



material used. For nearly all mixtures it is necessary to use material prepared by crystallizing a glass at a low temperature. Any composition lying in the area AEF (fig. 5) including the pyroxene mixtures E to F can, however, be crystallized to an 'equilibrium mixture' simply by cooling from the liquid condition.

# The Pyroxenes, Diopside-Clino-enstatite.

By using the results of the ternary system a diagram may be constructed for the pyroxenes which exhibits their behavior with change of temperature in a more striking manner than does the triangular diagram where temperature can be

represented only by means of isotherms. Such a diagram is shown in fig. 20. Thus the behavior of composition Di, En, is shown in the figure to be as follows: at 1552° forsterite crystallizes out and continues to crystallize down to 1523°. At this temperature pyroxene begins to crystallize out, and until the temperature 1420° is reached, the three phases forsterite, pyroxene and liquid co-exist. At 1420° both forsterite and liquid have disappeared and the whole consists of pyroxene. The diagram, then, expresses the nature of the phases present at any temperature in any mixture of given total composition. It does not, however, express the composition of the individual phases present in a heterogeneous mixture, inasmuch as this can be done only in terms of three components. It records the temperature at which any phase appears or disappears in a mixture of given total composition and therefore indicates the temperature at which a heat-effect takes place in that mixture, or, in other words, the temperature at which a heating-curve break is to be expected. It has been demonstrated that the true ternary equilibrium diagram, when boundary curves, isotherms and three-phase-boundaries are shown, also expresses these facts and has the advantage that it expresses the composition of the phases present at any temperature as well, but the ternary diagram is more difficult of rapid interpretation.

# Comparison of the Present Results with Earlier Work.

The system CaSiO<sub>s</sub>-MgSiO<sub>s</sub> had been formerly studied at this laboratory, the method of attack being principally the method of heating curves. The heat-effects indicated by the heating-curve breaks are usually quite adequate for the correct interpretation of equilibrium in the system, but it happened that in the present case they were not. The difference between the conclusions arrived at in the early work and those arrived at after making quenching experiments is the result of two factors. In the first place the heating-curve method is likely to overlook a change involving a small heat-effect when this change occurs at a temperature only a little higher than another involving a considerable heat-effect. The large effect at the lower point may completely mask the smaller effect which should be obtained at the higher point. It is true that by special treatment the higher point can often be fixed, in such cases, by the method of heating curves, but the fact remains that the existence of the higher point may not even be suspected and the special treatment not applied. Heatingcurve results are, then, likely to err in the direction of incompleteness.

In the second place, even when all heating-curve breaks have been obtained, it is not always easy to decide what the nature of the changes which have given the breaks may be. It is always possible that the materials on which a heating-curve is run is not itself an equilibrium mixture and the temperatures at which breaks occur are therefore, possibly, not the temperatures of equilibrium changes. When the attempt is then made to decide what change of phase has taken place at the temperatures of the breaks, the conclusions may be erroneous.

With the method of quenching, however, when supplemented by microscopic examination of the product, there is no room for doubt as to the nature of the phases present at equilibrium and the temperatures of all changes can be definitely fixed, even when there are two, or even more, at temperatures little removed from each other, and whatever may be the relative values of the heat-effects involved. The treatment can, moreover, always be made such that both the material started with and the final product represent equilibrium.

The above statements are not intended as an argument for the general superiority of the quenching method over the method of heating curves. The existence of a promptly reversible change, such as the inversion  $a-\beta$  quartz, can be easily missed when the quenching method is employed but may be readily detected by the method of heating curves. No fault can be found with the accuracy of the heating-curve break itself, but there is some danger of misinterpreting the breaks when the method is employed by itself in the study of equilibrium in a complex system.

Both the factors mentioned, viz.: the overlooking of certain changes and the obtaining of breaks which do not represent equilibrium changes, are involved in the results of the earlier work on the system  $CaSiO_a$ -MgSiO<sub>a</sub>.

The material on which the heating-curves were made was prepared in most cases by cooling a mixture from a temperature at which it was liquid to room temperature, crystallization taking place freely. It has been shown, in the discussion of the course of crystallization, that, when mixtures are allowed to crystallize in this manner, the resultant product consists, for the more calcic mixtures, 100–75 per cent diopside, of homogeneous pyroxene. By virtue of undercooling, somewhat more magnesian mixtures, extending perhaps as far as 65 per cent diopside, may also consist of homogeneous pyroxene if the cooling has been at the proper rate. In the earlier work, therefore, on finding that all mixtures extending from diopside to  $Di_{e5}En_{a5}$  gave a homogeneous product it was concluded that solid solution extended as far as  $Di_{a5}En_{a5}$ .

The more magnesian preparations, however, crystallize to a mixture of forsterite, pyroxene of variable composition and

free silica. Since the microscope showed inhomogeneity, and since the forsterite was not recognized as such, but was considered to be the high-temperature form of  $MgSiO_s$  (a-MgSiO<sub>s</sub>), these mixtures were considered to lie beyond the limits of solid solution.\*

The thermal results obtained seemed to be in accord with these conclusions, for these more magnesian preparations gave two heating-curve breaks, one of which appeared to be interpretable as the result of inversion of  $\beta$ -MgSiO<sub>s</sub> to a-MgSiO<sub>s</sub> and the other, as the result of eutectic-melting between MgSiO<sub>s</sub> and diopside solid solution.

The heating-curve breaks obtained on the more calcic mixtures (those that crystallized to homogeneous pyroxenes) should indicate the temperature of equilibrium changes and should therefore agree with the quenching results. This they do. Heating-curve results obtained on the more magnesian, inhomogeneous material, not itself at equilibrium, may indicate other changes. The completed results of the ternary system make it possible, however, to state what effects should be observed in this inhomogeneous material.

Since the material contains free silica and medium-calcic pyroxene there should be a notable melting-together of these two at temperatures corresponding to the flat portion of the boundary curve tridymite-pyroxenes (1370°-1380°; see fig. 7). Since forsterite is present also there should be melting of it with a further quantity of pyroxene at temperatures corre-sponding to the flat portion of the boundary curve pyroxeneforsterite (1387°-1389°). The melting should in each case give a heating-curve break and it was approximately at these temperatures that breaks were obtained in the earlier work. As already pointed out, the lower of these two breaks was at that time considered probably due to inversion in MgSiO, but this involved the difficulty that the break could not be obtained in MgSiO, itself. It has been shown by Bowen and Andersen that this suspected inversion in MgSiO<sub>s</sub> has no real existence inasmuch as the material called a-MgSiO, has proven to be forsterite Mg<sub>2</sub>SiO<sub>4</sub>. The break cannot, therefore, be the result of inversion." The presence of the break in all mixtures containing lime and its absence in pure MgSiO, is, however, in direct accord with the conclusion, stated above, that the break is due to the melting-together of silica and medium-calcic pyroxene. If either silica or calcic-pyroxene is absent the

\*The amount of silica is very small (2-3 per cent). It occurs in exceedingly minute particles speckled through some of the other crystals, the effect being merely to impart a dusty appearance to these crystals. It is to be noted that these minute inclusions were observed to be "more numerous in the mixtures which are rich in magnesia (70-97 per cent)."

break must disappear. In MgSiO<sub>3</sub> mixtures, therefore, even if crystallized in such a manner that they contain free silica, the break should not occur, since there can be no calcic pyroxene present.

In the earlier work it was noted that when the intermediate mixtures were crystallized from glass at a low temperature and a heating curve run on such material the lower break was not obtained. Preparations crystallized in this manner consist of homogeneous pyroxene. There is no silica and, therefore, the lower break is absent. It is clear that in the absence of either silica or medium-calcic pyroxene this lower break disappears, in fact, it must be absent in all mixtures of  $CaMgSi_2O_e$  and  $MgSiO_s$  when the preparation started with is an equilibrium mixture, i. e. homogeneous pyroxene.

Figure 20 shows that not only should the lower of these two breaks be absent in *all* pyroxene mixtures but the higher one, termed the eutectic in the earlier work, should also disappear in the more magnesian mixtures, 58-100 per cent MgSiO<sub>3</sub>, when they are crystallized in such a manner that they consist of homogeneous pyroxene. The finding of the higher break in the more magnesian mixtures is the direct result of the fact that the preparations were crystallized in such a manner that they consisted of forsterite, pyroxene of various compositions and free silica. The melting-together of pyroxene and forsterite gave the break.

In order to compare directly the behavior of homogeneous material and of inhomogeneous material of the above kind I have made quenchings of the two side by side, taking the mixture diopside 63 per cent. The quite different behavior of the two is displayed in the table below :

Temp.	Homogeneous	Inhomogeneous
$1382^{\circ}$	no change	stringers of glass formed
13 <b>9</b> 0°	no change	increased amount of glass
1398°	beginning of melting minute amount of glass	30-40 per cent glass

I have also run heating-curves on the mixture  $En_{s1}$   $Di_{19}$ . Homogeneous material, made by crystallizing the glass, gave no breaks at these lower points, whereas material crystallized by cooling the liquid gave a distinct break at 1372° owing to the presence of free silica.

In the earlier work a series of breaks recorded as the "upper points" (Table II, p. 8) were obtained in the more magnesian mixtures. These temperatures correspond very closely with the temperatures, located by quenching, at which the last of the pyroxene disappears (dissolves), leaving liquid and forsterite. The degree of correspondence is shown in Table V, columns II and III.

	INDIE V.	
II.	III	IV
	Final	Final
Heating	disappearance of	disappearance of
" Upper Point"	by quenching	by quenching
1424*	1425	1474
1427	1430	1484
1432	1440	1490
1474	1477	1515
1524	1523	1552
1543	1543	1558
1557	1557	1577
	Heating curve break '' Upper Point '' 1424* 1427 1432 1474 1524 1543	$\begin{array}{c} \text{II} \\ \text{III} \\ \text{Heating} \\ \text{curve break} \\ \text{``Upper Point''} \\ 1424^{*} \\ 1425 \\ 1427 \\ 1432 \\ 1432 \\ 1432 \\ 1474 \\ 1474 \\ 1524 \\ 1523 \\ 1543 \\ 1543 \\ \end{array} \\ \begin{array}{c} \text{III} \\ \text{Final} \\ \text{disappearance of} \\ \text{pyroxene determined} \\ \text{by quenching} \\ \text{transformed} \\ tr$

\* The figures given in column II are the values found in the earlier work corrected in terms of the extended gas-thermometer scale, see Day and Sos-man: The Melting Points of Minerals in the Light of Recent Researches on the Gas Thermometer, this Journal (4), xxxi. 341-349, 1911.  $\dagger$  The figures in column I are in terms of the components CaSiO<sub>3</sub> and

 $MgSiO_3$ ; see lower scale of figure 20.

A still higher break corresponding to the temperature at which forstorite finally disappears in the liquid was not obtained in the earlier work and it has remained for quenching to determine the existence and the limits of the temperature interval during which the various mixtures consist of forsterite and liquid (see Table V and figure 20).

Summary of Comparison of Results.-The comparison of the results of the earlier and the present work may now be summarized. The method of heating-curves was employed in the earlier work and the mixtures were crystallized in such a manner that some of them consisted of pyroxene of variable composition, forsterite and silica, and were not equilibrium mixtures. On this material two breaks were obtained, near each other, at about 1375° and 1385°. The lower break, formerly attributed to inversion, has been found by quenching to be due to the melting-together of silica and pyroxene and the higher break to the melting-together of forsterite and pyrox-No change occurs at the temperature of the lower ene. break in any mixture when the material started with is homogeneous pyroxene, as it should be at equilibrium. No change occurs at the temperature of the higher of these two breaks in the more magnesian mixtures when they consist of similar homogeneous material. The temperature recorded as the upper point in the earlier work corresponds with the temperature of final disappearance (solution) of pyroxene, leaving liquid and forsterite. The existence of a temperature interval during which the mixture consists of forsterite and liquid was overlooked in the earlier work but revealed by quenching.

### OPTICAL STUDY

Throughout the investigation the products of the various operations were examined under the microscope in order to identify the phases present. In the ordinary course of the work it was necessary to observe only a sufficient number of the properties of any phase to make its identification certain, but, whenever specially suitable material was obtained, determinations of all the measurable optical properties were made. In the following the values found for the various phases are recorded.

### Forsterite.

The properties of pure forsterite have been given in former publications from this laboratory and will simply be listed here without discussion.

Crystal system-orthorhombic; a:b:c=0.463:1:0.584Cleavage 010, 001 distinct. G=3.216Refractive indices,  $\gamma = 1.670$ ,  $\beta = 1.651$ , a = 1.635,  $\gamma - a = .035$ ,  $2V_{Na} = 85^{\circ}16'$ . Orientation c = b and  $a = c = Bx_a$ 

### Cristobalite and Tridymite.

Silica was found in the form of cristobalite in mixtures quenched from  $1500^{\circ}$  or higher and as tridymite in those quenched from about  $1400^{\circ}$  or lower. At intermediate temperatures it was usually possible to prove that both were present. These observations are in accord with Fenner's conclusion that tridymite and cristobalite are enantiotropic and the inversion point about  $1470^{\circ}$ , the change being decidedly sluggish.\*

Cristobalite occurred in the glass sometimes as sharply outlined octahedra, slightly modified by the cube. The cube was, however, usually the more prominent form and, by distortion, the crystals usually appeared as stout prisms. The double refraction was barely discernible with the aid of the sensitive tint plate.

Tridymite was in the form of broad thin plates which appeared as needles when turned on edge. The needle-shaped sections had quite marked double refraction, parallel extinction and negative elongation.

#### The Diopside-Clino-enstatite Series of Pyroxenes.

The compounds MgSiO<sub>s</sub> and CaMgSi<sub>2</sub>O<sub>s</sub> form a complete series of mix-crystals or solid solutions, crystallizing in forms corresponding with monoclinic pyroxenes. The existence of

\* Fenner, C. N.: The Stability Relations of the Silica Minerals, this Journal (4), xxxvi, 337, 1913.

complete solid solution is proved by the fact that any mixture between the two can be crystallized to a homogeneous crystalline mass which shows only the one kind of crystals. Complete solid solution is again proved, though further proof is unnecessary, by the character of the fusion surfaces found for the ternary system, i. e. the absence of any quintuple point (point at which liquid and three solid phases are in equilibrium). Moreover, any member of the series can be obtained in contact with liquid in the ternary system.

In order to prepare a pyroxene of a given composition, a mixture of the desired composition is converted to a glass, by quenching it from the liquid state, and the glass is then crystallized by heating at a temperature of from  $1300^{\circ}$  to  $1350^{\circ}$ . The heating is best prolonged for several days in order to increase the grain of the crystalline aggregate. The reasons for this procedure have already been stated in detail; suffice it to repeat here that, if the mixture is crystallized simply by allowing it to cool from the liquid state, the result is, for the more magnesian mixtures, pyroxene of variable composition (zoned pyroxene), forsterite and silica. The precaution is unnecessary in the more calcic mixtures, those containing up to about 35 per cent MgSiO<sub>2</sub>, 65 per cent CaMgSi<sub>2</sub>O<sub>6</sub>, for these do crystallize to homogeneous pyroxene if cooled quickly from the liquid state.

In the earlier work on these mixtures the material submitted to microscopic examination was crystallized simply by cooling the liquid and the result stated above was found—all mixtures as far as about 35 per cent  $MgSiO_s$ , 65 per cent  $CaMgSi_sO_s$ were found to consist of homogeneous pyroxene. The properties of these pyroxenes were carefully determined by Wright and Larsen and found to vary continuously with composition. In the present work it has been possible to show, by crystallizing from glass, that this continuous variation of properties does not cease with the 35 per cent  $MgSiO_s$  mixture, but extends as far as the pure  $MgSiO_s$  itself. The properties found for the pyroxenes as far as the 35 per cent  $MgSiO_s$  composition agree precisely with those found by Wright and Larsen.\*

Twinning.—The variation in the tendency to form twinned crystals appears to be continuous, though it is, of course, a property which does not admit of quantitative measurement. The twinning is always after 100. In pure clino-enstatite every grain when turned into the proper position shows narrow twinning lamellæ. In 80 per cent  $MgSiO_s$ , 20 per cent  $CaMgSi_2O_s$  the same is true, but the twinning lamellæ have a distinct tendency towards a greater average width. In 60 per cent  $MgSiO_s$ , 40 per cent  $CaMgSi_2O_s$  the breadth of the lamellæ is still greater; many of the grains show only two twinning

\*This Journal (4), xxvii, p. 38, 1909.

bands, though most of them are polysynthetically twinned. In 45 per cent  $MgSiO_s$ , 55 per cent  $CaMgSi_2O_e$  most of the grains are twinned only twice though many show several lamellæ. Closer to diopside the twinning is distinctly less frequent. In diopside itself most of the grains are untwinned, several show two twinned bands and only rarely is repeated twinning observed. This progressive increase in the tendency towards twinning was observed in mixtures crystallized by heating various glasses under the same conditions. It will be shown later that in the same pyroxene the tendency towards twinning varies when it is formed by different methods.

Extinction Angle.—The extinction angle on 010 can be measured very closely and shows the continuous variation in an excellent manner. The angle was found by measuring symmetrical extinctions against the trace of the twinning plane in those grains which showed this trace and the prismatic cleavage parallel to each other. By choosing such grains, a section in the prism zone was ensured and by choosing those in which there was no overlapping of the twinning lamellæ a section close to the clino-pinacoid was obtained. The overlapping of the twinning lamellæ is an especially delicate test in the present case because the lamellæ are usually much narrower than the thickness of the grain and a very slight turning from the clino-pinacoidal section gives a marked overlapping. For each pyroxene, measurements were made on ten or more grains and several measurements on each grain. An example is given below of the symmetrical extinctions found on different grains of composition CaMgSi<sub>2</sub>O<sub>6</sub> 37 per cent, MgSiO<sub>5</sub> 63 per cent.

c . c	30	31	(27)	32	31	30	29	30	30	(30)	1 27	31
c ~ c =	29	30	33	29	30	30	28	30	30	(34∫	29	30

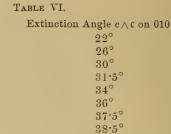
mean, after rejecting those pairs that are somewhat unsymmetrical (in brackets) =  $30^{\circ}$ .

Some compositions did not give quite as accordant results as the above. The measurements on  $CaMgSi_{\circ}O_{\circ}$  56 per cent-MgSiO<sub>3</sub> 44 per cent were, for example, as follows:

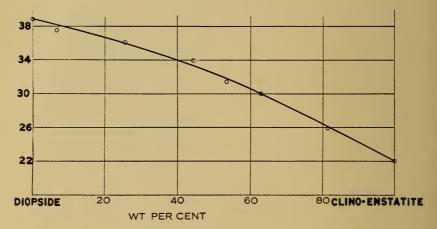
The angle  $c \wedge c$  for other compositions was found to be as given below in Table VI.

The curve indicating the change of extinction angle with composition (fig. 21) is convex upwards, that is, the angle increases more rapidly near the clino-enstatite end of the series.

Composition								
MgSiO,	100 %							
~~~ °	81 %							
66	63 %							
66	53.5%							
"	44 %							
66	25.5%							
66	7.0%							
Diopside								







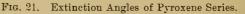


FIG. 22.

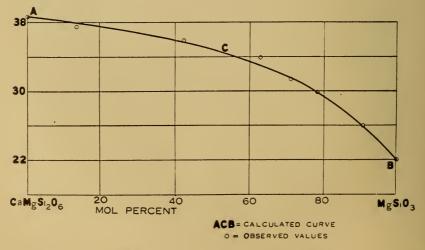
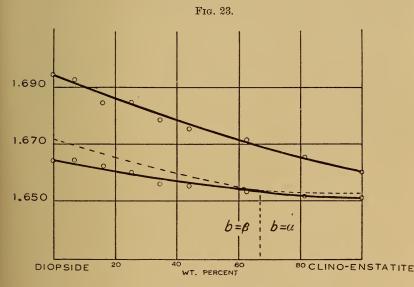
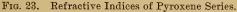


FIG. 22. Extinction Angles of Pyroxene Series.

If it is assumed that the molecular weight of clino-enstatite is the formula weight,  $MgSiO_s = 100.6$ , and that of diopside also the formula weight,  $CaMgSi_sO_s = 216.37$ , and the composition is plotted in mol. per cent, then the measured values of the extinction angles agree closely with the values calculated by means of Mallard's formula.\* In fig. 22 the circles indicate the measured values of the extinction angles plotted in this





manner and the curve ACB is calculated from the Mallard equation. The equation reads

$$\cot g \, 2a = \frac{n_1 d_1}{n_2 d_2} \cdot \frac{1}{\sin 2(i_1 - i_2)} + \cot g \, 2(i_1 - i_2)$$

where  $(i_1-a)$  is the desired extinction angle of a pyroxene mix-crystal containing  $n_1$  mols diopside to  $n_2$  mols clinoenstatite;  $d_1$  and  $d_2$  the birefringence of diopside and clinoenstatite respectively, and  $i_1$  and  $i_2$  their extinction angles. The agreement of the observed points with the calculated

The agreement of the observed points with the calculated curve is marked. It may be purely accidental, indeed the assumption that the molecular weight is equal to the formula weight for each of the compounds may be quite unwarranted, for if a near-equality of molecular volumes is necessary for complete solid-solution, the molecular weight of clino-enstatite

\* Bull. Soc. Min., iv, 101, 1881.

would have to be twice the formula weight in order to make the molecular volumes nearly equal and give likelihood of solid solution, but it is by no means certain that this similarity of molecular volumes is necessary. At any rate, the agreement seems worth recording.

Refractive Indices.—The refractive indices of the pyroxenes formed by crystallizing the glass were determined by matching with liquids in sodium light and then determining the refractive index of the liquid on the total refractometer. Only the maximum and minimum indices  $\gamma$  and  $\alpha$  can be determined by this method. The measured values of  $\gamma$  and  $\alpha$  are given in Table VII and are plotted in fig. 23. The average probable error of the values is  $\pm 002$ , though the accuracy is usually somewhat better in the compositions with low birefringence and occasionally not so good in those with higher birefringence.

TABLE	VII.
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Cor	mposition				
Diopside	Clino-enstatite	γ	α		
100		1.694	1.664		
92	8	1.692	1.664		
84	16	1.684	1.662		
75	25	1.684	1.660		
65	35	1.678	1.655		
56	44	1.675	1.655		
37	63	1.671	1.653		
19	81	1.665	1.651		
	100	1.660	1.651		

Optic Axial Angle.—The optic axial angle of various members of the series was measured on grains under the microscope. Sections showing the emergence of one axis were used for those having a large angle, but for a considerable range of compositions the angle is sufficiently small that sections showing the emergence of both axes were available. The material formed by crystallizing the glass at a low temperature was not entirely satisfactory for this purpose in compositions towards the magnesian end of the series, on account of the increasing prevalence of polysynthetic twinning towards that end. It was possible to prove, however, with this material, that the optic axial angle, beginning from the diopside end, grows smaller. In MgSiO, 63 per cent, diopside 37 per cent the angle is very small and the plane of the optic axes, as in all the more calcic members, is //010, normal to the twinning plane. In MgSiO<sub>3</sub> S1 per cent, diopside 19 per cent the angle is again small, but the plane of the optic axes is normal to 010 and parallel to the trace of the twinning plane.

It is evident that in some composition between these two, the value of the optic axial angle passes through zero. In order to study more closely this change in the plane of the optic axes, it was desirable to prepare crystals of known composition, in which the width of the individual twinning famellæ was greater than in material prepared by crystallizing glass of the pyroxene composition. It has already been shown that, when the three-phase-boundaries for the ternary system have been determined by the method of finding the temperature of beginning of melting of various mixtures (temperature method), a mixture can be chosen which, when held at a certain temperature, will give liquid, pyroxene of a certain composition and another crystalline phase. Thus a mixture of known composition can be chosen, held at a measured temperature and the composition of the crystals of pyroxene to be obtained can be predicted. It is not necessary, however, to depend on the prediction, for the composition of the pyroxene can be determined by measuring symmetrical extinctions on 010. A check is thereby obtained on the prediction and therefore, ultimately, on the determination of the three-phase-boundaries by the temperature method. The prediction is, therefore, an unnecessary part of the process, though very desirable since it removes the necessity of a number of trials.

When pyroxene crystals, embedded in glass, are prepared by this method it is found that the width of the individual twinning lamellæ is greater than in the same pyroxene prepared by the other method, It is, therefore, much less of a task to find a crystal which will give a good interference figure and a dependable value for the optic axial angle. In practice it is necessary to start with a mixture of suitable composition, in the form of glass, and to raise the glass quickly to the desired temperature. Mixtures containing a moderate excess of silica above pyroxene composition are more suitable than others, for, during the time necessary to raise the temperature to the desired point (2 or 3 minutes), no crystallization takes place in these somewhat viscous mixtures. All crystallization takes place, therefore, at the desired point, during the time the charge is held there, and it is thereby insured that all the pyroxene has the composition appropriate to this temperature. With less viscous, less siliceous mixtures, the charge cannot be raised to the desired temperature quickly enough to prevent some crystallization en route. Any pyroxene formed at a lower temperature will not have the desired composition and, once formed, it is very difficult to get rid of, for later crystallization is likely to take place about these early crystals. It is, of course, even more undesirable to start with material already

crystallized. In such a case it is often plainly discernible that the resultant pyroxene crystals have a different composition in their inner and outer portions.

It was desirable to resort to this method of growing the pyroxene crystals in a liquid, only in the case of the more magnesian pyroxenes, thereby to increase the width of the twinned bands and to facilitate optic axial angle measurements. The width of the bands is sufficiently great in the more calcic members, when formed by crystallizing glass of the composition of the desired pyroxene. The composition of the pyroxene is, of course, known absolutely, when prepared by the latter method. When prepared by growing the crystal in liquid the composition is known only as closely as it can be determined from extinction angle measurements (within 5 per cent MgSiO<sub>3</sub>). Other things being equal, the material whose composition is certain is preferable, but, for the purpose of studying the change in the plane of the optic axes, the crystals whose composition is known only approximately have the advantage already pointed out. Pyroxenes prepared by either one of these methods could

Pyroxenes prepared by either one of these methods could hardly be termed excellent material for optic axial angle measurement, but fortunately the change of angle is very great and the fact of continuous variation between the two end members readily fixed.

#### TABLE VIII.

Pyroxene Prepared by Crystallization of Glass.

Com	position		
Diopside	Clino-enstatite	Plane of Optic Axes	2 V
100		//010	$59^{\circ}\pm3^{\circ}$
75	25	//010	$56^{\circ} \pm 3^{\circ}$
65	35	//010	$47^{\circ}\pm6^{\circ}$
56	44	//010	$40^{\circ} \pm 6^{\circ}$
37	63	//010	very small
19	81	010	$20^{\circ} \pm 6^{\circ}$
·	100	010	$53^{\circ} \pm 3^{\circ}$

The composition of the pyroxene, which for monochromatic light is uniaxial, was placed between diopside 37 per cent and diopside 19 per cent by using pyroxenes crystallized from glass (Table VIII). By using pyroxene grown in a liquid (Table IX) it was placed within the narrow limits, diopside 35 per cent and diopside 30 per cent.

In figure 23 the refractive indices for the various compositions, as shown in Table VII, are plotted. The values for  $\beta$ are calculated approximately from the above determinations of Diopside—Forsterite—Silica.

### TABLE IX.

Pyroxene Prepared by Growing in Liquid.\*

I				II	III	IV	V	VI
Total Compositio	on o	f Cha	rge	Temper- ature	$c \wedge \mathfrak{c}$ of pyroxene	Composition of pyroxene from III, % diopside	2 V	Plane of optic axes
(Di 56 En 44) 9	97%	$SiO_2$	3%	$1375^{\circ}$	33•5°	54	$40^\circ \pm 3^\circ$	//010
"	"	"	٤٠	$1385^{\circ}$	31•0°	41	$20^{\circ} \pm 3^{\circ}$	//010
"	66	"	"	$1392^{\circ}$	29.7°	35	$10^{\circ} \pm 3^{\circ}$	//010
"	"	"	"	$1400^{\circ}$	$28.5^{\circ}$	30	$15^{\circ} \pm 3^{\circ}$	010
(Di 37 En 63) 9	95%	$\mathrm{SiO}_{2}$	5%	1410°	25.2°	17	$25^{\circ} \pm 3^{\circ}$	<u>_</u> 010

the optic axial angle. The curve for  $\beta$  is given because it presents graphically the reason for the observed behavior of the optic axial angle, the reason being, of course, that the values of  $\beta$  and a converge, become equal and then again diverge. A change from  $b = \beta$  to b = a necessarily takes place at the composition of the uniaxial pyroxene.

Summary of Optical Properties of Pyroxene Series.—The optical properties of the series of pyroxenes, diopside-clino-enstatite, may now be summarized briefly. With increasing MgSiO, the extinction angle decreases continuously from 38.5° to  $22^{\circ}$ , the mean refractive index falls from 1.676 to 1.654, the birefraction decreases from .030 to .009 and the optic axial angle, in the plane //010, grows smaller, passes through zero and opens again in the plane | 010.

The decreasing optic axial angle, refractive indices, birefringence and extinction angle were all observed by Wright and Larsen on those pyroxenes which were prepared formerly at this laboratory, namely those extending from diopside to about diopside 65 per cent, clino-enstatite 35 per cent.<sup>+</sup> In the present work these changes have been followed beyond this limit, in fact, to clino-enstatite itself.

G. Zinke,<sup>‡</sup> in an investigation of the system, diopside-MgSiO<sub>3</sub>, noted pyroxenes of small optic axial angle in some of his products. He also found, for one of these, an extinction angle of 32°. The pyroxenes observed by Zinke were, no doubt, some of the intermediate pyroxenes of the series, for the optical properties noted are those which the present

\*In each case the initial material was glass and the time of holding at the 

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investigation has shown to be characteristic of the intermediate pyroxenes.

Natural Pyroxenes with Analogous Optical Relations.— In the ordinary text-book descriptions of the pyroxenes there is commonly no mention of a series analogous to the pyroxenes prepared in the course of the present work. Occasionally, however, there is mention of pyroxenes poor in lime which show certain similarities with the magnesia-rich artificial varieties.\* In 1906 Wahl made a systematic study of such pyroxenes from a number of localities. Wahl's studies, both optical and chemical, show that there are natural, magnesiarich, monoclinic pyroxenes and they appear to form a series closely similar to the diopside-clino-enstatite series. Wahl terms those described by him, enstatite-augites.+ The natural minerals contain considerable iron and, therefore, differ from the iron-free varieties in many of their properties, but they show the same behavior of the optic axial angle, viz., in the varieties relatively poor in magnesia the axial plane is //010and the axial angle large; with increasing magnesia, as in the artificial varieties, the angle grows smaller, passes through zero and opens again in the plane normal to 010. Wahl was able to show that the axial angle for blue light passed through zero before that for red light in the ferriferous varieties (p. 39), an observation which the present writer was unable to duplicate in the non-ferriferous pyroxene on account of the extremely small dispersion. Wahl found moreover, that as the axial-angle decreased (magnesia increased) the extinction angle also decreased (p. 33).

### The Relation of Clino-enstatite to Enstatite.

It was no part of the plan of the present work to study the relation between clino-enstatite and enstatite, but some of the results obtained have a bearing on the problem and seem worthy of attention.

It has been demonstrated by Wright, Wahl and others that clino-enstatite is monoclinic in symmetry. In all other properties it is very similar to enstatite. The universal prevalence of twinning //100 in clino-enstatite has led Zambonini and others to conclude that enstatite is clino-enstatite in which the twinning is sub-microscopic; that the relation is one of polysymmetry. Some of those who support this view have pointed out that in meteorites and artificial melts clino-enstatite is found, in terrestrial rocks, almost universally, enstatite, and they have considered that the determining factor is the rate of cooling.

> \* Cf. Pigeonite-Winchell, Optical Mineralogy, p. 331. † Die Enstatitaugite, T. M. P. M. xxvi, 1–131, 1907.

According to this view, then, quick cooling, such as occurs in meteorites and artificial melts, gives coarse twinning which is visible under the microscope, whereas relatively slow cooling. as in terrestrial rocks, gives fine, sub-microscopic twinning. During the course of the present work it has been found that quick and slow cooling have precisely the opposite effects, at least, for these pyroxenes. When the crystals form instantaneously from an under-cooled liquid the twinning is very fine; when they are grown by holding for a couple of hours in contact with liquid the twinning bands are broad. It seems extremely unlikely, then, that the crystals of enstatite of terrestrial rocks, which undoubtedly grew in contact with liquid for a considerable period, would have twinning bands so fine as to escape observation. If twinning were present in crystals formed under these conditions the twinning bands would be broad and their presence unmistakable. The fact that no twinning bands are discernible leads the writer to believe that natural enstatite crystals cannot be identical with clino-enstatite and that the relation is not merely one of polysymmetry.

A further indication that enstatite and clino enstatite should be considered different allotropic forms is, of course, the fact that clino-enstatite and diopside form a complete series of solid solutions, whereas natural minerals point to limited solid solutions between diopside and enstatite.

It should be noted, moreover, that no orthorhombic pyroxene corresponding with enstatite ever crystallizes from any of the mixtures here studied, when they are crystallized by cooling from the liquid state. The writer believes that the so-called enstatite, often described as occurring in products formed by treating like mixtures in this manner, is really forsterite, for forsterite should be present and its presence is not noted.

## BEARING OF THE RESULTS ON PETROLOGIC PROBLEMS.

### The Series of Lime-Magnesia Pyroxenes.

The experimental work described throws some light on the physico-chemical meaning of zoned pyroxenes. In the mixtures dealt with, such zoning sometimes occurs and when formed during the normal course of cooling the inner zones are more magnesian, the outer more calcic. To be sure we are dealing with purely lime-magnesian pyroxenes, but it might be well to recall here that, in spite of the fact that we are prone to speak of the pyroxenes as ferro-magnesian minerals, the common pyroxene of igneous rocks usually contains lime, magnesia and iron in proportions in the order named.

Reference has already been made to the enstatite-augites of Wahl and attention called to their similarity in optical properties with the artificial pyroxenes. The analogy extends to some of their other relations. For example, Wahl has shown that, in a great variety of rocks bearing these enstatite-angites, the earlier pyroxene crystals are more magnesian, the later more calcic. This is sometimes true of the earlier and later parts (zones) of the same crystal, a fact which has been pointed out above for the artificial crystals.

It would appear, then, that pyroxenes more or less similar to the artificial lime-magnesia pyroxenes (differing from them principally in their iron content) have considerable importance in igneous rocks.

It has been shown in the optical part of this paper that, for the artificial lime-magnesia pyroxenes, the composition can be determined fairly closely from the optical properties. The ability to do so for the natural pyroxenes of rocks is very desirable and the present results may be considered a step in that direction. The lime-soda feldspars are at present the only isomorphous series of rock-forming minerals in which chemical composition and optical properties can be correlated with fair accuracy. Among recent studies in this direction that of Ford on the amphiboles may be noted. Until a great deal of such work has been accomplished, the determination of the proportions of minerals in a rock, as by the Rosiwal method, can, in the usual case, have little value.

### Resorbed Olivines in Natural Rocks.

It has been shown that in the artificial melts discussed, from which olivine is the first mineral to crystallize, the olivine is at a later stage either partly or completely redissolved, giving pyroxene by reaction with the liquid. This resorption takes place in the normal course of crystallization on cooling and is the necessary result of equilibrium between the phases. In natural rocks the resorption of olivine often takes place, an example occurring in the case of the Palisade diabase of New Jersey, where, in the contact facies, olivine with reaction rims of enstatite is observed.\* Such resorption has sometimes been assumed to imply some such drastic change as the sudden relief of the pressure to which the magma was subjected and the consequent instability of minerals formed under the higher pressure. Minerals exhibiting resorption are, moreover, sometimes assumed to have formed from a magma having a composition different from that of the rock in which we find them and, perhaps, to have sunk into a magma which exerted a solvent action upon them. In the case of olivine such assump-

\* Lewis, J. V., Ann. Rep't, State Geologist, New Jersey, 1907, 133.

tions are nunceessary. Resorption may have occurred during simple cooling under uniform conditions, the only change of composition being that in the still fluid portion of the magma as a necessary consequence of the separation of crystals.

#### Recurrent Crystallization.

It has been shown in the discussion of crystallization that, in certain of the artificial mixtures, forsterite may crystallize out, become completely redissolved (resorbed) and again crystallize out at a lower temperature. This behavior, in a comparatively simple system, illustrates how complicated the so-called 'order of crystallization' may be in a system so complex as an igneous magma. In natural rocks a great number of solid solution series are known to occur and there are a great many possibilities, or better necessities, of equilibrium in the liquid between orthosilicate and metasilicate molecules as exhibited, in the artificial system and in natural rocks, by pyroxene and olivines, between feldspar and feldspathoid molecules and of other equilibria which readily suggest themselves. The theoretical discussion of crystallization in such systems in terms of simple eutectics cannot lead to any useful conclusion.

We have, then, in the artificial system studied, a concrete example of the possibility of crystallization in 'two generations.' It is not necessary, however, that the two generations of any mineral, often observed by the petrographer, should have come about in a similar manner. Perfectly continuous crystallization may give the appearance of crystallization in two generations. The earliest formed crystals may continue to grow in size up to a certain point, when the increasing viscosity or the increasing ratio of crystals to liquid may necessitate the formation of new centers of crystallization. In such a case there may be larger phenocrysts and smaller groundmass crystals of a certain mineral though crystallization was perfectly continuous.

### The Significance of Zoned Crystals.

The distinction between the two types of crystallization described for the artificial, pyroxene-bearing melts should be carefully considered in any discussion of the crystallization of an igneous rock magma. In the first type of crystallization, the liquid is at equilibrium at any temperature with all the crystals, and with all parts of the crystals, existing in it. In the second type the liquid is at equilibrium at any temperature only with the crystals separating at that temperature. To realize the first type it is often necessary that crystals already separated should be redissolved and that mix-crystals already separated should change their composition, whereas in the second type no such changes take place. Between the extremes of perfect adjustment of equilibrium between the liquid and the early-formed crystals and complete lack of adjustment there is every stage of partial adjustment. If the mechanism of crystallization is considered, it is apparent that perfect adjustment must be exceedingly difficult to obtain. In order to change the composition of a mix-crystal there must be a diffusion of material in the solid crystal itself and an interchange of material between it and the liquid. In the meantime crystallization of a further quantity of mix-crystal of somewhat different composition is in progress and is almost certain to take place as a layer or zone about the early crystal as a nucleus, rather than to form a new nucleus. Unless diffusion in the solid can take place fast enough to bring about a change, the composition of this outer layer will remain different from that of the layer it surrounds, while still other layers are added. Cooling at an exceedingly slow rate might, perhaps, bring about perfect adjustment, but usually zoned crystals will result.

It is well known that zoned crystals are common in natural rocks. The significance of the formation of zoned crystals is great because, as has been shown in the discussion of crystallization of the second type, the temperature of final solidification is thereby very much lowered—the temperature and time interval of crystallization, therefore, much increased.\*

Even when the cooling is extremely slow, a factor other than zoning may intervene to bring about the same result of preventing the early crystals from participating in any interchange with the liquid necessitated by equilibrium at a lower temperature. This factor is the rising or sinking of crystals under the action of gravity as they grow in the liquid.

# Consequences of the Possible Sinking of Early Crystals in a Fluid Magma.

The idea that the sinking of crystals in a fluid magma has some importance in the differentiation of igneous rocks has recently been gaining ground. That such action must take place seems hardly debatable, only its relative importance is at issue.

In the melts here described, from our precise knowledge of equilibrium, we are able to determine definitely the effect of a possible settling of crystals. In discussing the crystallization

\* See also N. L. Bowen: The Melting Phenomena of the Plagioclase Feldspars, this Journal (4), xxxv, 597, 1913. of the melts, the behavior of a mixture of composition M, fig. 17, was described. If we imagine that the olivine crystals settled towards the lower layers, then, as the temperature of the point K is approached, the composition of these layers would lie between M and A and of some of the upper layers between P and K. On further cooling the various layers would behave quite differently, those having an abundance of olivine would crystallize to a mixture of pyroxene and olivine, those with only a small amount of olivine would have the olivine completely resorbed and would finally crystallize to a mixture of pyroxene and silica (cristobalite or tridymite). Thus the settling of crystals may bring about not merely a difference in the proportions of the minerals in various layers, but may produce a partially different assemblage of minerals.

The portions which crystallized to pyroxene and silica would, moreover, become completely crystallized at a lower temperature than would the other portions and might, perhaps, show an intrusive relation to the olivine-bearing portions. Such a result would be impossible if the minerals showed the simple eutectic relation, even if there were settling of crystals, for in this case all parts would have some share of liquid until the time of simultaneous final solidification of all the layers, assuming, of course, all the layers to have the same temperature. In the case of a difference of temperature in different layers, the cooler layers would necessarily become completely solid before the warmer layers when eutectic relations prevailed, however great a quantity of crystals had settled. In the melts described, however, the settling of olivine could bring it about that a lower, olivine-rich layer might become completely solid when at a higher temperature than an upper layer, poor in olivine, and still largely liquid.

But this result may be accomplished, not by the settling of olivine alone, but also by the settling of the early-formed, more magnesian pyroxenes and the continued concentration of calcic pyroxenes in the liquid. The crystallization would then tend towards crystallization of the second type and the result would be the same as when zoned crystals are formed. Here again one portion might become completely solid even when at a higher temperature than another portion still partly liquid. A similar behavior is possible in any melt that deposits mixcrystals of which one constituent has a considerably higher melting point than the other, as is notably the case with that very important rock-forming series, the plagioclase feldspars. Thus it seems possible that a homogeneous magma, containing substances capable of forming mix-crystals, as do all magmas, could become differentiated through crystallization into parts which gave evidence of having solidified at different

times and which had quite different compositions. Neither is it necessary, as it would be in the case of simple eutectic relations, that the part lying towards the cold contact should be the one giving evidence of having solidified first, for it would be possible to have the temperature of final solidification of such portions so lowered by the sinking out of crystals that they might still be largely liquid when a lower and hotter portion had already completely solidified.

To the writer it seems that the settling out from a basic magma of the more calcic plagioclases and the pyroxenes rich in magnesia and iron is the dominant control in the differentiation of the ordinary lime-alkali series of igneous rocks. Possibly causes other than gravity, which may bring about a similar relative movement of crystals and liquid, may be of equal importance, an example being the intrusion or forcing out of the liquid phase at a stage when most of the magma has crystallized. It would therefore be better to state that fractional crystallization, as opposed to fractionation in the liquid state, when aided by the processes mentioned, appears to be the prime factor<sup>\*</sup> in the differentiation of the series mentioned.

In making this result possible the occurrence of mix-crystals is one of the fundamental factors.

# Dissociation in the Liquid Phase and its Relation to Crystallization.

There is one question on which the behavior of the artificial melts throws some light and of which some mention might be made, that is the question of the state of combination of the various oxides in the liquid state. It has been maintained by some that the oxides must exist uncombined; at the time of crystallization they combine and the combinations may be different under different physical conditions. Unless this is true, it is stated, the same magma could not under different conditions give rise to different rocks. To this argument the objection has been raised that there is no evidence that the heat of combination is set free at the time of crystallization and that the oxides must therefore be combined. From the viewpoint of general chemistry, it might be stated that both views are right and both wrong. We must consider that in any melt there are certain amounts of the free oxides and of all possible combinations of these oxides.<sup>+</sup> The necessity of such

\*Cf. Harker, A.: Fractional Crystallization the Prime Factor in the Differentiation of Rock-Magmas. Communicated to 12th Int. Geol. Congress, Toronto, 1913.

Cf. Harker, A.: The Natural History of Igneous Rocks, p. 165.

an assumption is illustrated in the magnesia-rich mixtures of the present investigation and especially in the simple case of the mixture of composition  $MgSiO_3$ . The behavior of a liquid of this composition, when cooled, illustrates the fact that, in the liquid state, the whole cannot consist simply of the compound  $MgSiO_3$ . All possible compounds must be considered; that which separates in the solid form will be the one which, under the conditions, happens to be the first to reach its limit of solubility.

In the case of liquid of composition  $MgSiO_3$  we must consider that, among others,  $Mg_2SiO_4$  molecules are present and that, on cooling, the liquid becomes saturated with these at 1577°, forsterite separating out. On further cooling forsterite continues to separate, the liquid always remaining at the point of saturation with respect to that substance. At 1557° the liquid becomes saturated with respect to  $MgSiO_3$  and clinoenstatite begins to separate. In the liquid an equilibrium exists which can be represented by the equation

$$2 Mg SiO_{3} \longrightarrow Mg_{2}SiO_{4} + SiO_{3}$$

and at any temperature there is a definite equilibrium constant, that is, the relative proportions of the three compounds are fixed. When, at  $1557^{\circ}$ , MgSiO<sub>3</sub> separates from the liquid it is necessary that this reaction should proceed in the direction from right to left in order to maintain these proportions. This reaction lessens, however, the concentration of Mg<sub>2</sub>SiO<sub>4</sub> in the liquid and since the liquid must remain at the point of saturation with respect to forsterite, forsterite must dissolve. This cycle continues, forsterite dissolving and clino-enstatite precipitating, until the whole consists of crystalline clinoenstatite.

In all the compositions lying along the line between  $MgSiO_s$ and  $CaMgSi_2O_s$  as far as 75 per cent  $CaMgSi_2O_s$  we have, in the separation of forsterite, this direct evidence of the same equilibrium reaction in the liquid. It should not be assumed, because forsterite does not separate from liquid  $CaMgSi_2O_s$ and the mixtures close to it, that this reaction does not occur. On the contrary, it simply happens that liquid  $CaMgSi_2O_s$ becomes saturated on cooling with diopside first, and for this reason the whole crystallizes to diopside. Among others, a possible equilibrium in liquid diopside could be written

### $2\text{CaMgSi}_{2}\text{O}_{4} \rightleftharpoons 2\text{CaSiO}_{4} + \text{Mg}_{2}\text{SiO}_{4} + \text{SiO}_{2}$ .

Crystallization of diopside simply causes the reaction to proceed from right to left and the whole becomes solid diopside, the crystalline product, by itself, giving no clue to the state of combination in the liquid.

In summing up, then, it may be stated that any igneous magma or mineral melt may best be regarded from the viewpoint of the kinetic theory: all possible combinations and dissociations are going on simultaneously. At any temperature all the reactions have a definite rate and at equilibrium there are definite relative amounts of all the constituents. On cooling such a magma the first substance to crystallize will be that one of all those present which happens to reach first its point of saturation with respect to the liquid under the prevailing conditions. Under different conditions there may crystallize first an entirely different substance. This is true of the substance which crystallizes second and so on till all is solid. For this reason the same magma might give rise to different assemblages of minerals under different conditions. The whole reduces itself to a question of relative solubilities (relative degree of saturation) considered in conjunction with equilibrium between the molecules in the liquid phase.

### Freezing-Point Lowering in Silicate Mixtures.

Many attempts have been made to calculate freezing-point lowering in silicate melts and therefrom to calculate eutectic points of various pairs of minerals. Usually the law of freezing-point lowering in dilute solutions has been used. It is well known that this law cannot apply to concentrated solutions and that even the form of equation used for concentrated solutions need correction factors when there is association or dissociation in the liquid phase. The binary system, diopsideforsterite, exhibits an extreme case of variation from the simple rules. The addition of forsterite to diopside depresses the freezing-point an almost inappreciable amount—the eutectic point at the composition 12 per cent forsterite is only about 4°-5° below the melting-point of diopside. The microscope shows that there is no solid solution, so the explanation of this slight depression must be sought in a different direc-It has already been stated as probable that diopside is tion. dissociated in the liquid state and a possible equation for this dissociation was given.

### $2 \text{CaMgSi}_2\text{O}_6 \implies 2 \text{CaSiO}_3 + \text{Mg}_2\text{SiO}_4 + \text{SiO}_2.$

If forsterite is added to a liquid containing all the above molecules, a necessary result is the driving of the reaction from right to left and, therefore, the actual concentration of diopside molecules may be changed very little. At the freezingpoint of diopside the complex liquid is just saturated with diopside molecules. The addition of forsterite ( $Mg_2SiO_4$ ), if it affects very little the concentration of diopside molecules, should therefore change the freezing-point very little. The very

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### Diopside—Forsterite—Silica.

slight effect on the freezing-point actually observed may therefore be due to the existence of an equilibrium in the liquid such as that expressed in the above equation. The equation for the actual equilibrium is probably much more complicated than the above, but, if the reasoning is correct, should contain the molecule Mg<sub>2</sub>SiO<sub>4</sub> as one of the reaction products. In confirmation of this view that diopside is dissociated in the liquid state is the fact that, whereas the crystals of the CaSiO<sub>3</sub>-MgSiO, series show a sharp minimum on the curve of specific volumes at the composition of diopside,\* the glasses of the same series (undercooled liquid) show no minimum.<sup>+</sup> The smooth curve of specific volumes of the glasses does, however, lie distinctly below the straight line joining the volumes of the end members and may be considered to indicate, therefore, the formation of some of the denser diopside molecules in the liquid, but only in equilibrium proportions.

It is probable that more or less dissociation in the liquid state is common with silicates and, when mixed, they mutually affect each other in this respect. It is, therefore, not to be expected that, in the usual case, silicate mixtures should obey any simple law of freezing-point lowering. Disagreement with the law is, however, probably more apparent than real, for, in order to apply the law, a knowledge of the molecules present is necessary, whereas there is usually a complete lack of knowledge of this point, as well as of the heat-effects accompanying any molecular changes.

#### GENERAL SUMMARY.

The results obtained in the investigation of the three binary systems involved are first presented. The system diopside-silica shows the simple eutectic relation, as does also the system diopside-forsterite. The system forsterite-silica shows one intermediate compound MgSiO<sub>s</sub> (clino-enstatite) unstable at its melting-point.

In the ternary system it is found that clino-enstatite and diopside form a complete series of solid solutions (monoclinic pyroxenes) and therefore have a common field. As a further consequence of this unbroken series of solid solutions there is no ternary eutectic, the lowest point of formation of liquid in the system being the binary eutectic diopside-silica.

A brief theoretical discussion of solid solution in ternary systems is given in which the significance of certain lines, termed three-phase-boundaries, is pointed out. The results of

\* Allen, White, Wright and Larsen, this Journal (4), xxvii, 27, 1909. † Larsen, E. S., ibid. (4), xxviii, 263, 1909. the experimental determination of the three-phase-boundaries in the system being investigated are then presented.

The course of crystallization in typical mixtures is described and the value of the three-phrase-boundaries pointed out, especially their usefulness in determining the composition of mix-crystals separating at any temperature. In considering crystallization it is shown that crystallization may proceed according to two different methods; first, that in which the liquid is, at any temperature, in equilibrium with all the crystals and all parts of the crystals occurring in it; and second, that in which the liquid is in equilibrium at any temperature only with the crystals separating at that temperature. In a general way, crystallization of the second type is favored by quick cooling.

The importance of distinguishing between the two types of crystallization is great in the present system. It is shown that the difference between the conclusions arrived at in the present work and those arrived at in an earlier investigation of the pyroxene series carried out at this laboratory is due largely to the fact that in the earlier work crystallization of the second type occurred in many of the mixtures, whereas, if equilibrium is to be studied, crystallization of the first type must be obtained.

In the optical part of the paper the optical properties of the various crystalline phases are given. The properties of the series of monoclinic pyroxenes extending from diopside to enstatite vary continuously with composition. The artificial pyroxenes are compared with the enstatite-augites of Wahl.

In considering the bearing of the results on petrologic problems attention is called to the resorption of the olivine, forsterite, in the artificial mixtures and its probable relation to resorption of olivines in natural rocks. The consequences of the possible settling of crystals in a fluid magma (crystallization-differentiation) is discussed in the light of the facts known concerning the artificial mixtures.

Geophysical Laboratory

Carnegie Institution of Washington, Washington, D. C., June 23, 1914.

### ART. XX.— The Estimation of Iodine and Bromine in Haloid Salts by Means of Telluric Acid; by HARRIET ISABELLE COLE.

[Contributions from the Kent Chemical Laboratory of Yale University-cclxi.]

It has been shown in a previous paper<sup>\*</sup> from this laboratory that telluric acid may be used as an oxidizing agent to liberate bromine from hydrobromic acid and that the method may be relied upon to determine with accuracy amounts of bromine up to 0.3 grm. associated with 0.25 grm. of chlorine combined in the form of chloride. The present paper is the account of an attempt to extend this process to the estimation of iodine by finding the conditions under which telluric acid will react, first, with hydriodic acid to liberate the iodine quantitatively without a similar liberation of bromine, and second, with hydrobromic acid in such a way as to bring the reaction to completion without setting free chlorine from the hydrochloric acid formed in the reaction.

Telluric acid is not capable alone of bringing to completion the reaction with iodides to form hydriodic acid and then free iodine in solution, at such dilution that it will not also liberate some bromine from the bromide. The function of liberating the hydriodic acid so that the telluric acid may act as oxidizer has been performed by a very dilute solution of sulphuric acid, which after the removal of the iodine is then increased in order that the bromine of the hydrobromic acid may be similarly set free.

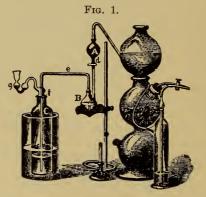
In the work to be described the telluric acid was prepared directly from the dioxide by precipitating tellurous acid from a hot solution of tetrachloride by means of water, and oxidizing with chlorine to telluric acid. Selenium present in the material may be removed by evaporating the telluric acid solution on a water bath. A slight reduction takes place in the presence of strong hydrochloric acid at this temperature and the selenium is first thrown out, the reduction being hastened by the presence of metallic tellurium. The filtered solution is re-chlorinated and evaporated in a current of air at room temperature. The telluric acid is washed with strong alcohol to remove traces of hydrochloric acid and recrystallized two or more times from water solution. In this way a very pure product may be readily prepared in considerable quantity.

The potassium bromide used was made by ignition and thorough fusion of potassium bromate specially prepared from purified bromine and potassium hydroxide. The potassium chloride was made by recrystallizing five times and thoroughly igniting pure potassium chlorate. The potassium iodide was prepared with great care, by acting with re-sublimed iodine upon iron wire, three-fourths of the iodine being

\* Gooch and Cole, this Journal (4), xxxvii, 219, 1914.

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added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the color of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine had been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was evaporated and recrystallized and the resulting salt carefully



ground in a mortar to insure a homogeneous product. This preparation gave by the arsenate method in three determinations, 0.4994 grm.; 0.4994 grm.; 0.4993 grm. of potassium iodide in 0.5000 grm. of salt weighed out.

The sulphuric acid used in the determinations was absolutely free from nitrous fumes, as an exceedingly slight trace will greatly increase the dilution at which chlorine is liberated.

Solutions of iodine and sodium thiosulphate of approximately N/10 strength were carefully standardized, the iodine against N/10 arsenite and the thiosulphate against the iodine with the use of starch as indicator. The halogen salts were kept over sulphuric acid in a desiccator and were weighed directly for each determination.

The form of apparatus used for the distillation and absorption of liberated bromine in the earlier work, and shown in the accompanying figure (fig. 1), was again used in the iodine and bromine determination, the smaller Voit flask being replaced therein, by an ether wash-bottle having the larger capacity of  $200^{\text{cm}^3}$ . All joints in the apparatus were of glass. The ether wash-bottle which served as the distillation flask was graduated with etched lines at  $10^{\text{cm}^3}$  intervals. A thick platinum wire so bent as to rest upon the bottom of the flask with the two ends upright was used as an aid in indicating the final volumes of  $70^{\text{cm}^3}$  and  $18^{\text{cm}^3}$ . The Drechsel bottle, which served as the receiver of the distillate, was kept cool by immersion in ice-water. A Kipp generator for the delivery of washed carbon dioxide was connected, as needed, with the separating funnel.

In the following preliminary tests the alkali halides and the telluric acid were introduced in solution into the distillation flask with  $15^{\text{cm}^3}$  of sulphuric acid of sp. gr. 1.015 (measured from a burette and prepared by diluting  $10^{\text{cm}^3}$  of concentrated acid to  $1000^{\text{cm}^3}$ ) and the total volume was made up to  $125^{\text{cm}^3}$  with water. The connection was made between the flask and the receiver charged with  $200^{\text{cm}^3}$  of a 1.5 per cent solution of potassium iodide, carbon dioxide was passed slowly through the apparatus, and the liquid in the flask, heated gradually at first, was concentrated by boiling to the volume recorded.

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Preliminary tests upon mixtures of the Halogen Salts. [Initial volume 125 cm<sup>3</sup> : H<sub>2</sub>TeO<sub>4</sub> 1 grm.]

KI taken	KBr taken	KCl taken	First final volume*	KI found	Error in terms of iodine	Second final volume†	KBr found	Error in terms of bromine
grm.	grm.	grm.	$cm^3$ .	grm.	grm.	$\mathrm{cm}^{3}$ .	grm.	grm.
			•	A				
0.5000			75	0.4993	-0.0001			
0.2000	0.5000		72	0.4995 (Trace due to	+0.0001			
	$0.5000 \\ 0.5000$		$50 \\ 50$	evolution				
	0.9000		- 50	(of bromine				
				В				
0.5000		0.2	65	0.1996	-0.0001			
0.5000		0.2	50	0.1996	-0.0001			
				С				
0.2000	0.2000	1	67	0.2009	+0.0008	17.5	0.1990	-0.0006
0.2000	0.2000		67+	0.1999	+0.0001	17.5	0.1995	-0.0003
0.2000	0.2000		67 +	0.1996	-0.0001	17.0	0.2002	+0.0001
				D		· · · ·		
0.1000	0.2000	0.2	67	0.1012	+0.0009	17.0	0.2030	+ 0.0018
0.1000	0.2000	0.2	67	0.1008	+0.0006	18.0	0.2004	+0.0005
0.1000	0.2000	0.2	67	0.0999	0.0000	1000	0.2016	+0.0009
0.1000	0.5000	0.2	67	0.1009	+0.0007	19.5	0.2007	+0.0004
0.2000	0.2000	0.2	67	1 0.0000			0 1000	
0.5000 0.5000	0.2000	$0.2 \\ 0.2$	64	$0.2009 \\ 0.2017$	+0.0008 +0.0014	$rac{20\cdot5}{19\cdot5}$	$0.1980 \\ 0.1957$	-0.0012 -0.0025
0.2000	0.2000	0.2	73	0.1996	-0.0001	$155 \\ 16.5$	0.1957 0.2015	+0.0023
	,	,	1				0.2010	+0 0003
0.3000	0.5000	0.3	65	0.3002	+0.0008	20.0	0.1994	-0.0003
0.3000	0.2000	0.3	67	0.2992	-0.0005	17.5	0.2026	+0.0012
0.3000 0.3000	0.2000	0.3 0.3	67	0.2996	0.0000	17.0	0.2026	+0.0015
0.2000	0.2000	0.3	67	0.2998	+0.0001	18.0	0.2018	+0.0010
0.0500	0.4000	0.3	67	0.0231	+0.0022	17.5	0.3995	-0.0003
0.0500	0.4000	0.3	65	0.0223	+0.0016	21.0	0.4002	+0.0001
0.4000	0.0200	0.2	1 00	. 0.9000	0.0000	120		
0.4000 0.4000	0.0200	$\begin{array}{ } 0.3 \\ 0.3 \end{array}$	63	0.3990	-0.0002 + 0.0001	$17.0 \\ 18.5$	$0.0207 \\ 0.0203$	+0.0004
	0 0 200	00	00	0 0990	+0.0001	10.0	0.0303	+0.0001

 $* H_2 SO_4$  of lower concentration.

+ H<sub>2</sub>SO<sub>4</sub> of higher concentration.

### 268 H. I. Cole—Estimation of Iodine and Bromine in

The preliminary tests of Table I, A, show that the iodine is completely eliminated from 0.5 grm. of potassium iodide during the process of concentrating to 75<sup>cms</sup> the solution containing 1 grm. of telluric acid and 15<sup>cm<sup>3</sup></sup> of the dilute sulphuric acid, sp. gr. 1015; and that no bromine is evolved from 0.5 grm. of potassium bromide similarly treated until the concentration of 50<sup>cm<sup>3</sup></sup> is reached. From the results given in B and C it appears that, while the presence of a chloride does not affect the determination of the iodine of the iodide, the presence of bromine tends to introduce slight errors of excess. On the other hand, in those determinations in which an excess of iodine is indicated the results show a slight deficiency in the bromine. This complementary relation of the errors of the iodine and the bromine points to an easier evolution of bromine if free iodine is present during concentration to a limit in the neighborhood of that at which the bromide by itself begins to evolve bromine. A similar phenomenon was noted in previous work\* when the presence of free bromine had the effect of raising the limit at which chlorine began to be evolved from a chloride.

In these tests the iodine collected in the receiver after the concentration of the solution to a volume of  $65^{\text{cms}}$  to  $70^{\text{cms}}$  was estimated by titration with N/10 thiosulphate, the receiver was recharged with  $200^{\text{cms}}$  of a 1.5 per cent solution of potassium iodide and connected with the distilling flask,  $10^{\text{cms}}$  of sulphuric acid [1 : 1] was then added through the separating funnel to the reaction mixture, and the solution concentrated as before to a volume between  $17^{\text{cms}}$ - $18^{\text{cms}}$ . The bromine was estimated by titrating with N/10 thiosulphate the iodine set free in the receiver.

The effect of the presence of free iodine upon the elimination of bromine from the bromide, as of free bromine upon the elimination of chlorine from the chloride, is clearly manifest in the results, although a part of the irregularity in the bromine determination was no doubt due to the difficulty in measuring with exactness the final volumes in so large a flask. So long as hydriodic acid remains undecomposed the formation of either iodic acid or a compound of iodine with chlorine or bromine is not possible, and so long as hydrobromic acid is present the formation of a compound in which the bromine will drag along chlorine is also an impossibility. The conditions of concentration at which the hydriodic acid and the hydrobromic acid, respectively, have been completely broken up while the free halogen remains in solution are points at which there is danger that the halogen less easily evolved will enter into combination with the volatile, free halogen. It is desirable, therefore, that the free halogen should be eliminated as it is evolved and from

solutions safely dilute. In the experiments of Table II, the expedient was adopted of introducing steam, with the carbon dioxide, so that the volumes might be held constant above the critical concentrations until the volatile halogen had been eliminated as set free.

#### TABLE II.

Preliminary Distillations in Steam from Flask. [Initial volume 100 cm<sup>3</sup> : H<sub>2</sub>TeO<sub>4</sub> 1 grm.]

KI taken	KBr taken	KCl taken	First final volume*	KI found	Error in terms of iodine	Second final volume	KBr found	Error in terms of bromine
grm.	grm.	grm.	cm <sup>3</sup> .	grm.	grm.	cm <sup>3</sup> .	grm.	grm.
				А				
$0.2000 \\ 0.2000$	$0.3000 \\ 0.3000$	$0.3 \\ 0.3$	$63.0 \\ 55.0$	0·1992 0·1996	$ \begin{array}{c} -0.0003 \\ -0.0001 \end{array} $	$19.0 \\ 18.5$	0·3019 0·3001	$^{+0.0011^{1}}_{+0.0001^{2}}$
0·3000 0·3000	$0.2000 \\ 0.2000$	$\begin{array}{c} 0.3 \\ 0.3 \end{array}$	$\begin{array}{c} 66.5 \\ 70.0 \end{array}$	$0.2996 \\ 0.2993$	$\begin{vmatrix} 0.0000 \\ -0.0002 \end{vmatrix}$	$20.0 \\ 20.0$	$0.1999 \\ 0.1998$	$-0.0001 \\ -0.0001$
0·5000 0·5000	$0.5000 \\ 0.5000$	$0.3 \\ 0.3$	$63.5 \\ 52.0$	$0.4985 \\ 0.4989$	$\begin{vmatrix} -0.0006 \\ -0.0003 \end{vmatrix}$	<sup>3</sup> 19·0 <sup>3</sup> 17·5	$0.4973 \\ 0.4986$	$-0.0016 \\ -0.0008$
				В				
$\begin{array}{c} 0.0200\\ 0.0200\end{array}$	$0.4000 \\ 0.4000$	$\begin{array}{c} 0.3 \\ 0.3 \end{array}$	$52.5 \\ 64.0$	$0.0206 \\ 0.0200$	+ 0.0004 + 0.0001	17·0 18·5	$0.4036 \\ 0.4036$	$^{+\ 0.0021}_{+\ 0.0021}$
$\begin{array}{c} 0.0200\\ 0.0200 \end{array}$	0·3000 0·3000	0.3	$\begin{array}{c} 64.0 \\ 63.0 \end{array}$	$0.0201 \\ 0.0200$	+0.0001 + 0.0001	$17.0 \\ 19.5$	$\begin{array}{c} 0.3031 \\ 0.3026 \end{array}$	+ 0.0018 + 0.0015
$0.0200 \\ 0.0200$	$0.0200 \\ 0.0200$	$0.5 \\ 0.5$	$62.5 \\ 66.0$	$0.0200 \\ 0.0200$	+0.0001 +0.0001	$17.5 \\ 19.5$	$0.0240 \\ 0.0235$	+0.0028 + 0.0021
* 11 90	) of low		ntration		11 60	of high	07 007 001	ntration

 $H_2SO_4$  of lower concentration.

 $\frac{1}{2}$  slow boiling below 30 cm<sup>3</sup>

 $+H_2SO_4$  of higher concentration.  ${}^{3}[\mathrm{H}_{2}\mathrm{TeO}_{4} = 0.2 \mathrm{grm. added.}]$ 

In Table II the results indicate that with the use of steam the iodine may be removed from potassium iodide at volumes ranging between 70<sup>cm<sup>3</sup></sup> and 52<sup>cm<sup>3</sup></sup>, but there seems to be a tendency toward a very slight deficiency in the iodine (A) except when small amounts (B) of the iodide are used; while the bromine determinations are high if the boiling is continued after the complete removal of that element, as is the case when the concentration is carried to 17cms after the prolonged boiling. Rapid concentration after a volume of 30<sup>cm<sup>s</sup></sup> has been reached tends to lessen the error.

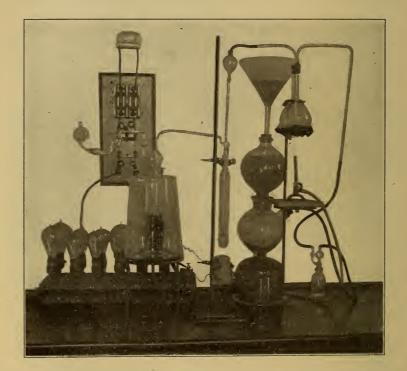
With the apparatus used in these experiments much difficulty was encountered in regulating the final volumes, which cannot be read with an accuracy of more than 5<sup>cm<sup>3</sup></sup>. The exact and final readings of volumes recorded in the table were determined after the experiment by removing the solution to a

AM. JOUR. SCI.-FOURTH SERIES, VOL. XXXVIII, No. 225.-SEPT., 1914. 19

graduate and reading the volume while still warm. For the final experiments, therefore, an apparatus (shown in fig. 2) was devised which permits more exact reading of the volumes.

A tubular flask  $25 \cdot 6^{\text{cm}s}$  high and  $3 \cdot 2^{\text{cm}}$  in diameter with a capacity of  $150^{\text{cm}s}$ , and provided with a ground-glass stopper and delivery tube extending to the bottom of the flask, was substituted for the distillation flask. Etched lines at  $1^{\text{cm}s}$  in-

F1G. 2.
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tervals in the locality of final volumes furnished a very accurate and simple means for determining the concentrations. An asbestus collar wound with nichrome wire (offering a resistance of 16 ohms) was used on a 110 volt current (with a 12 bulb lamp-board) as a means for heating, and was lowered on the flask as the solution evaporated. Steam was passed in at such a rate that the solution never became highly colored with the liberated halogen. A series of tests, Table III ( $\Lambda$ ), shows that all the bromine eliminated from 0.5 grm. of potassium bromide can be removed by concentrating from a volume of  $70^{\text{cm}^3}$  to a volume of  $28^{\text{cm}^3}-25^{\text{cm}^3}$  with the aid of steam.

### TABLE III.

Distillation in Steam from Tubular Flask. [Initial volume 100 cm<sup>3</sup> : H<sub>2</sub>TeO<sub>4</sub> 1.0 grm.]

					······································			
KI taken	KBr taken	KCl taken	First final volume*	KI found	Error in terms of iodine	Second final volume†	KBr found	Error in terms of bromine
grm.	grm.	grm.	cm <sup>3</sup> .	grm.	grm.	cm <sup>3</sup> .	grm.	grm.
				A				
	0·3000 0·3000 0·3000					25 28 26	0·3001 0·3002 0·3000	$\begin{array}{c} + 0.0001 \\ + 0.0001 \\ 0.0000 \end{array}$
				В				
0·2000 0·2000	$0.3000 \\ 0.3000$	$\begin{array}{c} 0.3 \\ 0.3 \end{array}$	66 66	$0.2000 \\ 0.2000$	$  \begin{array}{c} +0.0001 \\ +0.0001 \end{array}  $	$\begin{array}{c} 24\\ 24 \end{array}$	$0.3003 \\ 0.3001$	+0.0001 + 0.0001
0·3000 0·3000	$0.2000 \\ 0.2000$	$\begin{array}{c} 0.3 \\ 0.3 \end{array}$	65 60	$0.2995 \\ 0.2996$	$ \begin{array}{c c} -0.0001 \\ 0.0000 \end{array} $	$\begin{array}{c} 25\\ 24 \end{array}$	$0.2004 \\ 0.2004$	+0.0002 + 0.0002
0·5000 0·5000 [0·5000	$0.5000 \\ 0.5000 \\ 0.5000$	$\begin{array}{c} 0.3 \\ 0.3 \\ 0.3 \end{array}$	$\begin{array}{c} 64\\ 60\\ 64 \end{array}$	$0.4989 \\ 0.4989 \\ 0.4989$	$\begin{array}{c} -0.0003 \\ -0.0003 \\ -0.0003 \end{array}$	$^{1}23$ $^{1}24$ $^{1}23$	$0.4995 \\ 0.4995 \\ 0.5018$	$\begin{array}{c} -0.0003 \\ -0.0003 \\ +0.0010 \end{array}$
0·5000 0·5000	$0.5000 \\ 0.5000$	$\begin{array}{c} 0.5 \\ 0.5 \end{array}$	62 64	$0.4993 \\ 0.4994$	$-0.0001 \\ -0.0000$	$\begin{smallmatrix}&1&23\\&1&23\end{smallmatrix}$	$0.4999 \\ 0.4998$	$-0.0001 \\ -0.0001$
$0.0200 \\ 0.0200$	$0.4000 \\ 0.4000$	$\begin{array}{c} 0.3 \\ 0.3 \end{array}$	$\begin{array}{c} 64 \\ 64 \end{array}$	$0.0201 \\ 0.0200$	+0.0001 + 0.0001	$\begin{array}{c} 25\\ 24 \end{array}$	$\begin{array}{c} 0.4009 \\ 0.4009 \end{array}$	$^{+0.0005}_{+0.0005}$
$\begin{array}{c} 0.0200\\ 0.0200\end{array}$	0·3000 0·3000	$\begin{array}{c} 0.3 \\ 0.3 \end{array}$	$\begin{array}{c} 64 \\ 64 \end{array}$	$0.0205 \\ 0.0205$	+0.0004 + 0.0004	$\begin{array}{c} 24\\ 24\end{array}$	$0.2997 \\ 0.2998$	$-0.0001 \\ -0.0001$
$0.0200 \\ 0.0200$	$0.0200 \\ 0.0200$	$0.5 \\ 0.5$	$\begin{array}{c} 65\\ 64 \end{array}$	$0.0200 \\ 0.0200$	+0.0001 + 0.0001	$\begin{array}{c} 24\\ 24\end{array}$	$0.0213 \\ 0.0201$	+0.0007 + 0.0001
* $H_2SO_4$ of lower concentration. + $H_2SO_4$ of higher concentration.						ntration.		

In the final tests recorded in Table III (B) the solution (consisting of the three halogen salts ranging as high as 0.5 grm. each with 15<sup>cm<sup>3</sup></sup> of sulphuric acid [sp. gr. 1.015] and 1 grm. of telluric acid) was concentrated to a volume of  $64^{cm^3}$ - $66^{cm^3}$  for the removal of the iodine; and after the addition of 10cm<sup>2</sup> of sulphuric acid [1:1] was evaporated to a volume of  $24^{cm^3}$  for the removal of the bromine. On large charges the amount of telluric acid consumed by the oxidation of the iodide is calculated from the iodine found in the receiver and replaced before determining the bromine in order to insure an excess of 0.5 grm. of telluric acid at the final concentration.

The results of these experiments show that the method may be relied upon to determine with accuracy amounts of iodine up to 0.35 grm. (0.5 grm. of potassium iodide) and of bromine up to 0.3 grm. (0.5 grm. of potassium bromide) associated with

 $<sup>{}^{1}</sup>$ [H<sub>2</sub>TeO<sub>4</sub> = 0.3 grm. added.]

0.25 grm. of chlorine combined in the form of chloride (0.5 grm. of potassium chloride).

According to the procedure found to be effective, the three haloid salts are introduced into the tubular flask with 50<sup>cm<sup>3</sup></sup> of water. The flask and the inlet tube of the receiver, the latter charged with 200<sup>cm<sup>3</sup></sup> of a 1.5 per cent solution of potassium iodide, are connected after moistening the surface of the ground-glass joint. Telluric acid, 1 grm., dissolved in 15<sup>cm</sup> of sulphuric acid, sp. gr. 1.015, measured from a burette is introduced through the separating funnel with sufficient water to make the volume 100<sup>cm<sup>3</sup></sup>. Carbon dioxide and steam are passed very slowly through the solution and the boiling mixture is not allowed to concentrate below 100<sup>cm<sup>3</sup></sup> until all traces of color due to liberated iodine has left the solution. The mixture is then evaporated, with only enough steam to prevent the return of any color, to a volume of 64<sup>cm<sup>3</sup></sup> to 67<sup>cm<sup>3</sup></sup>. The amount of heat is regulated by the lamps in the resistance board and the furnace is always kept just below the surface of the solution in the tubular flask. At the final volume the source of heat is withdrawn and as soon as the apparatus is cool enough to be conveniently handled the receiver is disconnected and the free iodine in the receiver and trap is titrated with standard sodium thiosulphate. The receiver is then again charged with 200<sup>cm<sup>3</sup></sup> of 1.5 per cent potassium iodide solution and connected after moistening the surface of the ground-glass joint with sulphuric acid to serve as a lubricant and lute. Sulphuric acid, 10<sup>cm<sup>3</sup></sup> of the [1:1] mixture, is introduced through the separating funnel and carbon dioxide is passed very slowly through the apparatus. As soon as the boiling mixture shows any discoloration steam is passed in at a rate just sufficient to compensate for the vapor carried over until all color is removed, when the concentration is slowly continued with the help of steam to a volume of 30<sup>cm<sup>3</sup></sup>, from which point the remaining solution is rapidly boiled to a volume of 24<sup>cm<sup>3</sup></sup>. The furnace is removed and, as soon as the apparatus is sufficiently cool to disconnect, the free iodine in the receiver and trap is titrated with standard sodium thiosulphate and taken as the measure of the bromine liberated.

By the procedure described it is possible to determine with a good degree of accuracy any amount of iodine or bromine up to 0.3 grm. when associated in the haloid salts with amounts of chlorine up to 0.25 grm. The entire operation need not occupy more than two hours and a half.

In conclusion the author gratefully acknowledges her indebtedness to Professor Gooch for his valuable advice and assistance given during the progress of this work.

### ART. XXI.—Octahedral Crystals of Sulphohalite;\* by HOYT S. GALE and W. B. HICKS.

DURING a call at the office of Dr. S. P. Sadtler in Philadelphia two small octahedrons were noted by Mr. Gale among a collection of some hanksite crystals that had come from Searles Lake, California. Inquiry developed that the crystals were unidentified and were supposed to be alum, but that they had not received particular attention. Dr. Sadtler kindly offered to give one of the crystals for further examination. which accordingly was brought to Washington. Specific gravity determinations showed that it could not be alum and suggested sulphohalite, although the few specimens of this mineral that had been previously described are of dodecahedral The index of refraction of the unknown crystal was form. determined by Mr. Larsen but no record of the index of refraction for sulphohalite could be found. Accordingly, it was decided to make a chemical analysis. As this would necessitate the destruction of the crystal in hand, Dr. Sadtler was informed of the developments and kindly presented the other specimen for reference. Hence one of the crystals has been used in the investigation and the other deposited in the U.S. National Museum.

The two crystals were almost identically alike, each a little over a centimeter in diameter, slightly yellowish and clouded, transparent to translucent, resembling in color and substance, but not in form, the hanksite crystals among which they were included in the collection referred to. The crystals are reported to have been collected by Mr. Moerk, having been taken by him direct from the drillings in the saline deposits at Searles Lake, from the sand bucket at the drill holes. It is believed that, like the other described occurrences of sulphohalite, these originally occurred in association with the hanksite crystals in the main salt body of that deposit, and therefore at a depth of less than 100 feet.

Minor cubic and octahedral faces were mentioned in the previous description as being present on the dodecahedral crystals, but the material described in this paper is unique in that the octahedron is the only form present. The broken surfaces show no indication of any cleavage and the fracture is irregular and hackly. The specific gravity was determined as about 2.5. The mineral is isotropic and the refractive index for sodium light was kindly determined by Mr. Esper S. Larsen as 1.455.

\* Published by permission of the Director of the U. S. Geological Survey.

The mineral is readily soluble in water, fuses below red heat, and has no water of crystallization. It contains large quantities of sulphates, chlorides, fluorides and sodium, and a trace of potassium. The analysis on a 0.24 gram sample was carried out in platinum. In reporting the results enough sodium has been calculated to the oxide to combine with the SO, to form the molecule  $Na_2SO_4$ , and the remainder of the sodium reported as Na. The analytical data are as follows (W. B. Hicks, analyst):

Per cent	Calculated for 2Na <sub>2</sub> SO <sub>4</sub> . NaCl.NaF Per cent
SO <sub>3</sub> 42.00	41.61
$Na_{2}O$ $32.50$	32.25
Na 11.35	11.97
Cl 9·19	9.23
F (by difference) 4.71	4.94
Loss at 200° C 0.25	
100.00	100.00

The result of the investigation identifies the specimen conclusively as sulphohalite, and confirms the previous analysis\* by Penfield of this rare mineral.

\* This Journal, (4), ix, p. 425, 1900.

### ART. XXII.—A Problematic Fossil from the Catskill Formation; by FRANCIS M. VAN TUYL and FRITZ BERCKHEMER.

DURING a recent geological excursion of the students of Columbia University in the Delaware Water Gap region of Eastern Pennsylvania, Mr. C. W. Honess and Mr. F. M. Van Tuyl discovered in the Catskill red shale in a cut of the Delaware, Lackawanna & Western Ry., a short distance east of the station of Henrysville, a very peculiar organism which, on account of the scarcity of fossils in this formation and the singularity of its characters, seems to be worthy of description.

### Rectogloma problematica, n. g.; n. sp.

(See Fig. 1, nat. size.)

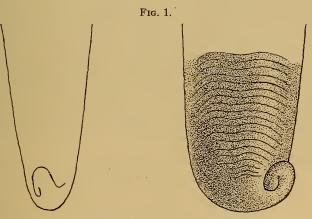


FIG. 1. Rectogloma problematica. Nat. size.

Professor Grabau has generously consented to let us undertake this work.

The fossil occurs in a bed of red shale 5 or 6 ft. thick which is interstratified with other red beds. There are no marine fossils associated, nor do such fossils occur in adjacent layers. We have not been able to identify the form either specifically or generically, and have given it the name *Rectogloma problematica*, a description of which follows:

Form slightly tapering, elliptical in transverse section, about two-thirds as thick as wide; apex terminating in a spiral coil. Surface marked by closely-placed sinuous sutures which gradually disappear on the lateral margins. Distance between sutures 1 to 3<sup>mm</sup>, very gradually decreasing towards the apex and disappearing completely on the apical coil. Sutures arching upwards with a slight depression near the middle, continuing a slight distance interiorly.

Upper extremity of fossil unknown. Apical coil spiral and laterally compressed, lying in the plane of the greatest diameter and consisting of about one whorl. Another specimen in our possession varies from the form described. It is only half as broad, even in the early stages, the suture lines are about half as far apart and the sides are more nearly parallel. This possibly represents a different species.

The fossil stands vertically in the bed with the spirally coiled apex downwards. This is the relationship exhibited by all the specimens found in place. The more perfect specimens, upon which the description is based, are now in the Paleontological Museum of Columbia University.

The affinities of the organism are somewhat obscure. One would at first sight take it for an abnormal cephalopod, on account of its apparent distinct septation, The only slight continuation of the sutures interiorly and their disappearance on the lateral margins, as well as the absence of a siphuncle and the non-septate character of the apical coil, are, however, not in favor of this view. But these negative characters may be due, in part, to the imperfect preservation of the fossil in the red shale. John M. Clarke\* describes Orthoceras specimens from the Oneonta sandstone occupying a position in the beds similar to that of our organism, but his forms exhibit undoubted cephalopod characters.

Paleontological Laboratory, Columbia University.

\* N. Y. State Mus. Bull. 39, vol. viii, pp. 167-171, 1900.

Bigelow—Determination of the "Solar Constant." 277

### ART. XXIII.—The Determination of the "Solar Constant" by Means of Computations Based on the Data of Balloon Ascensions; by FRANK H. BIGELOW.

It is well known that the value of the "solar constant" as derived from pyrheliometer observations, extrapolated by the Bouguer Formula  $I=I_{o}p^{m}$ , is found to be something less than 2.00 gr.cal/cm.<sup>2</sup> min. On the other hand, Abbot's ordinates in the bolometer spectrum energy curve are best satisfied by an initial effective temperature at the sun of about 6900°, corresponding with which the solar radiation at the distance of the earth is about 4.00 gr.cal./cm.<sup>2</sup> min. This wide discrepancy has been the subject of research in connection with the writer's development of non-adiabatic meteorology, and the results of an extensive computation are here summarized, the method of procedure being described in Bulletins No. 3, No. 4, Oficina Meteorologica Argentina, 1912, 1914; this Journal, Dec. 1912, April 1913; Bigelow's Treatise on Meteorology, 1914.

If  $T_o$  is the temperature,  $P_o$  pressure,  $\rho_o$  density,  $R_o$  gascoefficient on the level  $z_o$ , satisfying  $P_o = \rho_o R_o T_o$ , the corresponding  $P_1 = \rho$ ,  $R_1 T_1$  on the  $z_1$ -level are computed from the observed temperatures  $(T_1, T_o)$  by

(1) 
$$\frac{\mathbf{P}_1}{\mathbf{P}_0} = \left(\frac{\mathbf{T}_1}{\mathbf{T}_0}\right)^{\frac{nk}{k-1}}, \quad \frac{\rho_1}{\rho_0} = \left(\frac{\mathbf{T}_1}{\mathbf{T}_0}\right)^{\frac{n}{k-1}}, \quad \frac{\mathbf{R}_1}{\mathbf{R}_0} = \left(\frac{\mathbf{T}_1}{\mathbf{T}_0}\right)^{\frac{n}{k-1}},$$

where  $n = \frac{T_a - \overline{T}_o}{T_1 - T_o}$  per  $(z_1 - z_o)$  meters; 1000 for example. Thence, R is variable,  $Cp = R \frac{k}{k-1}$  is variable,  $k = \frac{Cp}{C_o}$ . The working gravity equation becomes

(2) 
$$-Cp_{a}(T_{a}-T_{o})=g(z_{1}-z_{o})=-\frac{P_{1}-P_{o}}{\rho_{10}}-\frac{1}{2}(q^{2}_{1}-q^{2}_{0})-(Q_{1}-Q_{o})$$

 $T_s$  is the adiabatic temperature at  $z_1$ ;  $T_s - T_o = -9^{\circ} \cdot 87$  per 1000-meters for example;  $\rho_{10}$  is the mean density in the column  $(z_1 - z_0)$  for same value of n;  $(q_1 \ q_0)$  are the observed velocities.

(3) 
$$(Q_1 - Q_0) = (W_1 - W_0) + (U_1 - U_0) = P_{10}(v_1 - v_0) + (U_1 - U_0)$$

 $(Q_1 - Q_0)$  is the free or non-adiabatic heat,  $(W_1 - W_0)$  the work,  $(U_1 - U_0)$  the inner energy,  $(v_1 - v_0)$  the change of volume. Hence,

(4) 
$$\frac{Q_1 - Q_0}{v_1 - v_0} - P_{10} = \frac{U_1 - U_0}{v_1 - v_0} = K_{10} = c_1 T_1^{a_1}.$$

(5) 
$$J_a = c_1 T_1^{a_1} - c_0 T_0^{a_0}$$
. (b)  $J_o = c_1 T_1^{4} - c_0 T_0^{4}$ 

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 $K_{10}$  is the mean radiant energy in the stratum  $(z_1 - z_0)$ , and it is equal to a selective absorption for the coefficients  $(c_1, c_0)$ , and exponents  $(a_1, a_0)$ , as computed from the temperature observations. The corresponding black body radiation is  $J_0 = (c_1 T_1^4 - c_0 T_0^4)$ .

It is evident that the temperatures  $(T_1, T_0)$  in the successive strata can be taken from the observations in balloon ascensions up to 25,000 or 30,000 meters, and then the series of computations can be extended upward to the vanishing limit of the atmosphere, by assuming for trial certain temperatures  $T_1$ , which shall produce such values of  $P_1$ ,  $\rho_1$ ,  $R_1$  in (1) as will finally satisfy the gravity equation (2) without important residuals. By means of such trial temperatures the computations have been made for four balloon ascensions: Uccle June 9, Sept. 13, Nov. 9, 1911, Huron, S. Dak., Sept. 1, 1910, extending up to 80,000 or 90,000 meters, and thence there have been derived for the entire atmosphere on every 1000-meter level the dynamic data  $(P_1, \rho_1, R_1, T_1)$ , the thermodynamic data  $(Cp \cdot Cv \cdot S \cdot W \cdot U \cdot c \cdot a \cdot J_a \cdot J_0)$  and the Kinetic Theory data  $(H \cdot U \cdot q \cdot \gamma \cdot K \cdot n \cdot N \cdot 1_{max}, v \cdot m_h \cdot e)$ . This will be published in full in Bulletin No. 4, O. M. A.

### The "Solar Constant" and the "Effective Radiation."

The following summary of the data for sea level will give an idea of the outcome of the computations, which were conducted in the (M. K. S.) system, but transformed in the summations into gr.cal./cm<sup>2</sup>. min.

### Summary of the Results of the Computations on Three Balloon Ascensions for the Values of the Thermodynamic and Radiation Energies.

Station and Date of the Observations. Height in meters for 0°A, by computation.	Uccle June 9, 1911 70,000	Uccle Sept. 13, 1911 80,000	Uccle Nov. 9, 1911 90,000
$\Sigma \left[ y(z_1 - z_0) \right]$ gravity acceleration	9.5792	11.0895	12.4565
$\Sigma \left[-\frac{1}{2} \left(q_{1}^{2} - q_{0}^{2}\right)\right]$ kinetic energy of circulation	0.0000	-0.0006	+0.0002
$\Sigma \left[ -(\tilde{Q}_1 - Q_0) \right]$ free heat (non-adiabatic)	5.4250	6.6676	8.6590
$\Sigma \left[g(z_1 - z_0) + \frac{1}{2}(q_1^2 - q_0^2) + (Q_1 - Q_0)\right]$ summary	4.1542	4.4219	3.7975
$\Sigma \left[-\frac{P_1 - P_0}{P_{10}}\right]$ hydrostatic pressure	4.1146	4.1608	3*9386
$\Sigma \left[ \mathbf{J}_{0} = c_{1}^{1_{0}} \mathbf{T}_{1}^{4} - c_{0}^{4} \mathbf{T}_{0}^{4} \right]$ black body radiation	3.9690	3.9261	*3.5373

\* This value is omitted from the mean because of Sun's large Zen. Dist.

$\Sigma [K_1 - K_0]$ radiation energy	1.4528	1.4672	1.4802
$\Sigma \left[\frac{Q_1 - Q_0}{v_1 - v_0}\right]$ free heat per vol. change	0.0000	-0.0087	+0.0352
$ \sum_{i} \left[ \mathbf{P}_{i}^{-1} - \mathbf{P}_{i}^{0} \right] $ pressure difference	1.4602	1.4404	1.4085
$\sum \left[ J_a = c_1 T_1^{a_1} - c_0 T_0^{a_0} \right] \text{ selective radiation} \dots$	1.4603	1.4610	1.4395

General mean of the thermodynamic data  $J_0$  General mean of the black body radiation data  $J_0$  3.9476 General mean of the radiation and pressure data  $J_1$  1.4516 General mean of the selective radiation data  $J_1$  1.4536

It will be noted that the thermodynamic and the black body radiation agree upon 4.00 gr.cal./cm<sup>3</sup>. min. as the amount required to raise a solid atmosphere at 0°A, through the liquid air state, into the conditions P.  $\rho$ . R. T. now existing from the surface to the top. Since this action is continuous 4.00 cal. is the true value of the "solar constant" and not 2.00 cal. as given by the pyrheliometer. The thermodynamic and selective radiation data agree that there is an absorption of 1.45 calories from the top down to the surface, which is in a condition to continuously emit the same amount of radiant energy.

We reproduce more specifically the values of J on several levels, that is the total amount from the top to the given level, for Sept. 13, 1911, in order to develop the corresponding curve of absorbed radiation.

### The Equation for Temperature Equilibrium. (7) Effective radiation inward = $I = A - J_a - B$ . I = B.

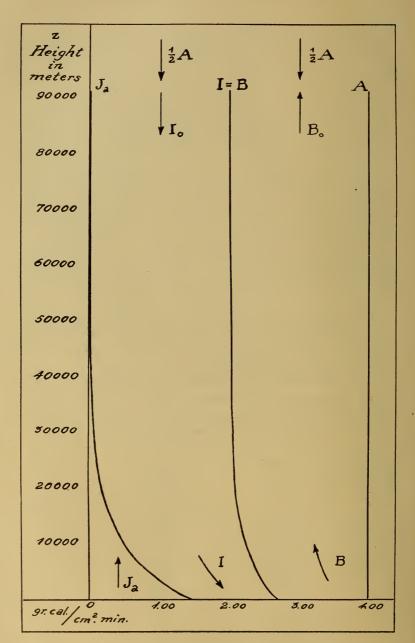
Z	Ja	$\frac{1}{2} (4.00 - J_a) = I = B$	A
90000	0.0000	2:000	4.000
		2.000	
		2.000	
•		2.000	
		1.999	• • •
46000	0.004	1.998	• • •
36000	0.034	1.983	
26000	0.100	1.950	66
16000	0.258	1.871	د.
6000	0.806	1.297	66
000	1.461	1.270	4.000

A = Solar constant 4.00

I = Effective radiation from 2.00 to 1.27

B = Return radiation from 1.27 to 2.00

 $J_{s} = Absorbed$  and emitting radiation from 1.46 to 0.



### Gram calories per centimeter square per minute.

×.,

The effective radiation,  $I=A-J_a-B$ , is built up of the total solar radiation A=4.00, neutralized in the lower levels by the emitting radiation  $J_a$  from 1.46 to the vanishing quantity at about 40,000 meters, and the return radiation B=I on every plane during steady temperatures. The pyrheliometer at any station observes the "effective" radiation I, and never the solar constant, which is A=2I on the upper level where  $J_a=0$ . The depth of m in the Bouguer Formula is about 3000 meters for each constant p in the lower levels. The value of p changes from p=0.83 at sea level, through p=0.86, p=0.89,  $p=0.92 \dots p=1.00$  in the upper levels, so that,

(8) 
$$I = I_0 p_1^{m_1} \cdot p_2^{m_2} \cdot p_3^{m_3} \dots \cdot p_n^{m_n}$$
.

The total solar constant A=4.00 is neutralized by  $J_a$  and by the return radiation B which is continuous, otherwise the temperatures would change in values. At night I=B=A=0, and the nocturnal radiation proceeds from  $J_a$  only.

If the spectrum energy of a 6900° black body radiation is computed, and the ordinates summed for  $\Delta \lambda = 0.05\mu$ , the sum is 80.30; if the Abbot observed ordinates are summed for Washington, D. C., the result is 51.19; for Mt. Wilson (1780 m.) it is 59.55; for Mt. Whitney (4420 m.) it is 61.38; for the topmost curve (8000 m.) it is 67.26. Hence by division the ratios for the absorbed parts of the spectrum are readily found. Similarly, divide the values of  $J_a$  by A on the same levels, and we obtain the ratio of absorption.

Station	Washington 34 m.	Mt. Wilson 1780 m.	Mt. Whitney 4420 m.	Assumed 8000 m.
Bolometer spectrum	<b>-</b> 0.363	0.258	0.236	0.162
Thermodynamics	0.362	0.287	0.225	0.163
•			•	

This shows that the energy lost in bolometer spectrum is the same as  $J_a$ , and it is absorbed in the lower levels.

Oficina Meteorologica, Buenos Aires, Argentina. March, 1914.

### SCIENTIFIC INTELLIGENCE.

1. Method for Cleaning Diatomaceæ; by E. R. DARLING (communicated).—There are a number of methods to be found in various books on microscopy for cleaning diatomaceæ. None of which proves to be perfect in all details. The method generally resorted to is to boil with nitric acid. This does not, however, remove all of the organic matter, and leaves a mounted specimen contaminated with black specks. Another method is to boil the specimen with sulphuric acid and potassium chlorate. This too has its disadvantage as in boiling neutral potassium sulphate is formed, this salt being sparingly soluble in water. The following method, which is a modification of that of Edwards,\* will be found to work with great success.

The sample is first dried, and then about five grams taken and well washed with distilled water. The washing is best done by placing the sample in a filtering paper fitted to a glass funnel, and replacing the water as it runs out. The washing is complete when about 250<sup>cc</sup> has run through. A hole is then punched in the apex of the filter paper and the sample washed into a 250<sup>cc</sup> beaker with concentrated hydrochloric acid, about 50<sup>cc</sup> being required. This is allowed to boil gently for 30 minutes, 100<sup>cc</sup> of hot water is then added, and the whole filtered. The sample is washed with hot water until it gives no white coloration when a drop is added to a weak solution of silver nitrate. The sample left on the filter paper is then washed into the beaker with 50<sup>cc</sup> of concentrated nitric acid and gently boiled until red fumes cease to be given off. This is then diluted with hot water, filtered, and washed until free from acid.

The above method removes all the mineral matter except silica diatomaceæ, and a large part of the organic matter. The product from the last operation is removed to a beaker by means of a small spatula. To this is added a mixture of concentrated sulphuric acid and water, 8 parts of acid and 2 parts of water. In mixing care should be taken to add the acid to the water. This is boiled for about 30 minutes, or until the organic matter is charred. As soon as the acid starts to boil weigh out about 2 grams of potassium chlorate and add to the acid in small quanti-ties until the solution becomes colorless. The acid solution is then poured into 250<sup>cc</sup> of distilled water, filtered, and washed free from acid. The product is then washed into a beaker with about 20° of concentrated hydrochloric acid and gently boiled for about 15 minutes. It is then diluted with hot water, filtered, washed first with distilled water acidified with hydrochloric acid and then with hot water until free from acid, which is determined by adding a drop of a weak solution of silver nitrate.

By the addition of the potassium chlorate to the sulphuric acid solution the organic matter is destroyed. The neutral potassium sulphate which is formed is changed into the chloride by the addition of the hydrochloric acid. The chloride is soluble in hot water and is removed in this way. When thus purified the diatomaceæ should be kept in a mixture of 6 parts of alcohol and 4 parts of water to prevent them from matting together.

\* Quart. Jour. Micr. Sci., vol. vii.

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# AMERICAN JOURNAL OF SCIENCE

### [FOURTH SERIES.]

ART. XXIV. — Experiments on the Active Deposit of Radium; by E. M. WELLISCH, Assistant Professor of Physics, Yale University.

### Introductory.

1. In a previous paper<sup>\*</sup> the experimental result was described, that when radium emanation is mixed with any gas there is a definite limit to the fraction of the active deposit which settles on the cathode in an electric field. This limiting value is independent of the pressure of the gas, provided the latter is high enough to prevent appreciable recoil on to the walls of the containing vessel; it is however, in general, dependent on the nature of the gas with which the emanation is mixed. The values assigned in the previous paper were 89.2 per cent for air and hydrogen, 80.7 per cent for carbon dioxide and 10 per cent for ethyl ether.

The physical meaning of this limiting value is that it represents the fraction of the total number of deposit particles which possess a positive charge at the end of the recoil path, before either columnar or volume recombination have had a chance to become operative. The small value of the limit in the case of ethyl ether was surprising and was ascribed to the large density of ionization produced by the deposit particle during its motion of recoil. It had previously been shown that with air or hydrogen the deposit particles are either positively charged or neutral; it became of interest to ascertain whether negatively charged particles were present when the emanation was mixed with ether. This was the immediate purpose of the present investigation, but, as will be seen later, the field was greatly extended as the experiment progressed.

\* Wellisch, this Journal, xxxvi, p. 315, October, 1913.

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 226.—October, 1914. 20

### Experimental Procedure.

2. It is unnecessary to enter here into any detailed description of the apparatus and the experimental method, as these were in all respects the same as previously described. The essential features of the method were as follows : the emanation mixed with any gas was introduced into a cylindrical vessel with a central electrode and remained there under the desired conditions of potential, pressure, etc., until radio-active equilibrium was established. The emanation was then blown out by means of a strong current of air and the amounts of active deposit on the central electrode and on the case were measured separately, the proper corrections being made for the decay of the deposit after the emanation had been removed. The ionization currents were measured by means of an electrometer which had a sensitiveness of 180<sup>mm</sup> per volt. Arrangements were made for the addition of suitable capacities when the currents were large.

### Distribution of the Active Deposit in Ethyl Ether.

3. In this series of experiments the vapor was obtained by evaporation from the liquid; it was dried by phosphorus pentoxide and admitted into the testing vessel which had previously been evacuated. The other was then removed till the pressure in the vessel was only a few mm., a fresh lot of ether was introduced as before and this process of fractionation was repeated about five times. In the final stage the ether was introduced through the radium solution and after passage through the drying agent was admitted into the testing vessel.

The following table exhibits the results obtained for the distribution of the active deposit for various pressures of the ether and for different potentials applied to the case of the testing vessel.

Pressure mm.	Potential volts.	Percentage deposit on central rod.
82	+750	$9 \cdot 1$
87	-750	9.2
82	-160	9.6
88	- 20	9.2
89	+ 20	10.0
89	-160	9.2
93	+ 4	10.4
80	- 2	10•4
87	0	10.3

TABLE I.

### Wellisch—Experiments on Active Deposit of Radium. 285

The results show that the application of either a positive or a negative potential is without any decided effect on the distribution of the active deposit. In the experiments described in the previous paper approximately the same value was obtained for the deposit on the central rod as in the above series; however, the assumption was there made that the neutral particles were distributed on the central rod and the case in the proportion of the areas exposed. This assumption is not justifiable; it is in fact easy to obtain a theoretical expression which will give approximately the relative distribution on rod and case which results from the process of diffusion.

Let us consider a cylindrical condenser of infinite length, the radius of the inner electrode being a, and that of the outer b.

Let q be the number of deposit particles that are produced per cc. per second in the gas as a result of the disintegration of the emanation.

Let n be the number of deposit particles present per cc. in the gas at a region distant r from the axis.

Let D be the coefficient of diffusion of the deposit particles. Then, if there be no applied electric field, we will have, using cylindrical co-ordinates, as the equation for the steady state

$$D\left(\frac{d^{2}n}{dr^{2}} + \frac{1}{r}\frac{dn}{dr}\right) = -q \tag{1}$$

The solution of (1) is given by

$$n = -\frac{q}{4\mathrm{D}}r^2 + \mathrm{C}_1\log r + \mathrm{C}_2 \tag{2}$$

where  $C_1$  and  $C_2$  have yet to be determined.

Inasmuch as the deposit particles adhere to the exposed solid surfaces, the concentration in the gas will be zero in the vicinity of the metal, i.e. n = 0 for r = a and r = b.

We deduce 
$$C_1 = \frac{q}{4D} \cdot \frac{b^2 - a^2}{\log b - \log a}$$
  
and  $C_2 = \frac{q}{4D} \frac{a^2 \log b - b^2 \log a}{\log b - \log a}$ 

The concentration at any place r is then given by

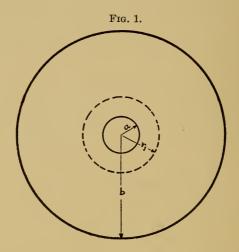
$$n = -\frac{q}{4D}r^{2} + \frac{q}{4D} \cdot \frac{b^{2} - a^{2}}{\log b - \log a} \log r + \frac{q}{4D} \frac{a^{2} \log b - b^{2} \log a}{\log b - \log a}$$
(3)

Inasmuch as the concentration is zero at r = a and r = b, it is obvious that there must be a position  $r_1$  where the concentration is a maximum.

By differentiating (3) with respect to r we find

$$r_1^2 = \frac{b^2 - a^2}{2 \log \frac{b}{a}}$$

In the steady state the deposit particles may be regarded as streaming towards the central rod or the case according as they are situated within or without the cylinder  $r = r_1$ . (Fig. 1.)



The relative distribution on central rod and case will then be proportional to the volumes cut off by the cylinder  $r = r_{1}$ .

i. e. 
$$\frac{\text{activity on central rod}}{\text{total activity}} = \frac{\pi (r, {}^2 - a^2)}{\pi (b^2 - a^2)}$$
$$= \frac{1}{2 \log \frac{b}{a}} - \frac{a^2}{b^2 - a^2} \qquad (4)$$

The first term, which in most cases is the more important, is the same as the electrical capacity per unit length of the condenser.

By integrating equation (3) the total number of deposit par-

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ticles in the gas which are present in the steady state in the volume corresponding to a height l of the condenser, is seen to be

$$\frac{\pi q l}{8 \mathrm{D}} \left( b^2 - a^2 \right) \left\{ \frac{b^2 + a^2 - \frac{b^2 - a^2}{\log \frac{b}{a}}}{\log \frac{b}{a}} \right\}$$

When a = 0, i. e. if the central rod be absent the number present becomes  $\frac{\pi q b^{*l}}{8D}$ ; this case is of special interest in connection with the determination of D (v. Section 6).

Let us now proceed to apply equation (4) in order to estimate the fraction of the total activity which should appear on the central rod in a diffusion experiment, i. e. when the central rod and the case are metallically connected. It is of interest here to observe that the expression obtained in (4) for this fraction is determined wholly by geometrical conditions, being independent of the nature of the gas, pressure, amount of emanation, etc.

For the vessel employed  $a = .0915^{\text{cm}}, b = 2.9^{\text{cm}}$ 

$$\therefore \frac{1}{2\log \frac{b}{a}} = .145 \; ; \; \frac{a^2}{b^2 - a^2} = .001$$

### fraction = $\cdot 144$

This is greater than the fraction 105, which was obtained for the activity distribution as a result of a series of diffusion experiments under varied conditions; however, it should be remembered that expression (4) refers to an indefinitely long cylinder, and there is no doubt that the corrections for the diffusion to the top and bottom would bring the calculated and observed values into closer agreement.

Another diffusion experiment was performed with a central rod of thin steel, the radius being  $015^{\text{cm}}$ . The value obtained for the fraction of the deposit on this rod was 066; the value calculated from (4) is 095.

To revert to the experiment when the emanation was mixed with ethyl ether, we see, therefore, that the values given in Table I indicate that very approximately all the deposit particles are uncharged and reach the electrodes as a result of diffusion. The limiting value of 10 per cent, which was assigned in the previous paper, is incorrect, on account of the erroneous assumption which was there made with regard to the diffusion distribution.

It may not be out of place here to draw attention to the fact that nothing has been said with regard to the charge carried

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by the deposit particle at the moment of formation; what is here asserted is that the particles are uncharged in ether at the end of their recoil path even in the presence of electric fields which are easily able to prevent recombination of the gaseous ions.

It is probable that if the concentration of the emanation were sufficiently great the deposit particles in ether would form positively and negatively charged aggregates, as has been shown later (section 5) to occur for the deposit particles in air.

### Distribution of Active Deposit in Air, Hydrogen and Carbon Dioxide.

4. A slight correction has to be made for the limiting values of the cathode deposit in air, hydrogen and carbon dioxide, owing to the fact that in the previous paper the diffusion correction was made on the assumption that the diffusion distribution was proportional to the areas of the exposed surfaces. The experimental values (p) uncorrected for the diffusion of neutral particles, which were obtained for the percentage cathode deposit, were as follows : air 89.4, H<sub>2</sub> 89.4, CO<sub>2</sub> 81.1.

The corrected values, which give the number of positive particles expressed as a percentage of the total number of particles, are obtained by evaluating the expression  $\frac{200 \ p-2,100}{100}$ .

These values are : air 88.2, H, 88.2, CO, 78.9.

The broken curves given in fig. 2 of the previous paper, which exhibit the dependence of the cathode deposit on the amount of emanation when small potentials are applied to the case, would take slightly different positions if the proper diffusion correction were made. The effect of this correction would be to make each activity curve lie still further below the corresponding ionization curve than it actually does in the diagram; this would bring out, with greater emphasis than before, the fact that the rate of recombination between the positively charged deposit particles and negative ions is greater than between the positive and negative ions among themselves. Inasmuch as this point is brought out clearly by the curves there given, and as, in any case, the actual shape of any one of the curves depends upon the particular vessel employed, it was not thought desirable to reproduce the corrected curves.

### Experiments with large Amounts of Emanation.

5. It was shown in Section 3 that when the emanation mixed with any gas is introduced into a cylindrical vessel the amount

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of active deposit in the gas (i. e. gas activity) when the steady state is established is inversely proportional to the coefficient of diffusion (D) of the active particles in the gas. If therefore we could determine the amount of active deposit in the gas at any time we would be able to obtain the value of D. The determination of this coefficient is of importance in the theory of diffusion because the particles are of relatively large mass and also because they are present in extremely small number.

Before describing the method employed for determining the amount of active deposit in the gas it is of interest to record that when relatively small amounts of emanation were employed the gas activity was found to be a definite fraction of the total activity. With larger amounts of emanation, however, variations of such an exceptionally large order were found to occur in the values of the gas activity that it became of interest to make a systematic investigation. The results obtained in this connection are given in the present section; the determination of D by the use of relatively small amounts of emanation is described in the next section.

In the experiments now to be described it was not found necessary to determine the total amount of the active deposit present in the gas. The experimental procedure may be briefly described as follows: approximately  $2\frac{1}{2}$  millicuries of radium emanation\* mixed with air was introduced through drving tubes and cotton wool into the cylindrical testing vessel, which was closed at the top with a rubber stopper, no central rod being present. Several hours and occasionally a few days were allowed to elapse in order that any dust present in the gas might have a chance to subside. The outer case was connected to any desired potential, but as there was no inner electrode, the electrical conditions inside the cylinder were not disturbed. When conditions were steady an electrode permanently connected to earth was introduced for one minute and then withdrawn, the cylinder being again closed by the rubber stopper. It was demonstrated repeatedly during the course of the investigation that less than 1 per cent of the amount of emanation escaped during the process of introducing and withdrawing the central electrode; the decay of the emanation was examined from day to day and in this way the loss could be estimated. It was found that the most convenient method of comparing the activities of rods which were introduced under different conditions was to measure the activity at any convenient period after removal and then to calculate the activity corresponding to the lapse of a definite period from the time when the rod was originally

\*Kindly supplied by Professor Boltwood.

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withdrawn. The definite period chosen was 4 hours 40 minutes. The measurements of the activity were made at a sufficiently long time after removal, so that thenceforth the activity decayed with the period of RaB.

These experiments were designed to furnish information with regard to the activity accumulating in the gas; by repeating them from day to day we could ascertain how this gas activity varied as the amount of emanation decreased through disintegration. In addition to these experiments electrodes were often introduced with various potentials applied to the case and allowed to remain for several hours before removal; their activity was estimated in the same manner as before. Moreover advantage was taken of these long exposure experiments to determine the relative amount of emanation in the vessel. This was accomplished by measuring the ionization current by means of a sensitive Siemens Halske galvanometer ( $4.5 \times 10^{-9}$  ampère per cm. when unshunted); in measuring the current a potential of 1000 volts was applied because with potentials of only a few hundred volts there was evidence of abundant recombination, so that with these small potentials the currents would not be proportional to the amount of emanation.

Two distinct series of experiments were made in this connection; in each instance about  $2\frac{1}{2}$  millicuries of emanation were introduced and each series occupied a little over one month. Several hundred measurements of the activity were made under various conditions, but for the sake of brevity only a few results which are most typical are here given (Table II). These, however, are sufficient to illustrate the interpretation which is given later.

The column headed 'accumulation' gives the time during which the deposit particles were allowed to accumulate in the gas before the insertion of a central electrode. This time is reckoned from the time of withdrawal of the electrode which had been previously inserted. Exposures referred to as 'long' were for periods of over twelve hours.

The point of chief interest in connection with the results of this table is the large amount of deposit which goes to the central electrode with negative potentials applied to the case.

The results are readily explained on the view that there are present in the gas charged aggregates of active deposit. These aggregates diffuse very slowly and therefore accumulate in the gas so that in the steady state there is a large amount of gas activity. Experiments 15, 16 and 17 in conjunction show that the amount of charged activity in the gas constitutes alone approximately half the total amount of active deposit in radioactive equilibrium with the emanation. The slow rate with

### TABLE II.

No.	Date 1914	Electrode removed		tion m.	Duration of exposure h.m.	Potential on case volts	Activity (after 4 h. 40 m.)	Satura- tion cur- rent×10 <sup>8</sup> ampère	
1	1 May	12.45 р. м.		10	2 5	-990	2.72	52.8	
23		$\begin{array}{c} 3.30 \\ 4.6 \end{array}$	2	$\frac{44}{20}$	1	$-990 \\ 0$	$5.95 \\ .03$		
4		4.30		$\tilde{23}$	1	220*	.09		
$\begin{array}{c} 4\\ 5\end{array}$	2 May	11.00 А. М.			long	-400	5.58		
$\begin{array}{c} 6 \\ 7 \end{array}$	ĩ	12.25 р. м.	1	24	1	-400	5.21		
7		12.39		13	1	-400	3.24		
8	4 May	9.28 A. M.	1	26	long	+160	$5.44 \\ 1.42$		
$\begin{array}{c c}9\\10\end{array}$		10.55 1.45 р. м.	$\frac{1}{2}$	$\frac{26}{49}$	1	$^{+160}_{+990}$	$\frac{1.42}{5.72}$		
11		5.23	~		3 38	+990	11.40	25.9	
12		5.241		1212 1212 1284		+ 990	·30		
13	5 May	3.15		1	4 29	- 990	.51	22.3	
14		$3.16\frac{8}{4}$		84	1	-990	•06		
15	8 May	10.23 А. М.			long	+990	5.28	12.1	
16	9 May	12.15 р. м.	25		1	-990	1.18	0.94	
17 18		$2.50 \\ 7.55$	$\frac{2}{5}$	34	1 1	$+990 \\ 0$	$1\cdot49\\\cdot01$	8.34	
19	11 May	11.15 а. м.	1	45	1	-990	.67	5.81	
20	15 May	10.20	96	40	1	-80	.06	0.01	
$\tilde{21}$	10 MLWJ	11.30	1	9	î	+ 80	•10	2.69	
22	16 May	10.55	20		1	- 4	$\cdot 004$		
23		2.15 р. м.	3	19	1	+ 4	·006		
	* Alterna	ting 60 cycle	•						
	(after 25 m.)								
24	20 May	4.21 р. м.	96	20		-160	8.77	•91	
$\begin{array}{c c} 25\\ 26 \end{array}$	01	5.0		$\frac{38}{30}$	1	+160	9.43		
26 27	21 May	$7.15 \\ 8.10$	7	$\frac{30}{54}$	· 1	-160 + 160	$\frac{6.67}{8.77}$		
28	22 May	3.35	18	04	1	+160 + 160	6.17		
29	an may	4.45	10	9	1	-160	4.42		
30	23 May	7.5	$2\overline{5}$	, in the second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second s	1	-160	1.15		
31		8.00		54	1	+160	2.20		
32	25 May	7.14	26		1	-160	•19		
33		7.48		33	1	+160	.52		

#### Emanation introduced 29 April, 1914.

which the particles diffuse is well shown by the smallness of the activity in the absence of any applied potential (3 and 18). With a large positive potential applied to the case the inner electrode, if exposed for one minute, receives practically all the positively charged aggregates, plus the positively charged deposit particles formed in one minute; the former is however, in the circumstances to which Table II refers, comparatively ł.

small (12). A large applied negative potential brings over similarly the negatively charged aggregates.

An essential condition for the presence in the gas of a large amount of active deposit is that sufficient time should be allowed for the particles to accumulate. Experiments 10 and 12 show well the difference which results from varying the time allowed for accumulation. From a knowledge of the activity resulting from a long exposure (cf. 11) it is easy to calculate by the aid of standard transformation formulæ the activity which should result from an exposure of one minute in the absence of any accumulation. The theory gives that the former activity is 40 times the latter, which shows that the activity in experiment 12 is due practically entirely to the formation during one minute; experiment 10 shows in consequence the preponderating influence of the deposit which has been allowed to accumulate in the gas.

There is abundant evidence that the aggregates owe their charge to the ions present in the gas. Experiments 13, 14 and 16 bring out this point most clearly; in experiment 13, where the duration of exposure is long, the ions are removed from the gas by the applied field and the activity measured is due practically entirely to the diffusion of the neutral deposit particles; in experiment 14 there has not been sufficient time for accumulation of deposit in the gas and the consequent formation of aggregates; in experiment 16 the central electrode receives the negatively charged aggregates. Moreover for long exposures there is more deposit on the central rod with an applied potential of -400 volts than with -990 (cf. 1 and 5). With the former potential it was easy to show by readings of the ionization current that there was considerable recombination of the ions; this implies the presence of ions in the gas and hence an increased number of charged aggregates of active deposit.\* Experiments 16 and 17 or 20 and 21 show that the amount of positively charged gas activity is slightly greater than the amount which is negatively charged; the ratio is roughly the same as that of the mobilities of the negative and positive gas ions; in other words, the amounts of positive and negative activity are roughly in the same proportion as the numbers of positive and negative ions present in the gas.

More direct evidence that the aggregates acquire their charge from the ions present in the gas is furnished by investigating the effect produced by causing Röntgen rays to pass through the gas. A beam of fairly intense Röntgen rays passed through the aluminium bottom of the vessel for about 15 minutes before the introduction of the electrode; the rays con-

\* Of course the charged aggregates also suffer recombination, but they acquire a fresh charge from the ions present in the gas.

tinued to pass during the exposure (1 minute) of the electrode and were switched off when the electrode was removed. These experiments were performed only when the original batch of emanation had decayed considerably; on this account the extra ionization produced by the rays was relatively all the stronger. It will be seen from the table given below that both the positive and negative gas activity were considerably increased as a result of the extra ionization.

Date	Duration of	Potential	Activity
1914	exposure	on case	
2 June	1 min. 1 min. 1 min. 1 min.	-160 - 160 + 160 + 160 + 160	·15 1·80 X-rays 1·92 3·05 X-rays

In these measurements the activities were measured 25 minutes after removal of the electrodes; the capacity of the electrometer system was only 1/21 of its previous value.

The second part of Table II is a continuation of the results obtained as the emanation decayed still further. The activity of the central electrode being relatively small is now determined by measurements made 25 minutes after its withdrawal from the emanation, the capacity of the electrometer system however remaining the same as before. The chief point of interest in connection with this table is the rapidity with which the charged gas activity falls off when the amount of emanation decays beyond a certain value. In Table I the amount of charged gas activity is approximately proportional to the quantity of emanation in the vessel as measured by the saturation current (cf. 2, 16 and 19). If in Table II we calculate the ratio of the gas activity obtained with one minute exposure and -160 volts to the saturation current, we obtain for the five successive days the following numbers :

### 9.65, 9.74, 7.90, 2.62, .50

A careful examination of all the results obtained indicates that the proportion of charged deposit present in the gas contained in the cylindrical vessel without a central electrode remains approximately constant over a wide range; but when the emanation has decayed until the saturation current obtained when a central electrode is introduced is about  $5.0 \times 10^{-9}$ ampère this proportion suffers a sudden diminution in magnitude. A current of  $5.0 \times 10^{-9}$  ampère implies the production of  $3.23 \times 10^{19}$  pairs of ions per second in the vessel and as the volume of the vessel was  $326^{cc}$  the number (q) of ions

produced per cc. per second is approximately 10<sup>\*</sup>. If we assume that the value of the coefficient of recombination (a) is unaltered by the presence of the emanation and take for a the value assigned by Townsend, viz.,  $3400 \times e$ , then the number of ions of each sign present per cc. in the vessel is

 $\sqrt{\frac{q}{a}} = 7.95 \times 10^6.$ 

When the density of ionization in the gas falls below this amount there seems to be a rapid diminution in the amount of charged activity in the gas. When the emanation decays still further the active deposit particles in the gas appear to be uncharged and in amount to be a constant fraction of the total amount of deposit in equilibrium with the emanation. It appears from the results that aggregation of the deposit particles ceases fairly abruptly at the critical stage, but there is also evidence that a considerable fraction of the deposit particles in the gas can still be charged even after they have ceased to aggregate. Aggregation implies a slow rate of diffusion, which is made manifest by the very small amount of deposit collected on a central rod in the absence of an electric field. It is easy to tell, by measuring the proportionate activity collected on such a rod, the stage when aggregation practically ceases. As stated before, aggregation ceased fairly abruptly when the saturation current was  $5.0 \times 10^{-3}$  ampère, but evidence at any rate of negatively charged deposit particles in the gas was found even with the current as low as 10<sup>-</sup> ampère.

The general effect seems to be that the active deposit atoms situated in the gas charge up, both positively and negatively, in appreciable numbers when the density of ionization exceeds a certain amount; the atoms thus charged act then as nuclei of condensation and build up aggregates of active particles when these are present in sufficient quantity.

There is, of course, a possibility that both the aggregation and the charging-up may be conditioned by the presence in the gas of foreign nuclei, such as traces of dust particles, etc. Against this view, however, is the fact that practically identical results were obtained in different series of experiments when in every instance great care was taken to exclude foreign matter. Such matter might, however, have been introduced on the insertion of the electrode. It should, in this connection, be mentioned that when the emanation had decayed so that the saturation current was in value between  $5.0 \times 10^{-9}$  and  $10^{-9}$  ampère, the number of charged particles for any given amount of emanation, although small, was subject to irregular variations.

# Coefficient of Diffusion of the Active Deposit of Radium.

6. An expression was given in Section 3 for the amount of active deposit present in the gas contained in a cylindrical

vessel when a steady state is established, such that the production of fresh deposit from the emanation is balanced by diffusion to the surface. This expression is, however, only approximate, as it neglects the diffusion to the top and bottom of the cylinder; inasmuch as the exact expression comes out with surprising simplicity, it seems desirable to present here the exact theory.

Let ABCD represent a longitudinal section of the closed cylinder (without any central electrode). Let q be the number of active deposit particles produced per cc. per second from the emanation.

Let the axis of the cylinder be taken as the axis of z, and let the origin be midway between top and bottom.

Let 2l be the height of the cylinder, and b its radius.

Using cylindrical co-ordinates we have as the equation of the steady state

$$\mathbf{D}\left\{\frac{\partial^2 n}{\partial r^2} + \frac{1}{r}\frac{\partial n}{\partial r} + \frac{\partial^2 n}{\partial z^2}\right\} = -q \tag{1}$$

where n is the number of particles per cc. at (r, z). The boundary conditions are n=0 when r=b for all values of z n=0 when  $z=\pm l$  for all values of r.

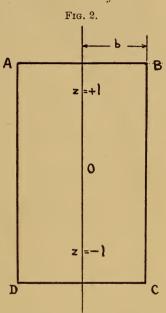
At the point O, i. e. at 
$$\begin{array}{c} r = 0 \\ z = 0 \end{array}$$
 we must also have  $\frac{\partial n}{\partial r} = 0$  and

$$\frac{\partial n}{\partial z} = 0$$

T

$$N = n + \frac{q}{4D} (r^2 - b^2)$$
(2)

(1) becomes 
$$\frac{\partial^2 \mathbf{N}}{\partial r^2} + \frac{1}{r} \frac{\partial \mathbf{N}}{\partial r} + \frac{\partial^2 \mathbf{N}}{\partial z^2} = 0$$
 (3)



with the conditions N = 0 when r = b for all values of z (i)

$$N = \frac{q}{4D}(r^2 - b^2) \text{ when } z = \pm l \text{ for all values}$$
  
of r (ii)

At 
$$\begin{pmatrix} r=0\\ z=0 \end{pmatrix}$$
  $\left\{ \begin{array}{c} \partial \mathbf{N}\\ \partial r \end{array} = 0 \text{ and } \begin{array}{c} \partial \mathbf{N}\\ \partial z \end{array} = 0$  (iii)

The function  $N = AJ_{o}(ar) (e^{az} + e^{-az})$ , using the usual notation of the Bessel functions, is a solution of (3), which satisfies the condition (iii). We have the constants A and a at our disposal. (i) will be satisfied if a be a root of  $J_{o} (\lambda b) = 0$ . This equation has an infinite number of real positive roots,  $\lambda_{1}, \lambda_{2}, \ldots, \lambda_{n}, \ldots$  Now, if we can expand  $\frac{q}{4D}(r^{2}-b^{2})$  as a series

$$\sum_{n=1}^{\infty} \mathbf{A}_{n}(e^{\lambda_{n}l} + e^{-\lambda_{n}l})\mathbf{J}_{0}(\lambda_{n}r)$$

it is easy to see that

$$N = \sum_{n=1}^{\infty} A_n (e^{\lambda_n z} + e^{-\lambda_n z}) J_n(\lambda_n r)$$
(4)

will be the solution of (3), which will satisfy all the conditions of the problem.

Carslaw\* gives the following expression for the coefficient

 $B_n$  in the expansion  $f(r) = \sum_{n=1}^{\infty} B_n J_0(\lambda_n r)$  where  $\lambda_n$  is as above:

$$\mathbf{B}_{n} = \frac{2}{\bar{b}^{2}} \frac{\int_{\bullet}^{b} rf(r) \mathbf{J}_{o}(\lambda_{o}r) dr}{\{\mathbf{J}_{o}'(\lambda_{n}b)\}^{2}}$$

So that in the case under consideration, we have

$$\mathbf{A}_{n} = \frac{2}{b^{2}} \frac{\int_{0}^{b} r \frac{q}{4\mathrm{D}} (r^{2} - b^{2}) \mathbf{J}_{o}(\lambda_{n}r) dr}{(e^{\lambda_{n}l} + e^{-\lambda_{n}l}) \{\mathbf{J}_{o}'(\lambda_{n}b)\}^{2}}$$
(5)

We have next to determine the integral

$$\int_{0}^{b} (r^{\mathfrak{s}} - b^{2}r) \mathbf{J}_{0}(\lambda_{\mathfrak{n}}r) dr$$
(6)

\* §126. Fourier's Series and Integrals, Macmillan, 1906.

By making use of the integral  $\int_{0}^{x} x^{n} J_{n-1}(x) dx = x^{n} J_{n}(x)$  together

with the known relations subsisting among the Bessel functions of adjacent order\* the following indefinite integrals were obtained: (for the sake of brevity the analysis is omitted)

$$\int x J_{0}(x) dx = x J_{1}(x)$$
$$\int x^{3} J_{0}(x) dx = 2x^{2} J_{0}(x) + (x^{3} - 4x) J_{1}(x)$$

Applying these to (6) and utilizing the fact that  $J_o(\lambda_n b) = 0$ we obtain  $-\frac{4b}{\lambda_n^3} J_i(\lambda_n b)$  as the exact expression of (6)

From (5) we obtain  $\mathbf{A}_{n} = -\frac{2}{b^{2}} \frac{qb}{\mathbf{D}\lambda_{n}^{3}} \frac{1}{(e^{\lambda_{n}l} + e^{-\lambda_{n}l})\mathbf{J}_{n}(\lambda_{n}b)}$ 

and from (2) and (4) in conjunction

$$n = \frac{q}{4\mathrm{D}} (b^2 - r^2) - \frac{2q}{b\mathrm{D}} \sum_{n=1}^{\infty} \frac{1}{\lambda_n^3} \frac{e^{\lambda_n z} + e^{-\lambda_n z}}{e^{\lambda_n l} + e^{-\lambda_n l}} \frac{\mathrm{J}_{_0}(\lambda_n r)}{\mathrm{J}_{_1}(\lambda_n b)} \quad (7)$$

Now the total number of active particles in the gas is given by

$$G = 4\pi \int_0^{r=b} \int_0^{z=l} nr dr dz$$

Using (7) and also the integral  $\int_0^b r J_0(\lambda_n r) dr = \frac{b}{\lambda_n} J_1(\lambda_n b)$ 

we deduce, as the expression for the total number of active particles in the gas contained within a cylinder of height 2l and radius b when the steady state is established

$$G = \frac{\pi q b^4 l}{4D} - \frac{8\pi q}{D} \sum_{n=1}^{\infty} \frac{1}{\lambda_n^5} \frac{e^{\lambda_n l} - e^{-\lambda_n l}}{e^{\lambda_n l} - \lambda_n l}$$
(8)

where  $\lambda_1, \lambda_2, \ldots$  are the roots of  $J_0(\lambda b) = 0$ .

So far no approximation at all has been made, so that the series (8) is the exact solution of the problem; the first term was obtained in Section 3 as the approximate solution when the diffusion to the top and bottom was neglected.

\* Cf. Gray and Mathews Bessel Functions, p. 13.

The cylinder used in the present experiment had a height of  $14^{\text{cm}}$  and a radius of  $2.9^{\text{cm}}$ . So that we have l = 7.0 and b = 2.9.

Using Gray and Mathews' Tables, the following are the first five values of  $\lambda_n$  :

$$\begin{split} \lambda_1 &= \cdot 829 \ ; \ \lambda_2 &= 1 \cdot 93 \ ; \ \lambda_3 &= 2 \cdot 98 \ ; \ \lambda_4 &= 4 \cdot 07 \ ; \ \lambda_5 &= 5 \cdot 15 \\ \frac{e^{\lambda_n l} - e^{-\lambda_n l}}{e^{\lambda_n l} + e^{-\lambda_n l}} \ \text{is practically indistinguishable from unity and} \\ &\sum_{n=-1}^{3} \frac{1}{\lambda_n^5} = 2 \cdot 592. \end{split}$$

From (8) we obtain for the number of active particles in the gas in the steady state :  $G = 103 \cdot 1 \frac{\pi q}{D}$ . (9)

Without the correction for vertical diffusion we obtain  $123.8 \frac{\pi q}{D}$  i. e. 20 per cent in excess. Let Q be the number of particles produced per minute in the gas contained in the cylinder

$$\therefore \mathbf{Q} = \frac{120\pi b^2 lq}{\mathbf{Q}}$$
$$\therefore \frac{\mathbf{G}}{\mathbf{Q}} = \frac{103\cdot 1}{120} \quad \frac{1}{b^2 l} = \frac{\cdot 0146}{\mathbf{D}}$$
$$0146 \frac{\mathbf{Q}}{\mathbf{Q}}.$$
(10)

so that  $D = .0146 \frac{Q}{G}$ .

It is apparent from the above that to obtain D we must determine the ratio  $\frac{Q}{G}$ ; in order to accomplish this, it is necessary to measure the ionization currents resulting from Q and G under similar conditions. Put briefly, the method employed was to deposit certain ascertainable fractions of Q and of G on a central rod introduced into the cylinder in the manner described in Section 5. These deposits could then be compared by measuring the ionization currents to which they gave rise in a second cylinder; it was easy to verify from the decay curves thus obtained that these fractions were deposited on the rod chiefly in the form of RaA.

The experimental procedure was as follows: the emanation, mixed with air carefully dried and freed from dust, was passed into the cylinder and allowed to remain for several days. A

potential of -160 volts was applied to the case, and an earthed rod was introduced for one minute and then withdrawn, the cylinder being closed as before with a rubber stopper. About half an hour later the experiment was repeated with rod and case both earthed; after another interval of about half an hour the experiment was repeated with earthed rod and +160 volts applied to the case. The activities of the rods were measured about 25 minutes after withdrawal when the decay curve is practically flat; on this account no correction had to be made for the decay of RaA during the exposure of the electrode.

The activity deposited on the rod in the first experiment (-160 volts) will be due to two causes; in the first place, the rod will receive a certain fraction (f) of the activity (G) in the gas at the time of introduction; it will also receive a certain fraction (k) of the neutral deposit particles formed during the exposure (1 minute). Suppose a fraction p of the deposit particles are positively charged when a potential of 160 volts is applied; this fraction p of course takes into account a small amount of columnar recombination which is independent of the amount of emanation in the vessel.

In the second experiment (0 volts) the rod will receive fG together with the fraction (k) of all the deposit particles formed in one minute. In the third experiment (+160) the rod will receive the same as in the first experiment together with pQ.

If a, b, and c represent on an arbitrary scale the measured ionization currents due to the active deposit collected on these rods and if m denotes a factor of proportionality between amount of deposit and ionization current, including also the correction for decay from the maximum value, we will have the following relations:

$$fG + k (1-p)Q = m.a \quad (-160 \text{ volts})$$
  

$$fG + kQ = m.b \quad (0 \text{ volts})$$
  

$$fG + pQ + k (1-p)Q = m.c \quad (+160 \text{ volts})$$

We deduce

$$pQ = m.(c-a)$$

$$k = \frac{b-a}{c-a}$$

$$\frac{Q}{G} = \frac{f(c-a)}{a-(1-p)b}$$
(11)

The assumptions made in obtaining the above relations may at first sight appear doubtful in their applicability; still they appear to be entirely justified by experience. The separation of Q into pQ positive and (1-p)Q neutral has been justified repeatedly by the author in numerous experiments. The AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXVIII, NO. 226.—OCTOBER, 1914.

separation of G and Q as far as diffusion effects are concerned is merely an application of the undoubted principle that in diffusion processes we may treat any large number of atoms chosen at random as a separate gas to which the laws of dif-fusion may be applied. Finally there is the most important assumption that the activity in the gas is entirely neutral. In order that this should be the case it is necessary, as explained in the previous section, that the experiments should be performed with small amounts of emanation; all the deposit particles in the gas appeared to have lost their charge when the saturation current fell below 10-° ampère. The method of putting this point to experimental test was to perform the three experiments with various amounts of emanation in the testing vessel; if a, b and c remained in constant proportion over the series this was taken to imply the absence of any appreciable quantity of charged gas activity because it has already been shown that the amount of charged activity decreased extremely rapidly with decreasing amounts of emanation. The fact that we are thus restricted to the use of small quantities of emanation means of necessity an extremely small value for the activity in the first experiment in which the chief contribution comes from the gas activity; on this account every precaution was taken in measuring the corresponding ionization current, the electrostatic shielding being made thorough and the measuring vessel preserved carefully from radio-active contamination.

A very large number of experiments were performed to obtain the ratios a:b:c. There was little difficulty in getting an accurate determination of the value  $\frac{b}{c}$ ; this came out 1/9 for practically all the experiments. The most accurate determination of the ratio  $\frac{a}{c}$  is 1/20; this was obtained about 8 times under favorable measuring conditions. Still the ratio 1/15 was obtained on a few occasions; of course there was always the possibility in these instances of the presence in the gas of charged deposit, but the amount of emanation was as always quite small. The ratio was never less than 1/24. The value of p was taken as  $\cdot 83$ ; this value represents the fraction of the active deposit that settles on the cathode when 160 volts is applied to the case, the quantity of emanation being supposed to be so small that volume recombination is absent (v. Section 4). The value of f was taken as  $\cdot 10$ , this value representing the fraction of the deposit that settles on the central rod in the absence of an electric field (v. Section 3). It was ascertained experimentally that the exposure of one minute afforded ample time for this fraction to reach the central rod.

If we take the ratios a:b:c as 9:20:180 then we have from equations (10) and (11) D =  $\cdot0445$ ;  $k = \cdot064$ .

With a:b:c = 12:20:180 we deduce D = 029. With a:b:c = 9:24:216 we deduce D = 061.

The value  $D = 0.0445^{\text{cm}^2} \text{ sec}^{-1}$  represents the most probable value for the coefficient of diffusion of uncharged atoms of radium active deposit in dry air at a pressure of one atmosphere and at room temperature. The other values for D are to be regarded merely as extremes between which the true values of D appear to lie.

The value obtained for D is smaller than the values which have been obtained experimentally for the diffusion of radium emanation in dry air. In the case of the emanation the values obtained are not very different from  $\cdot 10$ . The value of D for the active deposit is approximately the same as that found by Townsend for the diffusion of a gaseous ion in air.

#### The Experiments of Eckmann.

7. In the Jahrbuch der Radioaktivität (1912) Gerhard Eckmann describes the results of a series of experiments bearing on the diffusion and distribution of the active deposit particles of radium. These experiments cover in many respects the same ground as those here described; this fact was not recognized till the present series was completed. Eckmann's work may be for convenience summarized under the following heads:

- (1) distribution of the deposit in electric fields :
- (2) investigation with regard to aggregates :
- (3) determination of the coefficient of diffusion (D).

With regard to (1) he comes to the conclusion that about 98 per cent of the particles are positively charged, the remainder being negatively charged. This is of course opposed to the results of the present investigation. Eckmann assumes that the total deposit is the sum of the deposits obtained on a central electrode when it is first raised to a high positive and then to a high negative potential. The present experiments show that this assumption is incorrect, the 2 per cent which is obtained in the latter instance being due to the diffusion to the central electrode of a small fraction of the neutral particles. Eckmann ascribes the deposit on the anode to negatively charged particles and accordingly neglects a considerable amount of deposit which settles on the case of his vessel.

Eckmann's work with regard to aggregates anticipates to a large extent that described in the present paper. He shows

that they are charged and is undoubtedly correct in his assumption that they owe their charge to the ions present in the gas. He shows also that the anomalous results obtained by Debierne<sup>\*</sup> in a series of experiments with regard to the diffusion of radium active deposit can be explained by taking into consideration the formation of aggregates. The present experiments bring out several new points of interest but on the whole serve merely to confirm the results of Eckmann in this connection.

With regard to the determination of D, Eckmann collected the total amount of gas deposit on a piece of gauze; he found for the particular vessel which he employed that this deposit was equivalent to a formation for six minutes; in other words,

 $\frac{Q}{G} = 1\frac{2}{8}$  (with the notation of Section 6). He then employed

the formula  $G = \frac{\pi q^4 b l}{4 D}$  (Section 3) in order to estimate D,

which came out as  $\cdot 06$ ; this formula however neglects the diffusion to top and bottom which was important for the cylinder which he used. It is of interest to apply formula (8) in order to evaluate D; we find b given as  $4^{\text{cm}}$  and l equal to  $8^{\text{cm}}$ .

Equation (10) of Section 5 becomes now

$$\mathbf{D} = \cdot 0266 \frac{\mathbf{Q}}{\mathbf{G}} \; ; \;$$

using Eckmann's experimental value for  $\frac{Q}{G}$  given above, we

have D = .0443.

Such an excellent agreement with the most probable value obtained in the present investigation must be to some extent fortuitous, but there can be little doubt as to the order of magnitude of D.

#### Summary.

8. It is advisable to give here a brief synopsis of the results obtained in the series of experiments dealing with the active deposit of radium, including for the sake of convenience several results previously published.

Suppose a quantity of radium emanation is mixed with a dry dust-free gas; of the active deposit particles which are produced a certain fraction are positively charged, the remainder being neutral. This fraction depends upon the nature of the gas but not upon its pressure provided the pressure be high enough to prevent any appreciable recoil on to the walls

\* Debierne, Le Radium, vi, p. 27, 1909.

of the vessel. The values of this fraction are for air,\* hydrogen and carbon dioxide respectively 88.2, 88.2 and 78.9. When the emanation is mixed with ethyl ether practically all the deposit particles are neutral.

In a previous paper the view was put forward that the distribution of charge among the deposit particles had its origin in the motion of recoil of these particles when expelled from the atoms of emanation. The recoil atom during its motion produces a large number of ions and in all probability is ionized itself so that it acquires a positive charge; however it is always liable to lose its positive charge by collision with an electron and all the more readily in the case of those gases or vapors such as carbon dioxide and ether where the electrons do not quickly leave the columns.<sup>+</sup> The general effect to be expected from such a process is that when the deposit particles are brought to relative rest among the gas molecules there will be a definite fraction positively charged, the remainder being neutral.

Let us now consider what happens after formation of the deposit atoms and let us for convenience in exposition assume that the emanation is situated in a cylindrical vessel with a central electrode.

If we wish to bring over to the cathode all the positively charged deposit particles an electric field must be established of sufficient strength to prevent both the columnar and volume recombination with negative ions to which the particles are subject. In this connection it should be pointed out that the recombination between these particles and the negative ions is more intense than that between positive and negative ions. As long as the electric field is large enough to prevent volume recombination the fraction of the total deposit which settles on the cathode is independent of the amount of emanation in the vessel because if there is now any loss after formation it is due to columnar recombination which is conditioned by the value of the electric field.

With large values of the electric field the neutral deposit particles reach the electrodes by the process of diffusion; let us now consider the process at work when there is no electric field present or when the electric field is so small that there is considerable volume recombination present in the What happens in these cases depends on the amount of gas. emanation in the vessel. With fairly large quantities of emanation the active particles which exist in the gas form

\* It is of interest to record here that Lucian has found the number 94.9 for the fraction of the deposit particles of actinium which are formed with a positive charge in air. † Cf. Wellisch and Woodrow, this Journal, xxxvi, p. 214, Sept., 1913.

large aggregates which acquire positive and negative charges from the ions present in the gas; the aggregates become then of course liable to lose their charge by recombination, but they can then regain it as before, so that on this account a moderately small field is able to bring over to the central electrode either as anode or as cathode a considerable amount of active deposit. In fact with negative potentials applied to the vessel, the active deposit on the central electrode (anode) increases with increasing potential because over a wide range the number of ions present in the gas remains approximately constant; but when the applied potential becomes large enough to effect a diminution in the number of ions present in the gas the anode activity diminishes. In the circumstances now under review the number of charged deposit particles in the gas is in general greatly increased by the production in the gas of extra ionization, e. g. by means of Röntgen rays.

The formation of large aggregates appears to cease abruptly when the concentration of the emanation and the density of ionization sink below certain values; the deposit particles remaining in the gas may still carry electric charges, but as the emanation decays still further the deposit atoms in the gas are practically all neutral and reach the electrodes through diffusion. On this account the general process becomes again the relatively simple one of electric convection and diffusion to which reference has previously been made.

Under conditions which are such that the deposit atoms in the gas no longer form aggregates nor are charged by means of gas ions their coefficient of diffusion through dry air at one atmosphere pressure and at ordinary room temperature (about 20° C.) is approximately  $\cdot045^{\text{cm}^2} \text{ sec}^{-1}$ .

Sloane Laboratory, Yale University, June 17, 1914.

# ART. XXV.—The Optical Properties of Roscoelite; by FRED. EUGENE WRIGHT.

THE mineral roscoelite has long interested chemists and mineralogists, because of its high vanadium content. At first it was considered by J. Blake, its discoverer, to be a chromium mica, but an analysis by Genth\* of the material collected by Blake from the Stockslager Mine, Eldorado Co., Cal., proved it to be a vanadium mica of so unusual composition that Blaket gave it a special name. A second analysis of the mineral was made by Roscoet in the same year with results similar to, but not identical with, those obtained by Genth. Two decades later Hillebrand§ established, by a series of careful determinations on pure material, its chemical character; a discussion by Clarke of Hillebrand's results brought out the relation of roscoelite to the other members of the mica group.

Turner, Ransome, \*\* Lindgren ++ and others have investigated its geological mode of occurrence not only in California, but also in Colorado, Oregon and Australia. In these papers its optical properties are mentioned briefly, but nowhere, so far as I have been able to find, has an effort been made to ascertain these properties more accurately. The object of the present note is to present the results of measurements on two samples of material from the Stockslager Mine, the original locality. For these I am indebted to Dr. Hillebrand, and desire to express, herewith, my appreciation of his kindness. This material is not part of the sample which served for the chemical analysis, but it is from the same mine and is similar in every respect to the original. The first sample was given to Dr. Hillebrand by Dr. Geo. F. Becker, to whom it had been sent by Mr. Ryland J. Becker; the second sample was presented to Dr. Hillebrand by the late Prof. A. H. Chester. Of these samples the first is coarser-grained and more homogeneous, and better adapted for optical work.

Sample No. 1 consists of loose flakes of practically pure roscoelite. Occasional inclusions of a dark red to opaque substance, possibly iron oxide, are scattered through the flakes, but they are so intergrown that separation by heavy solutions

\* This Journal, (3), xii, 32, 1876.

† Ibid., p. 31. 1 Proc. Roy. Soc., xxv, 109, 1876.

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This Journal, (4), vii, 451, 1899.
Ibid., p. 454.
Ibid., p. 455.
U. S. Geol. Surv. Bull., 262, 9, 1905.
Mining and Sci. Press, lxxxii, 252, 1901. U. S. Geol. Surv., 22d Ann. Rept., pt. 2, 643, 1901.

is of little avail. The micaceous flakes are relatively large (up to  $2^{mm}$  in length) and in the aggregate are irregular in shape and size and show the characteristic wavy surfaces of the micas. They are elastic and easily bent. Their color is olive-green; the luster, splendent, almost submetallic and bronze-like. Cleavage after 001 is perfect; after 010, good. The hardness is not satisfactorily determinable on the minute flakes, but it is apparently 2.5 to 3.

Under the microscope the flakes are olive-green to greenbrown in color and noticeably pleochroic, although much less intensely so than lepidomelane or biotite. In thin flakes the pleochroism is  $\gamma =$  green-brown,  $\beta =$  olive-green and a = olive-green. Absorption  $\gamma > \beta \ge a$ . The absorption is fairly strong, thick sections appearing practically opaque. Crystallographically, the flakes are usually bounded only by the cleavage faces 001 and less perfectly by 010. The prism faces are rarely developed and ordinarily such terminations are wanting altogether. On the whole, the cleavage after 010 appears more highly developed in roscoelite than in other members of the mica group.

The basal flakes do not extinguish uniformly, but are frequently divided into areas running parallel with the direction of elongation of the flakes and extinguishing at small angles (up to  $2\frac{1}{2}^{\circ}$  were measured) with the common line of junction. The appearance of these areas is frequently that of twinning lamellæ, and it is perhaps possible that such is the case, but since the optical orientation is very nearly the same in any two adjacent lamellæ-the optic axial plane of the one making an angle of 5° or less with that of the second and the acute bisectrices in both lamellæ being practically parallel-the appearance of such lamellæ with noticeable extinction angles on basal sections would place the mineral in the triclinic system. This is, however, hardly probable in view of the universal monoclinic nature of the micas. To test this deduction attempts were made to produce etch figures on cleavage flakes. Both hydrofluoric acid and sodium hydroxide were used as etch media, and in both instances with only poor results. The best figures were obtained by immersing the flakes for 30 seconds in hot commercial hydrofluoric acid. The etch figures were comparatively rare, but, when observed, were either five-sided or six-sided, and in every instance appeared to be symmetrical to the cleavage lines after 010, the plane of symmetry. The results, however, were not very satisfactory, and too much stress cannot be placed on them. The flakes occur frequently in radial rosettes, and it is possible that the observed difference in extinction positions of two adjacent lamellæ is due to actual difference in orientation resulting from radial growth.

The refractive indices were determined by the use of refractive liquids of known index. Because of the strong absorption and structure of roscoelite, however, the phenomena thereby observed were not sufficiently distinct for accurate measurements and the refractive indices for sodium light may be in error  $\pm 0.003$ :  $\gamma = 1.704$ ,  $\beta = 1.685$ ,  $\alpha = 1.610$ . Compared with the other members of the mica group these refractive indices are remarkably high and are evidently due in part to the high vanadium content.

The optic axial angle was measured on a number of different flakes and found to vary noticeably from flake to flake. Measurements were made by use of (1) the double screw micrometer eyepiece on sections normal to the acute bisectrix, (2) the improved Fedorow stage, and (3) the substage apertometer. In sodium light the observed values ranged from  $2E = 42^{\circ}$  to 69°, while in lithium light 2E varied from 34° to 60°, and for the green mercury light  $(546\mu\mu)$  values of 2E up to 75° were obtained. The axial dispersion is strong with  $2V_{v} > 2V_{v}$ . Dispersion of the bisectrices was not detected with certainty. An abnormal shift in interference colors near the position of total extinction was noted in some of the grains and may have been due either to a slight dispersion of the bisectrices or to the overlapping of crinkled flakes. On many of the sections the negative bisectrix was found to be inclined up to  $4^{\circ}$  with the axis of the centered microscope. This may have been the result, in each case, of a slight tilting of the cleavage flake, on which crumpling and warping of the plane surface is the rule. The crinkling is most pronounced along lines about normal to the cleavage traces of (010) and is often so regular that it resembles, at first glance, polysynthetic twinning lamellæ. The gliding movement has probably taken place along the usual gliding plane  $\rho$  (205) which plays an important rôle in the production of compression figures on mica.

With the aid of percussion figures and the unusually distinct cleavage after (010), the plane of the optic axes was found to be perpendicular to the plane of symmetry. Roscoelite belongs, therefore, to the first group of micas of E. Reusch. Its optical orientation is  $b = \gamma$ ,  $a \land \beta$ , either zero or a small angle not over  $4^{\circ}$ .

The birefringence is strong, and the interference colors are, as a rule, high. On basal cleavage flakes the selective absorption of the mineral is so strong that abnormal interference hues in green and olive-brown appear and dominate in every section. A peculiar apple-green interference color is, in fact, characteristic of roscoelite.

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Sample No. 2 is finer than No. 1 and is more or less mixed with free quartz, but it is practically identical with No. 1 in its optical properties :  $\gamma = 1.692 \pm 0.005$ ;  $\beta = 1.682 \pm 0.005$ ;  $a = 1.615 \pm 0.005$ .  $2E = 55^{\circ}$  to  $80^{\circ}$ . Dispersion of optic axes strong  $2E_v > 2E_r$ . Pleochroism and absorption as in Sample 1. Interference colors often abnormal, especially on cleavage flakes. Gliding planes normal to cleavage after (010) less frequent than in No. 1, but not rare. The roscoelite of both samples is remarkably fresh and unaltered. Sharp crystal outlines were not observed, and are evidently not characteristic of this member of the mica group.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

# ART. XXVI.—Geological Notes on the Andes of Northwestern Argentina; by HAROLD S. PALMER.

# PART I—A SECTION ACROSS THE CORDILLERAS. PART II—THE CALCHAQUÍ GRABEN.

(A paper based on observations made while assisting Professor Isaiah Bowman on a geographical expedition to the Central Andes in 1913, under the auspices of the American Geographical Society of New York.)

### Introductory.

THE Central Andes, namely that part of the Andes between the so called "Knot of Vilcanota" in southern Peru and the minor chains of northwestern Argentina, constitute a mountain region distinct from the Peruvian and Colombian Andes on the north, and from the Andes of Chile to the south. They are characterized by the presence of a steep, faulted eastern scarp, cut by torrential streams and covered with a heavy forest growth, and further by a flexed and faulted western scarp, which, as shown by its elevated beaches, has been modified by wave erosion. The chief feature, however, which distinguishes the Central Andes from the rest of the Andean Cordillera, is the north-south line of high interior basins, flanked on the east by mountain ranges inclosing structural valleys which drain south and east to the broad Argentine Pampas. These border ranges are in turn fronted by the socalled pre-Cordillera, including such extra-marginal ranges as the Serrania de San Antonio, the Serrania de Lumbrera, and others near Córdoba and Tucuman. The stratigraphy exhibited in the walls of the through valleys of the eastern border ranges and the entire Andean Cordillera is characterized by sediments. chiefly sandstones and shales, of great thickness, in places as much as two miles. Practically all of this great sedimentary series shows features characteristic of deposition on land or in shallow water, and is to be regarded therefore as of terrestrial There is, however, a thin basal portion with marine origin. fossils, which are probably of Lower Jurassic age. It is with the basal portion that this article will largely deal. A reconnaissance trip from Salta, Argentina, to Calama, Chile, gave an opportunity to study the entire sedimentary series in which it occurs, in the Calchaquí Valley. Several structure sections were also made and typical rock and fossil specimens collected. The time for study was necessarily limited by the conditions of travel, but the results seem to be of interest on account of the geographical and structural relations of the sedimentary strata to the Paleozoic schists and slates, to the Tertiary volcanic

rocks, and to the Pampean formations. In addition, fossils were found, though the series of sediments in which they occur

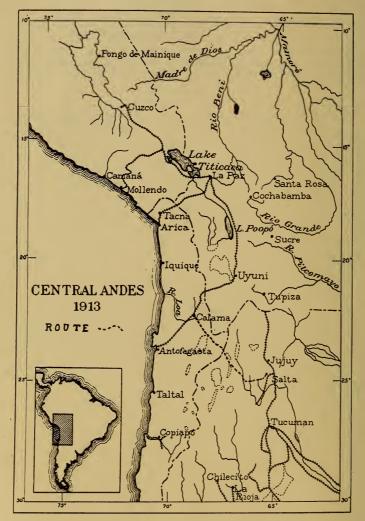


FIG. 1.

FIG. 1. Location map of the Central Andes, showing part of the route of the Central Andean Expedition of 1913.

is in general singularly barren of fossils, in spite of its great thickness and wide geographical extent.

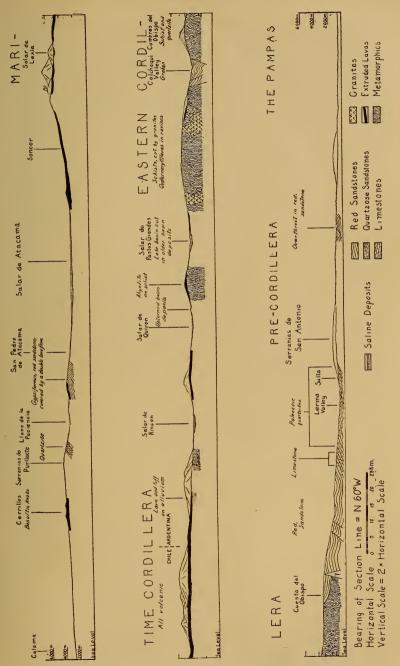


FIG. 2. Diagrammatic structure section from Calama, Chile, to a point on the Argentine Pampas 600 kilometers away and bearing S.  $60^{\circ}$  W. The profile is compiled from barometric observations.

FIG. 2.

In order to make more clear the relations of the detailed discussion of the Calchaquí Valley, there will be discussed briefly in Part I, the general structure of the whole group of mountain ranges and interior basins of northwestern Argentina and the adjacent portion of Chile. The section (fig. 2) is a diagrammatic representation of the structures encountered along the route. It is intended to show the various structural belts constituting the southern part of the Central Andes. The details of structure shown on the section are not precisely those found on the line of the section, but are rather generalized. It should be noted that the scale is so small that accurate graphic representation is impossible, and consequently the type of structure is suggested, rather than the actual forms reproduced. The section represents conditions along a line 600 kilometers (370 miles) long, drawn from some indefinite point on the Argentina Pampas through Salta to Calama, Chile, in the direction, N. 60° W. In no case did the route depart more than 40 kilometers (25 miles) from the line of the section.

The section discussed in the present article runs from Lat. 25° S. at the eastern end, to Lat. 22° 30′ S. at its western end. The western end joins up with the section made by G. Courty,\* on the line of the Antofagasta-Bolivia Railway. At the eastern end the section connects up with the work of Steinmann, Bodenbender, and Stelzner. These men worked mostly in the Córdoba region about 800 kilometers south of Salta, though reconnaissance trips were made north, and Steinmann in 1883 visited the Atacama desert.

The route of the present expedition had not been covered by geologists before, though it has been an important trade route for several centuries. Von Tschudi, between 1857 and 1859, travelled over part of the route, but made no geological observations.

Previous writers on other parts of the Central Andes have described three geologic zones which are characteristic of the region. The first zone is that of Silurian and Devonian "slates," cut by granites; it forms the Eastern Cordillera. The second is a single or repeated zone of Mesozoic sediments; and the third is a zone of "diorites" of post-Cretaceous age, forming the Western or Maritime Cordillera. The presence of these three zones is the habit of the Central Andes.

### PART I. A Section from the Pampas of Argentina, near Salta, across the Cordillera to Calama, Chile.

The Pampas of Argentina constitute a great, prairie-like plain, sloping from the Andean foothills with very gentle

\* "Explorations Geologiques dans l'Amerique du Sud," by G. Courty of the Crequi-Montfort expedition of 1903.

gradients eastward to the Atlantic Ocean. It is largely covered by a thick mantle of alluvium that conceals the structures of the older rocks. The alluvium represents the combined accumulation of materials decayed in situ and of materials carried down from the mountains. The Bermejo, Salado, and other rivers emptying into the Atlantic drain the Pampas. Along the western edge of the Pampas there are a few small mountains and ranges forming the previously mentioned pre-Certain of these ranges were observed from the Cordillera. railroad between Tucuman and Salta. These ranges are composed chiefly of Paleozoic quartzites and schists, which for the most part stand on edge. Farther east and beyond reach from the railroad there are a number of outcrops of a Mesozoic red sandstone, which is folded and overturned to the east, the commonest dips being to the west.

## Mesozoic Formations.

Leaving the Pampas and going westward into the foothills region one ascends through brown and gray Paleozoic quartzites, and then encounters a great succession of sediments, which include red and gray sandstones, red shales, a small amount of red conglomerate, and a little light-colored limestone. The succession of these could not be worked out fully. and no measurement of the thickness of the red sandstone, the upper formation, could be made. This upper formation is a brick-red sandstone, mostly of average coarseness, and wellcemented by a mixture of calcite and iron oxide. The individual beds are from three inches to six feet thick and are usually separated by thin beds or partings of shale. The sandstone beds are quite uniform in character, whereas the shales are quite variable, some being fine, others gritty, and others There are a good many beds or lenses of conglommicaceous. erate, containing pebbles of quartz, red sandstone, and shale, as well as a few of quartzite, mica schist, and granite. These pebbles are well-rounded and range in size from a quarter of an inch up to four inches in diameter. Cross-bedding is very common, especially in the conglomerate lenses, but can be detected in almost every outcrop. The thickness of these brick-red sandstones is at least 500 meters (1500 feet) and is probably between two and five times as much as that. The fossil evidence, which suggests that this formation is of Lower Jurassic age, is discussed in Part II under "Ages of the Formations."

Beneath this red sandstone formation there are at least two other formations which are believed to be Mesozoic on account of their structural and geographic relations. The relations between these two formations could not be ascertained. One of them is a fine-grained, closely bedded, white or yellow-white limestone, having a thickness of 60 to 100 meters (200 to 300 feet). There are a few oölitic bands in it from two to four feet thick. The other formation is a soft and mealy drab sandstone of fine texture. It has been but weakly cemented, so that its more gritty portions form a friable sandstone, and the remainder a gritty shale. The whole is so soft that outcrops are rare. It seems to have a thickness of 100 to 125 meters (300 to 400 feet).

Detailed study would undoubtedly enable the geologist to work out the sequence of the limestone and the shale, and possibly to subdivide them further on a lithological basis.

This series of three (or more) Mesozoic sedimentary formations is folded into roughly parallel anticlines and synclines. The folds average about north and south in trend, but the strikes vary from N.  $45^{\circ}$  W. to N.  $40^{\circ}$  E. Some of the anticlines are so big as to reveal in the canyons the basal quartzites and schists. Though most of the folds are open, some are closed and overturned towards the east. In a few cases there has been thrust faulting, with overthrust to the east, the throws measuring hundreds of meters. One such overthrust lies a few miles east of the Cuesta del Obispo, and has a throw of at least a hundred meters (300 feet), and possibly (if there were movements parallel to the plane of bedding) much more.

Since these sediments are fairly coarse and show much crossbedding, it is probable that they represent piedmont and flood-plain deposits formed by the erosion of a mountain system composed of the Paleozoic metamorphic rocks and their intrusions of granite. They were at the time of their origin very much like the superficial deposits now forming along the eastern foothills of the Andes. The presence of abundant calcite in the cement shows that the climate was and has been as arid as it now is, with a precipitation of less than 50 centimeters and in many places less than 25.

#### Paleozoic Metamorphic Rocks.

Between the Cuesta del Obispo and the Calchaquí Valley there are several alternations of Mesozoic sedimentary rocks and Paleozoic metamorphic rocks. This alternation is due to the rather deep erosion of the huge folds which once existed here. The Paleozoic metamorphic rocks are chiefly schist and quartzite, with a small amount of slate. It seems that the quantity of quartzite decreases as one goes west towards the Calchaquí Valley, where the Paleozoic consists almost entirely of schist and slate. The schist is mostly gray or gray-brown, but locally it is red, green, blue, and brown. The texture approaches the phyllitic, as there is not enough mica or coarse quartz to make it highly schistose. Some of it is very badly shattered, apparently by stresses in different directions applied at different times, which developed a strong, slaty cleavage in one, two or three directions. The high degree of this fissility is marked by the difficulty of neatly trimming a specimen. The constituents are in general so fine-grained that they are not distinguishable under the hand-lens. The rocks of this formation seem to be of sedimentary origin, as it is possible in some outcrops to trace the former bedding by the bands of quartzite now present. They have suffered so much compression that most of the original structure has been destroyed, though some outcrops show closed folds of five or ten meter radius, with many minor plications superposed on them.

The source of the materials forming these "metasediments," as it has been suggested we should call metamorphic rocks of sedimentary origin, is a problem that has yet to be solved, and which has, in fact, hardly been attacked. There is here a vast amount of material. Outcrops of this schist and quartzite formation occur more or less continuously over wide areas, and the original sediments must have been from one to three kilometers thick. These rocks form the major portion of the Eastern Cordillera for many hundreds of kilometers. Among the hypotheses as to the source of the materials are the following:

(1) That they were derived from a mountain area in what is now the Pampas region.

(2) That they were derived from an older system of mountains in the general region of the present-day Maritime Cordillera and Coast Ranges.

(3) "That they were derived from a land mass lying west of the present west coast of South America and which has now completely slumped in. In this case there would be two possibilities; first, that the sediments were geosynclinal, or second, that they were deposited on the edge of and just outside the then continental shelf. Such marginal deposits are known to be forming at the present day, but have not been recognized in the sedimentary record. This hypothesis would accord well with the idea that the Galapagos and other Pacific islands were formerly connected to South America.

Unfortunately no data were obtained which would tend to prove or disprove any of these hypotheses.

An interesting structural relation between the Paleozoic metasediments and the Mesozoic sediments is shown in the Calchaquí Valley. Though more fully discussed in Part II,

\* Suggested by Professor Joseph Barrell in a personal communication.

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this great graben is mentioned here as an element of the Cordilleran structure. A block of the red Jurassic sandstone has moved downward between two mountains of Paleozoic schists. This downfaulted block, or graben, is about 8 kilometers wide and at least 40 kilometers long (5 by 25 miles), and has dropped some five thousand feet, relative to the bordering metamorphic rocks.

# The Eastern Cordillera.

West of the Calchaquí Valley is the Eastern Cordillera, which in this region has no individual name. It consists of a



FIG. 3.

FIG. 3. Photograph taken on a lava-stream which flowed down the Quebrada de la Paya. The lateral valley directly opposite the camera was dammed, and a lake and characteristic lake deposits were formed.

great mass of Paleozoic schists into which have been intruded a number of granite and granite porphyry masses. One of these at Piedras Blancas is interesting on account of the cubical shape of the feldspars. These weather out without losing their peculiar form, and make an unusual sort of gravelly sand. Many of the ravines on the east flank of the Eastern Cordillera have had small streams of basic lava poured into them. The lava dammed up the valleys, making temporary lakes which are now drained, but whose recent existence is demonstrated by almost undissected lake beds; fig. 3 is from a photograph taken on such a lava flow and looking up a small side-valley in which lake deposits can be seen. The freshness of topographic form suggests that these flows are not older than late Pleistocene.

There are very few outcrops of the Paleozoic schists west of the Eastern Cordillera. Most of the region is covered with lava flows of Pleistocene age, by recent alluvial or piedmont deposits, or by deposits of saline residues. The great amount of volcanic material suggests that its eruption began long before the Pleistocene, and that it occurred intermittently through, possibly, the whole Tertiary. In the Quebrada de Soncor, a canyon which runs down from the Martime or Western Cordillera to the Salar de Atacama, there is exposed a more recent flow of glassy mica andesite about 15 meters thick. There is under this a less recent flow of hypersthene andesite porphyry, which has been cut to a depth of at least 50 meters. These flows, extending down from the Maritime Cordillera, have their western margins at the edge of the Salar de Ata-Along the margin of the lava flows there are a score cama. or more of cones of dacite porphyry from twenty-five to seventyfive meters high.

Since the lavas are not very old, erosion has not progressed far enough as yet to expose to any great extent the underlying formations. Only three such exposures were observed. One of these was on the northwestern margin of the Salar de Rincon, where there are flows of lava similar to those just described, except that they are on the eastern side of the Maritime Cordillera. These have been cut through so as to expose underlying alluvial deposits.

Again, in the valley of the Atacama River, north of San Pedro de Atacama, the lava cap is less thick, and under it are exposed at least one hundred and fifty meters of partially consolidated sands and gravels of a strong red color. These sediments bear large quantities of gypsum, perhaps 10% by volume, indicative of arid conditions of deposition. The beds are moderately folded and tilted. The gypsum stands out in the form of horizontal shelves two or three inches wide, a structure due to its resistance to the scouring of the persistent northwest winds of the region. The lava here lies conformably on the sediments or nearly so.

On the southwestern flank of the Serranias de Purilacte there are exposed quartzites, which were probably the source of the sand and gypsum deposits just described. They seem to be of great thickness, perhaps a thousand meters, and are now tilted nearly vertical. The nature of the contact of the red, gypsiferous sediments and this quartzite is completely obscured by the broad alluvial deposits of the Llano de la Paciencia. Westward from the Serranias de Purilacte to Calama is a long alluvial slope, fully exposed to the nearly continuous northwest winds of the region. This wind has developed to a very high degree the characteristic desert pavement of windpolished and facetted pebbles. The only interruption to this long westward sloping expanse of alluvium is a group of knobs of augite andesite at Cerrillos.

# The Maritime Cordillera.

The Maritime Cordillera, which has been referred to above, consists of a long chain of volcanic peaks with their associated flows of lava. They extend the whole length of the Central Andes region and constitute a lava field, which in size is comparable with the Columbian field of North America and with the Deccan field of British India. Though the activity of these volcanoes began in the Tertiary, there are some which are still feebly active. Smoke and steam issue from some, and the Franciscan monks of Salta tell of finding human implements and remains in the lavas near Antofagasta de la Sierra.

One contrasting point regarding the Eastern and Maritime Cordilleras is that of the relative heights of their peaks and passes. In the Eastern Cordillera the passes range from 5000 to 5400 meters (16,000 to 17,500 feet), but the peaks run only a small amount higher, that is, to 5500 or 6000 meters (18,000 or 20,000 feet). The passes have not been cut down very much, and the mountains are in extreme youth, or rather in the early stages of erosion in a new cycle. In the Maritime Cordillera, on the other hand, the passes are lower, averaging about 4600 meters (15,000 feet), but the peaks run up to 6000 meters (20,000 feet) and even to 7000 meters (23,000 feet). This is due to the fact that they are volcanic cones 1500 to 2500 meters (5000 to 8000 feet) high, built on a rather level surface at about 3600 meters (12,000 feet) above sea level.

#### Glaciation.

Though the mountains of the Maritime or Western Cordillera reach as a maximum an altitude of four and a quarter miles, they have suffered only slight glaciation. What glaciers there are now are but little more than snow banks on the tops of the very highest peaks. This absence of glaciation is due to the combination of extreme aridity and the comparatively high temperature of the region near the Tropic of Capricorn, the two factors sufficing to overcome the effect of these very high altitudes. In the Eastern Cordillera, where there is a

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slight precipitation at present, and where there must have been considerable precipitation in the moister climates of the glacial period, the mountains show signs of former glaciation. On the eastern aspect there are U-shaped valleys, terminal and lateral moraines, and empty cirques. Farther to the south the Andes bear plenty of snow, due to the combination of somewhat lower temperature and of much greater precipitation. To the north also there is more snow because of the far greater precipitation in the belt of the trade winds than in this dry horse latitude belt of northwestern Argentina and Chile.

### The Lines of Salt Lakes.

The Salars (or Salinas) of Pastos Grandes, Quiron, Rincon and Lexia lie in a series more or less along a north-south line and constitute the eastern chain of high, interior basins; while the Salar de Atacama constitutes the main portion of the western chain of basins. There are a number of other such intermontane basins, but only the above were encountered on the route of the expedition. In character they are very similar to the salt basins of the southwest of the United States, such as Death Valley, though at a greater elevation. Long erosion in the enclosed basins of this arid region has concentrated large deposits of the more soluble salts in their low portions. The salts include the usual residues from evaporation, chlorides of sodium, potassium and magnesium, borax, and some sulphates and carbonates. Evaporation is not complete in any of the basins, so that there are central lagoons of brine, surrounded by solid residues from evaporation. The lakes have hard borders with a firm, smooth deposit, the upper surface of which looks very much like a good asphalt pavement, and which has the same resilient feel under the mule's hoofs. Around this central area of salt, interspaced with open pools, there is a narrow zone of alluvium permeated with saline matter, and outside this again the salt-free margins of alluvial fans which, with gradients of 3° to 5°, run up to the mountains. In addition, the Salars of Pastos Grandes, Quiron and Rincon are partly surrounded by the inclined and dissected strata of an earlier period of basin deposition, separated from the present by dynamic disturbances, which tilted and faulted the deposits already formed and exposed them to erosion.

These basins vary markedly in size. The Salar de Lexia was the smallest observed, being about six by twelve kilometers. The basins of Pastos Grandes, Quiron and Rincon are fifteen to twenty-five kilometers wide by forty to fifty-five long. The basin containing the Salar de Atacama is about fifty by one hundred kilometers.

Fig. 4.

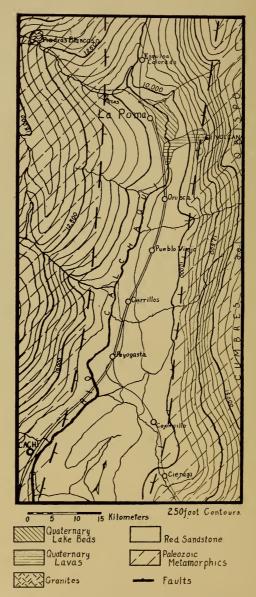


FIG. 4. Sketch map of the Calchaquí Valley made from the hachure map of the Crequi-Montfort Scientific Commission and barometric observations by the expedition. La Poma is at Lat.  $24^{\circ}$  35' S. and Long.  $68^{\circ}$  32' W.

# PART II.

## The Calchaquí Graben.

It was the good fortune of the expedition to remain at La Poma in the Calchaquí Valley for several days, so that it was possible to study a little more closely the structure of the graben there developed. The details in hand therefore warrant giving somewhat more space to this than to the other parts of the section covered by the expedition.

There is a block of Jurassic red sandstone about eight kilometers wide and at least forty kilometers long, bounded by two closely parallel normal faults, which separate it from the Paleozoic metamorphic rocks to the east and west. These faults were actually observed : the one at Ciénaga in the southeast corner of the map (fig. 4) and the other a little west of Pircas in the northwest corner.

### The Rocks.

The name "Jurassic red sandstone" is used in this article as a convenient and comprehensive term for a series of greatly varying sediments, having a total thickness of at least three thousand feet. They consist of red sandstones, shales and conglomerates, well cemented by a mixture of iron oxide and The color is brick-red, of much the same quality as calcite. that of the Triassic of the eastern United States, but of greater intensity. In the Calchaquí valley there is a great increase in coarseness toward the north end of the valley, and with this goes an increase in the amount of cross-bedding. Thus in the neighborhood of Cajoncillo there are about equal amounts of sandstone and shale, with only a very few lenses of conglomerate. North of Orusca this condition is reversed-the sandstone predominates over the conglomerates, but the shale is almost absent. In the Quebrada de la Paya (the canyon in which Pircas lies), with an extremely rapid change from a sandstone, the rock becomes a solid mass of conglomerate with mere partings of sandstone. The conglomerate seems to be especially characteristic of the upper portions and the marginal portions of the formation, for in ascending this Quebrada one passes through the western flank of an anticline until the great fault near Pircas is reached. The change from sandstone to conglomerate is very striking. Cross-bedding is everywhere developed and can be found in almost every outcrop, but is especially characteristic of the conglomerates. The angle of inclination of the cross-bedding is quite steep, ranging from 10° to 30°, indicating that the deposits were laid down in running water. Were these wind-laid deposits, the angle of the cross-bedding would be much lower.

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The red sandstone between the marginal faults of the valley is slightly folded and faulted internally. It has been thrown into open anticlines and synclines, whose axes trend north and south, i. e. parallel to the length of the valley. The steepest parts of the flanks of the folds dip about thirty degrees, but in the lesser folds the dips become in places as steep as sixty degrees. In a few cases thrust faulting has taken place, as for example at a point near Cerrillos illustrated in fig. 5. The





FIG. 5. Small overturned fold and small thrust fault in the Jurassic red sandstone near Cerrillos. The fault line is indicated by the arrow as it is obscured in part by debris.

photograph shows a cliff about one hundred and twenty feet high, exposing in section a thrust fault and a monoclinal, overturned fold. The beds are offset about two meters by the fault and about three meters by the fold. The average position of the beds on the long flank of the fold is N.  $40^{\circ}$  E., with a dip of 18° NW.

The broader structure of the red sandstone of the valley is shown in fig. 6, reproduced from a sketch made looking north from La Poma. The broad anticline and syncline are diagrammatically distinct in the field and are but slightly accentuated in the sketch. The photograph and sketch (figs. 5 and 6) show how slight has been the disturbance of the red sandstones forming the bottom of the valley. The relation of these folds to the marginal faults is discussed later.

The schists and quartities on either side of the valley are of great age and have been subjected to many crustal disturbances. As a result the original structures have been completely obliterated, and no statement can be made of the amount or kinds of mashing and dislocation that they have suffered.

# The Ages of the Formations.

As to the ages of the formations of this region but little can be said. Stelzner is quoted in the Argentine "Agricultural and Stock Census" of 1909 as follows:----"The sandstone in

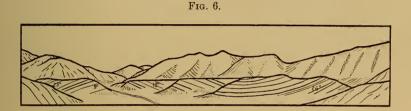


FIG. 6. Sketch section of the Calchaquí Valley, looking north from La Poma, showing a broad anticline on the west and a broad syncline on the east.

the provinces of Salta and Jujuy, of the Upper Cambrian formation, rests on the Archean, and on this is found the limestone and dolomite of Mendoza and San Juan and the sediments of the Lower Silurian. Thereupon follows a break in the continuity.... to the Rhætian. It includes a portion of sandstone and red psammite remarkable for its lack of fossils. Through the more recent researches of Bodenbender we know that on the Silurian limestones of the Jachal there are regular layers of schist and psammite, which perhaps represent the Upper Silurian. Fossils have not yet been found. The latter form a bed of gravel, psammite, and limestone with Devonian fauna, which is being studied ... by Dr. Kayser."

Dr. Rudolph Martin,\* a mining engineer of Salta, Argentina, has found trilobites in the quartzite near Salta, which prove that these metamorphosed sediments are of Paleozoic age. Wolff, Raimondi, Phillipi, Steinmann, and many other writers mention Silurian and Devonian rocks and fossils from many places on the eastern margin of the Cordilleras.

\* Oral communication.

The red sandstone seems to have been deposited in a tangential manner as regards time. That is the deposits are not contemporaneous, but vary in age from place to place. Thus Stelzner speaks of Rhætic psammites in the Salta and Jujuy region; Professor Bowman has found Cretaceous fossils at Pongo Mainique, Peru (Lat. 11° S.); and the fossils in the red sandstone of the Calchaquí region indicate Lower Jurassic. Though fossils are entirely wanting in this red sandstone formation throughout the whole eastern border of the mountains in Bolivia for a distance of seven hundred miles and are very rare in Argentina, the present expedition found a fossiliferous horizon at La Poma. Professor Schuchert was so kind as to study these and has tentatively identified *Cerithinella* armatum and a *Cerithium* (species ?), which are gastropods, suggestive of Lower Jurassic age. The collections of fossils included only the two species. Professor Schuchert also submitted the fossils to Dr. Stanton, who seemed to think that similar species had been identified by Moriche in the Jurassic of Chile, and that he would expect to find them in the Jurassic of Argentina. Dr. Stanton further said : "I should hesitate to say positively that these fossils are Middle Jurassic, or even that they are Jurassic, on the basis of their unsupported evidence. There are so many forms of similar appearance at various horizons in the Mesozoic and Cenozoic that I should consider it unsafe to make a definite determination of age on such forms alone, unless I could be absolutely sure of a specific determination."

At the point where the fossils were found, a little south of La Poma and close to the river, a section of about 20 meters was measured. As this section is at the center of a large anticline, it is the base or near the base of the formation. The section is as follows, from the top down :

An indefinite thickness (1,000 meters or more) of red sandstone, shale, and conglomerate.

30<sup>cm</sup> – micaceous sand, or soft sandstone.

180<sup>cm</sup> – a heavy, single bed of sandstone.

250<sup>cm</sup> — sandstones and shales. The sandstone is in bcds averaging eight centimeters in thickness and is prominently cross-bedded.

125<sup>cm</sup>-variegated shales; green, purple, and yellow.

210<sup>cm</sup>— soft, fine-grained yellow sandstone, in beds of 1 to 5 centimeters.

60<sup>cm</sup> - variegated shales.

60<sup>cm</sup>— fine-grained, yellow to brown and gray sandstone. Alternating layers are hard and soft, some approaching quartzites.

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70<sup>cm</sup> - fossiliferous, yellow to brown limestone, micaceous.

25<sup>cm</sup> – variegated shales and clay; yellow, brown, and green. 110<sup>cm</sup> – fossiliferous, gray-brown limestone.

 $7\frac{1}{2}$  meters — alternating gray clays, yellow shales, and gray-brown limestones.

The chemical and fossil character of this basal portion point to the early conditions of deposition of this formation as being marine while the later conditions, as indicated by the nonfossiliferous, conglomeratic, and cross-bedded character of the upper part of the formation, must have been those of terrestrial deposition.

## The Marginal Faults.

At Ciénaga there was observed a perfectly clear example of normal faulting. The fault is best shown on the southwest

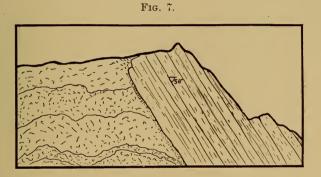


FIG. 7. Sketch looking south at the Ciénaga fault on the east side of the Calehaquí graben. Paleozoic quartzite and slate to the east and Jurassic red sandstone to the west, separated by fault breccia.

wall of the quebrada. To the west there is sandstone with a westward dip of  $58^{\circ}$ . This was separated by a brecciated zone about three meters wide from Paleozoic schists and quartzites. Fortunately the metamorphics at this point included a few bands of quartzite by means of which a little of their structure could be made out. A sketch of this fault as it appeared in this outcrop is reproduced as fig. 7. This might be interpreted as an unconformity but for the presence of the fault-gouge and breccia.

The fault on the western side of the graben at Pircas was not so diagrammatically clear as the eastern fault at Ciénaga. The Pircas fault appears most clearly on the north wall of the quebrada, where of two adjacent and very steep spurs the

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westernmost is composed wholly of Paleozoic schists for its entire visible height of a couple of hundred meters. The easternmost of these spurs is, on the other hand, composed entirely of red sandstone. There is a great deal of brecciated material in the gully between the two spurs. The hypothesis that this is a contact due to original sedimentation is untenable, for the red sandstone dips westward into the metamorphics, and the necessary thickness of red sandstone can not be accommodated by a reversal of dip in the zone covered by the breceia.

FIG. 8.



FIG. 8. Looking eastward from the middle of the Calchaquí valley to the Cumbres del Obispo opposite La Poma. Note the mature upper slopes, the smooth middle slopes, and the very young gullies in the lower slopes. The folded Jurassic red sandstone is seen in the middle ground and the crumpled and fissile Paleozoic metasediments in the background. This figure is to be compared with figure 9.

Owing to the conditions of work and the rough topography it was impossible to examine the nature of the contact between the Jurassic red sandstone and the Paleozoic metamorphics at other points. Below are given several arguments of circumstantial nature, which have led to the conclusion that both of the marginal faults extend the whole length of the valley.

The Cumbres del Obispo, 1200 to 2100 meters higher than the valley, lie on the eastern side of the Calchaquí depression, and their whole slope towards the valley is very smooth. The main points suggestive of the continuation of the fault along the base of the Cumbres del Obispo as a line of inherent weakness are as follows:

(1) The abnormal profiles of the ravines show that the gradients along the lower slopes of the otherwise exceptionally smooth mountain flank have been steepened in recent times. (See fig. 8.)

(2) The mountain flank has a very straight outline from north to south. In other words, contours drawn on this flank would approximate to straight lines, a condition not to be expected as a result of erosion, pure and simple, on schists of variable resisting power.

(3) There are several small volcanoes, now extinct, located on or very close to the line of contact. For example, "El Volcan" near La Poma.

(4) The Argentine Weather Bureau reports from its station at La Poma occasional slight earthquakes, which are of local origin and have purely local effects, as if crustal adjustment in the immediate vicinity were still in progress.

From these lines of evidence it is concluded that the Ciénaga fault continues northward along the base of the Cumbres del Obispo, forming the contact between the Jurassic red sandstone and the Paleozoic metamorphic rocks.

The argument for the southward extension of the western fault from Pircas is by analogy to the eastern fault. The contact between the metamorphics and the sandstone is strikingly brought out by the great contrast in color between these two rocks. From any vantage point in the central portion of the valley both the eastern and western contacts can be traced with ease for ten or a dozen kilometers to the north and south. The contact on the west side is strongly deflected by every spur and gully which it crosses, the deflection being vertical, not horizontal, which indicates that the contact-plane is very steep at all points. In view of this uniformity it is argued that the western boundary is a fault extending southward along the valley from Pircas.

The eastern fault is not a line of uniform displacement, but of somewhat differential movement. The fault is of the rotary type. This is seen by comparing figures 8 and 9. Both were taken from about the middle of the valley looking eastward to the Cumbres del Obispo. Fig. 9, which was taken six or eight kilometers north of La Poma, shows slopes much more maturely dissected than figure 8, which was taken about opposite La Poma. Since the slopes are less mature to the south, there must either have been more recent movement or have been greater movement.

### The Amount of Displacement.

The amount of the faulting must be of the same order as the height of the mountains on either side of the valley, presuming that the region had moderate relief at the time when the red sandstones were deposited and that the faulting belongs to the cycle of uplift and erosion which has made the present mountains. Were the Jurassic red sandstones deposited in what was already a rather narrow canyon, the amount of the

FIG. 9,



FIG. 9. Looking eastward from the middle of the Calchacuí valley to the Cumbres del Obispo six or eight kilometers north of La Poma. Note that the very young gullies in the ridge in the background are restricted to the lowermost portions of the mature slopes. Ledges of Jurassic red sandstone in the foreground dip under the camera. The well stratified rocks across the valley are also of Jurassic red sandstone. The upper slopes and the snow-capped peaks in the background are of Paleozoic metasediments Compare with figure 8.

throw would be lessened. On the other hand, if erosion has been more effective on the tops of the mountains than in the valley, the throw may have been greater than the present height of the mountains. Presuming that these two factors partly counterbalance each other, the height of the mountains must be an approximate measure of the amount of throw of these faults.

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There are a few anticlines in the sandstone in the neighborhood of Payogasta by which the metamorphics are brought close to the level of the valley floor, so as to be exposed in small gullies. On account of this relation we can not consider the base of the sandstone as much below the present valley floor.

Considering the mountains on either side of the valley as 1200 to 2000 meters high, the throw of the faults would be from one to two kilometers (three-quarters of a mile to a mile and a quarter).

#### The Relation of Folding to Faulting.

A graben, or down-faulted crust-block, may attain its position and structure as the result of any one of several processes. It may have settled vertically under gravity as the result of the pulling away of its sides by tensional forces in the earth's crust, in which case it would find expression as a crust block of downward-tapering cross section. Conversely, an upwardtapering wedge-shaped crust-block may be depressed by compressive forces acting horizontally on oppositely inclined thrust fault planes. It may have remained lower while the side blocks were pushed up, or it may have been a separate great slice caught in a fault zone subjected to oscillatory movement, the upward movements taking place dominantly on one of the graben walls, the downward movements occurring chiefly on the other. The last two causes might cooperate with either of the first two in attaining the final result.

The general relations of the Calchaquí graben, which bear upon this problem, are as follows:

The region is one of folded and overthrust rocks, which have been cut by normal faults, as is true of all the eastern border of the Central Andes. It is improbable that there could have been a period of crustal tension, as all the structures which have been described are of types due to compression. It is also improbable that the Calchaquí graben block has remained at a constant level in the presence of such tremendous and widespread forces as those which built the Andes.

It is clear that faulting has occurred on both sides of the block and that the block has suffered compression. These two facts, which are the dominant facts of its structure, are explained by the hypothesis that in the elevation of the Andes faulting occurred on this eastern margin and that due to the oscillatory nature of the fault movements the block was relatively depressed. There is no evidence at hand to show whether the folding of the Jurassic red sandstone took place before, during, or after the faulting. It is slightly more probable, perhaps, that faulting and folding occurred simultaneously, for it is probable that in the release of the vertical forces in the crust, horizontal stresses and strains would have been developed.

That the habit of the Jurassic red sandstone and its related red sandstones in northwestern Argentine is one of block-faulting seems certain. Pierre Denis<sup>\*</sup> has described the Serrania de la Lumbrera, one of the elements of the pre-Cordillera, as an up-faulted block with gentle folds. Bailey Willis, in a personal communication to Professor Bowman, said that he depended to quite an extent on the dominant block-faulting of the region in locating wells for the water-supply for the Argentine Government's new railroad.

Résumé.

In summing up the geologic history of the region traversed by the Expedition we find evidence of the following periods and events:

(1) The deposition of Paleozoic (and possibly Archean) sediments.

(2) The metamorphism of these to schists, quartzites and slates by regional processes in mountain-making movements at the end of the Paleozoic. This was either accompanied by, or followed by, the intrusion of granites and granite porphyries.

(3) The erosion of these to maturity.

(4) The deposition on the eastern side of the Cordilleras of Jurassic sediments, with a marine basal portion, but chiefly terrestrial.

(5) A period of vertical movements, probably oscillatory and differential in character, forming the Calchaquí graben; these were accompanied by horizontal compression normal to the axis of the Cordilleras, which folded and faulted the Jurassic rocks.

(6) A period of great volcanic activity, yielding rhyolites and andesites, beginning in the Tertiary and running into the Pleistocene and recent.

(7) Some glaciation in the Eastern Cordillera.

(8) The present period of erosion, with very slight volcanic activity.

\* Annales de Géographie, July 15, 1913, Paris.

# ART. XXVII.—Geology of Bermuda Island; Petrology of the Lavas; by L. V. PIRSSON.

Introductory.—The samples obtained from the Bermuda well, described in the preceding number of this Journal, do not afford material well suited for petrographic study. In the zone of sedimentary deposit down to 700 feet frequent chips and pebbles occur, sufficiently large to furnish thin sections of the usual size, but this material has been greatly altered by atmospheric agencies. In the zone below this, where firm rock is encountered which, buried beneath the sea, has never been exposed to the atmosphere, the drill reduces the rock to the condition of a sand varying from fine to medium in size, and only a few somewhat larger pieces occurred in the samples studied by the writer. The difficulty is enhanced by the extreme density, compactness, or fine grain of the rocks. In order to obtain sections sufficiently thin to observe the groundmass components it is necessary to grind them to thicknesses below 0.02 millimeter, which is not an easy operation with small grains. The sections first prepared were those made from the larger chips from the sedimentary zone and from them it was thought that they were of altered augiteandesite, as stated in the preliminary paper.\* Further study of the fresher material has shown that this was not correct and, as will be seen, the lavas have a quite different character from andesite.

Sections have been prepared from nearly all the samples and while they all yield some information, especially with respect to the larger phenocrystic minerals, in a number of them, cut with especial care as thin as possible by Mr. W. Harold Tomlinson, areas occur which are fairly well suited for the study of the very fine groundmass. In all the sections this groundmass is more or less altered, and in most cases very much changed. When the petrographic work was nearly finished I received a letter from Dr. H. H. Thomas of the Geological Survey of Great Britain, in which he stated that he had also had the opportunity of studying a set of samples from the Bermuda well, received by the Survey through the British Colonial Office. From his statement it seemed that he had found some better material and had therefore better sections than the writer, and I requested him to send me the results of his observations on the petrography of the lavas. This he has most kindly done, and he has also added some microphotographs. Dr. Thomas' letter sums up so well the petrographic characters

\* This Journal, vol. xxxvi, p. 70, 1913.

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of these rocks that I quote from it freely, with reproductions of two of his photographs, and then present additional observations of my own :

"It would appear that the igneous rocks are mostly, if not entirely, lavas of the alkali group, and that they fall under two main heads.

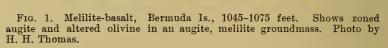
a Feldspar-free basalts, including melilite-basalt.

b Lavas of monchiquitic and lamprophyric affinities.

Judging by the fragments and powders it seems that the basaltic



Fig. 1.



rocks are in excess of other types, but the lamprophyric and monchiquitic ones appear to predominate in the upper 100 feet of the igneous rocks, occur at depths of 1045-1075, 1140, and their presence is suggested at various positions in the basaltic types.

The Basalts.—Inferred solely from the powders these are compact, dark gray rocks consisting of a deeply colored augite and fresh and decomposed olivine as microporphyritic crystals set in a base of some feldspathoid mineral. Feldspar appears extremely rare and it is evident that most of the rocks are free from it.

Two fragments of the basalts, from 1045–1075 feet, were large enough to furnish sections and both proved to be melilite-basalt. The microscope reveals the fact that the microphenocrysts consist of olivine and augite while the matrix is composed of a later generation of augite, of melilite, apatite, primary analcite, a little biotite, and some spinellid, probably both magnetite and perovskite.

The augite phenocrysts are fairly strongly colored, yellowishgreen and zoned, the outer layer darker with purplish shade, such as is usually associated with a higher percentage of titanium. Olivine is completely decomposed and represented by pseudomorphs in serpentine, calcite, and a pleochroic (bright green to yellow) micaceous mineral. Its size is about that of augite.

The groundmass consists of narrow elongated crystals of brownish augite forming a complicated lattice whose interstices are filled with colorless melilite with typical cross-striation and "pflockstruktur." It is roughly tabular to the base, but seldom shows crystal outline. Apatite is abundant in slender, wellformed prisms.

Perovskite is inferred to have been present in the undecomposed rock, from the occurrence of brownish, almost opaque, octahedral crystals which seem to have been partially changed into a granular aggregate or titanite. Small, clear patches without definite outline consist of analcite which appears to be original. The melilite, when in close proximity to these patches or projecting into them, takes an idiomorphic habit and occurs as well-formed tables flattened parallel to the base. A microphotograph of the rock is seen in fig. 1.

Lamprophyric and Monchiquitic Rocks.—It is probable that all the rocks which fall under this heading might be classed with the monchiquites in a broad sense, the essential constituents being augite, biotite, and analcite, with apatite as an important accessory. Olivine appears absent in all cases. Augite and biotite are interchangeable, with all gradations between all augite and all biotite. The various types, therefore, find their parallels in the fourchite and ouachitite of Williams and Kemp.

The best fragments of these rocks come from the depth of 1140 feet. They are moderately fresh, compact, gray rocks without phenocrysts, consisting of elongated crystals of a brownish and purplish augite and deep red biotite in a somewhat decomposed base. This base consists of calcite and analcite, the latter often in clear areas, and is traversed in all directions by slender needles of apatite. A photograph of this type is seen in fig. 2.

Rocks of this character have been met with at 1002-1022 and at 1045-1075 feet, in the latter almost free from augite, and they were the most prevalent in the upper 100 feet of the igneous rocks, though much decomposed.

Keratophyre.—The only distinctly feldspathic rock found comes from the higher portion of the well. A section from a fragment in the sample from 550–554 feet proved the rock to be allied to the keratophyres, since it consists of a fine-grained aggregate of albite and microperthite enclosing a few larger albites, rare flakes of biotite, and fairly abundant needles of apatite."

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The condensed statement by Dr. Thomas sums up well the chief characters of these rocks. But judging from my own preparations the monchiquite type is as common as the melilite-basalt. Since, however, the specimens are chance chips and grains, the largest individual piece being less than half a pea in size, which are mingled together between the points indicated in the list of samples, there is no way of

FIG. 2.

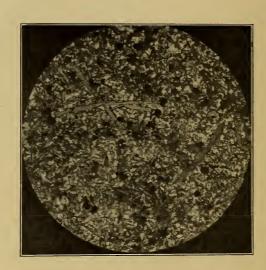


FIG. 2. Biotite Monchiquite, Bermuda Is. Large biotites in fine-grained groundmass. Photo. by H. H. Thomas.

definitely settling this point. The following are the results of my own study of the lavas:

### Melilite-basalt.

The following minerals have been found in the sections: iron ore, apatite, perovskite, angite, biotite, olivine, melilite, orthoclase, nephelite, and analcite. The *augite* as a phenocryst is usually well-crystallized with the forms a, (100); b, (010); m, (110); and s,  $(\overline{101})$ ; elongate on the vertical axis and sometimes flattened parallel to a, (100). The largest embedded crystal seen measured  $4^{mm}$  along the b axis and half that perpendicularly. The regular cleavage is well developed. The angle of extinction is large,  $c \land c$  up to  $45^{\circ}$  or more, the birefringence high. The color is brownish varying to olive and as noted above there is often a deeper purplish border, recalling the titaniferous augites seen in certain nephelinites. Like those, it is pleochroic and shows a dispersion of the bisectrices. The augites of the groundmass are similar, though not markedly zoned, rather evenly developed in the prism zone and relatively long columnar on the vertical axis. The sections are, therefore, lath-shaped. While sometimes unaltered, they are often in part, or wholly, replaced by granular masses of carbonates. In several cases it has been observed that where the augites of the groundmass project into or lie in areas of analcite the common variety described is replaced by ægirite or ægiriteaugite. Similar cases have been noted by Cross\* in the phonolite of Cripple Creek, and by the writer in analcite-basalt from the Little Belt Mts.,† and is one indication of the original nature of, at least, some of the analcite.

*Biotite* occurs only as a small occasional flake in the groundmass.

Olivine, in an altered condition, has been found in only one case by the writer, embedded in the section. A few isolated fragments, some altered to greenish serpentine, others very fresh, have been found in the powders, but the amount is so small in comparison with augite that it must be considered a rather rare phenocryst in the Bermuda lavas. The decomposition products indicate a variety rich in iron.

*Iron ore* is well distributed, usually in small crystals rather evenly scattered through the groundmass. The square outlines indicate the octahedron, and that it is probably magnetite. The most notable fact about the iron ore is the way in which, in the solid lavas below 700 feet, it appears unchanged, even in groundmasses much altered, while in the zone above that level it has largely gone into limonite.

Apatite occurs in slender colorless needles in the groundmasses and occasionally in larger stouter prisms. On account of the suspected presence of melilite, whose optical properties are very similar to those of apatite (melilite o, 1.634; e, 1.629; o-e, 0.005; colorless, uniaxial, cleavage poor; apatite, o, 1.638; e, 1.634; o-e, 0.004; colorless, uniaxial, cleavage poor) a chemical test was made for phosphoric acid, since it had not been determined in the quantitative analysis. The finely ground rock was boiled in dilute nitric acid, filtered, and the filtrate evaporated to dryness. The residue was taken up in nitric acid, diluted, the insoluble silica filtered off, and in the filtrate molybdic acid solution gave an abundant test for phosphoric acid. This confirms the identity of the grains and needles.

*Titanite* was observed in several of the samples in isolated \*Geology of the Cripple Creek District, Colo., 16th Ann. Rep. U. S. Geol Surv. Pt. II. p. 35, 1895

Geol. Surv., Pt. II, p. 35, 1895. † Twentieth Ann. Rep. of the U. S. Geological Surv., Pt. III, p. 546, 1900. fragments in the powders and in a number of cases embedded in the sections of groundmass in the form of grains or aggregates of them. It is an alteration product of perovskite and augite, and the more altered the rock the more abundant it becomes. It is readily determined by its high index of refraction, strong double refraction, small optic angle, and marked dispersion of the optic axes, together with its color.

*Perovskite*, in unaltered, identifiable form, was not found in any section of the melilite-basalt, but the writer agrees with Dr. Thomas in considering yellowish masses as indicative of its former presence.

Melilite.—Strong suspicion was aroused concerning the possible presence of this mineral, both from the nature of the rock and from the chemical analysis. The difficulty in detecting it lay in the prevalent alteration which the groundmass has undergone. For the most part the colorless cementing substance consists of analcite or indeterminable whitish material thoroughly clouded with extremely minute specks and granules of calcite, such areas giving an aggregate high polarization effect. It is evident that the mineral substance has suffered a process of calcitization. Dr. Thomas was more fortunate in finding some yet unchanged areas in which it could be recognized, and encouraged by this, new sections were prepared and finally in one of them, from the sample mentioned by him, 1045–1075 feet, melilite was found with the characters he mentions. Between crossed nicols it has not been observed to have any abnormal interference color, only a gray, like apatite or nephelite. It is negative in these sections. The alteration of melilite into carbonates, chiefly calcite, is not mentioned by Rosenbusch, but has been recently described and discussed by Soellner in his paper on bergalite, the remarkable melilite rock from the Kaiserstuhl.\* This would be a natural form of alteration in a rock submerged in sea-water containing CO<sub>2</sub>. The material is not suited for observing the alteration of melilite into deeckeite described by Soellner. After the characteristic melilite with its peg structure had been seen and studied, it could be traced in many of the calcitized areas by minute remnants of the peg structure still remaining.

Nephelite, sodalite, hauynite.—Nephelite has been found in several cases in isolated fragments in the slides made from the rock powders, as recognized by its colorless character, negative uniaxial interference figure, refractive index close to balsam, and low interference color. Whether these fragments come from the melilite rock or from the monchiquite-like type, since the samples are mixtures, is uncertain, though it is thought to be probably present in both. Sodalite and hauynite were tested for

\* Mitt. d. Grossh. Bad. Landesanst, vii, pp. 438, 452, 1913.

chemically. Some of the sample of crushed rock at 1045 feet was first washed free from any adherent chlorides or sulphates coming from sea-water. These were at first present. The rock powder was then dried, ground fine, and boiled with very dilute nitric acid, and the solution filtered. Some of this filtrate on being evaporated yielded abundant gelatinous silica, from melilite of course, for the most part. Other portions tested for chlorine and sulphuric acid gave negative results, indicating the absence of sodalite and hauynite.

Feldspar; pseudoleucite.—Feldspar in the form of sanidine has been found in one or two isolated fragments in the rock powders, as at 980 feet. It was not observed in any of the "rock sections" with any certainty, save in one case. The reader must remember, however, that the largest "rock section" is not above 3mm. in diameter, while most of them are about 1mm, and with prevailing alteration and very dense texture the opportunities are not good. In the case referred to, the section, which is one of the largest, contains a whitish circular spot cut in half by the edge of the section, and about one and a half mm. in diameter. This consists, for the most part, of small, irregular, interlocked, granules of an alkalic feldspar mixed with some nephelite. The determination is difficult on account of the thinness of the section and the considerable degree of kaolinization, but some of the particles have a refractive index practically the same as balsam while others are lower and biaxial. The whole appearance of this area is similar to that of pseudoleucites from Brazil, Arkansas, Montana, and other places, as described by the writer and other petrographers. The chemical analysis given beyond suggests also the possibility of occasional leucite in these rocks. In addition the area contains masses of calcite, grains of secondary titanite whose grouped disposition indicates that they are secondary after augite microlites, and much altered perovskite.

Analoite.—The colorless isotropic areas with low refractive index are inferred to be largely of this mineral since many of them exhibit well the cubic cleavage which, as Evans\* pointed out, is one of the best characters in helping to determine it. That it is not sodalite is shown by the chemical test mentioned previously. The original nature of at least some of this analcite has been mentioned by Dr. Thomas and referred to under augite.

Texture.—The rock is holocryptocrystalline, microporphyritic in fabric and dopatic, the groundmass prismoid divergent, its character being determined by the interlaced prisms of augite whose interstices are filled by the anhedral felsic minerals.

\* Quart. Journal Geological Society, vol. lvii, p. 38, 1901.

Mode.—Both the character of the rock and of the sections which can be cut from it forbid any accurate computation of the quantitative actual mineral composition. Judging from what is seen in the sections and from the analysis presented later, a rough approximation in which only the chief original minerals are considered, might be, iron ore 8 per cent, apatite 2 per cent, olivine 5 per cent, pyroxene 35 per cent, melilite 35, analcite 15 per cent.

Classification.—The rock is evidently to be classed as a melilite-basalt, though from the relatively small amount of olivine it contains it is near the border line of a melilitite if, following the analogy of nephelinite and nephelite-basalt, that name should be applied to rocks of this class without olivine. A near relative of this rock would appear to be the cappaelite of Sabatini in Umbria.\*

### Lamprophyric Lavas.

These rocks occur chiefly in the upper layers of the unaltered lavas, but appear also in the samples taken at lower levels. Since the casing was discontinued at 785 feet, soon after the firm rock was reached, there must be some uncertainty as to their occurrence at the lower levels, since detached fragments from above, to some extent, must have been precipitated into the hole. Their appearance at some levels and not at others is, however, indicative that they belong to some extent in the lower zones. They have also been found in the upper zone of altered sedimentary deposits, as would naturally be expected, since they were apparently the latest forms of lava ejected.

As noted by Dr. Thomas, there is a considerable diversity among these rocks, and yet they are so closely related by transition forms and similarity in character of constituent minerals that it seems best to consider them as a single group. They are also closely related to the melilite-basalts, and it is not at all certain that there are not transitions in this direction also, or that they may not occur as varying portions of a single flow.

One variety, as found in a chip from the 1045–1075 sample, consists of a network of fine interlaced prisms of a brown augite so thickly packed that there seems not much space left for other minerals. It must form perhaps 75 per cent of the rock. In the interstices are analcite, occasional flakes of calcite, and a brownish, fibrous substance with aggregate polarization varying from feeble to strong in different spots of the same area. Sprinkled generally through this are small grains and octahedra of perovskite, more or less marginally converted

\* Boll. R. Comm. Geol. d'Italia, 1903, p. 376.

into a black decomposition substance. Masses and strings of secondary granular titanite are seen in places. Iron ore, olivine, and biotite appear to be entirely wanting in it, and, although it is one of the largest sections, containing about 12 square mm. of surface, it contains no phenocrysts. Considering the amount of mafic mineral present, this rock would perhaps classify best as an *augitite*, of alkalic affinities. It might be remarked, however, in this connection that rocks which have in many cases been classified as nephelinites, nephelite-, and leucite-basalts, etc., have quite as large a proportion of mafic minerals, so that if stress is to be laid upon the felsic component, as in their case, the rock would be called an analcitite, or perhaps a monchiquite, in lava form.

Another variety of this group, mentioned by Dr. Thomas, contains no augite, but is composed of abundant small biotites embedded in a felsic cement. The best example was found in a minute pebble at 554–573 feet. The biotite plates vary in pleochroism from rich chestnut brown to nearly colorless. They are accompanied by a great number of opacite pseudomorphs of elongate lath-like form which are seen by transitions to the unaltered biotite to be resorption products of former biotites. These and some iron ore grains and slender needles of apatite are cemented by a colorless substance which polarizes weakly in minute, patchy, ill-defined areas. Its precise nature cannot be determined, but it is thought to be a mixture of felsic minerals, perhaps nephelite, sanidine, and analcite. In other varieties intermediate between the two mentioned, in which both augite and biotite occur, the resorption products are wanting. Considerable variation may be noticed in the augites; they are sometimes chocolate-brown, sometimes yellowish-brown, and sometimes colorless. In regard to the felsic cement, it is sometimes analcite, as mentioned by Dr. Thomas, accompanied by calcite; in other cases, as at 995 feet, a colorless mineral of low birefringence, which is held to be nephelite, is also present; consequently, it is not certain that the analcite in such cases, at least, is primary. The texture of these rocks is similar to that of the groundmass of the melilite-basalts mentioned above, consisting of an interwoven mass of the mafic minerals with a colorless cement. While the minute size of the "rock sections" does not give a fair idea of the textures as to whether they are strongly porphyritic or not, the rather abundant fragments of phenocrystic augite which occur in the powders suggests that they are at least moderately so.

*Classification.*—The classification of these rocks in qualitative schemes offers some difficulties. Dr. Thomas has struck the most important thing about them in remarking that they are to be considered the effusive equivalents of monchiguites; and it is clear that they are lavas of lamprophyric character. The relative amount of mafic minerals and felsic cement is variable, and where the former is large the augitic types are much like those placed under augitite by Rosenbusch. The lamprophyric nature of many augitites is indeed commented on by this writer.\* The type, rich in biotite and without augite, could not, however, be placed with them; and those who demand a separate name for the effusive rocks as contrasted with the intrusive ones, would object to calling it ouachitite, which it is most like in composition and in genesis. The name of *bermudite* is suggested for consideration, to obviate this difficulty.

#### Chemical Composition.

It has not been possible to obtain thoroughly satisfactory material for an analysis of the Bermuda lava, partly because none has been found in the samples that was not altered, as previously observed, and partly because no definite solid mass large enough to afford the requisite quantity of substance was obtained. The fine granular samples are representative of the lavas between certain levels, and where pieces large enough to furnish sections occurred in them it was found, as previously noted, that two types of rocks were commingled. Therefore, there was no assurance in the analysis of one of the samples that one definite rock substance was being investigated, as would be the case when a solid piece of rock is available. Consequently an extended detailed analysis did not seem warranted, but, on the other hand, since the two rock types are much of the same general nature and the melilite-basalt in some is much in excess, it was thought that a partial analysis would be of some interest and would afford additional light on the nature of the lavas. This has been carried out by Mr. R. C. Wells of the chemical laboratory of the U.S. Geological Survey, to whom grateful acknowledgment is here made for this assistance. The analysis is given in No. 1 of the adjoining table, and those of some related rocks are added for comparison.

The analysis shows at once the character of the group of alkalic lamprophyres. An attempt has been made to compare it with the two kinds of rocks of which presumably the sample was composed, melilite-basalts and monchiquitic rocks. There are not many analyses of melilite-basalts available, and most of these are not recent, and, therefore, not made according to modern methods; they are consequently more or less defective. No. IV is given that of the typical rock from Hochbohl. The

\* Massige Gesteine, vol. ii, p. 1475, 4th ed., 1908.

# Petrology of the Lavas.

ANALYSES OF ALKALIC BASALTIC ROCKS.

No.	I	11	III	IV	V	VI	VII	VIII
SiO <sub>2</sub>	38.79	37.01	37.50	33.89	36.40	42.03	35.91	0.647
Al <sub>2</sub> Õ <sub>3</sub>	14.55	8.71	9.12	9.93	12.94	13.60	11.51	0.142
Fe <sup>2</sup> ,0 <sup>3</sup> ,	5.67	7.26	5.59	15.63	8.27	7.55	2.35	0.036
FeO	6.68	6.71	8.81		4.59	6.65	5.38	0.093
MgO	7.78	14.83	13.72	16.14	11.44	6.41	17.54	0.192
CaO	14.65	15.85	13.85	15.19	14.46	14.15	13.57	0.262
Na <sub>2</sub> O	2.78	2.63	2.69	2.86	3.01	1.83	1.75	0.045
K,Ô	2.54	1.84	0.63		0.92	0.97	2.87	0.027
$H_{2}O +$	1.99	1.78	2.35	2.90	2.36	1.08		0.110
H_0	0.62		1.05				9.40	
CÔ,	3.56		0.27	1.41	3.94			0.081
$\operatorname{TiO}_2$	0.80	3.21	3.21	0.64	0.42	3.70	0.23	0.010
$P_2O_5$	n. d.	tr	0.90	1.41	1.04	0.57	n. d.	
$Cr_2O_3$		0.14	0.02	tr				
Total	100.46	99.97	100.19	100.00	99.84	99.23	100.51	

- I. Melilite-basalt, mixed with some monchiquite. Bored well at 1110 feet, Southampton, Bermuda Island. R. C. Wells, U. S. G. S., analyst.
  II. Melilite-nephelite-basalt. Neuhöwen ("by Stetten"), N.W.
- II. Melilite-nephelite-basalt. Neuhöwen ("by Stetten"), N.W. from Engen, Hegau, Baden. Anal., Fr. Dr. S. Hezner. Rosenbusch, Elem. d. Gest., 3d edit., p. 467, 1910.
- III. Melilite-nephelite-basalt. Kilanea Landing, Kauai Is., Hawaii. Anal., W. F. Hillebrand. Contains 0.05 Cl, 0.04 NiO, 0.15 MnO, 0.07 BaO, 0.05 SrO, 0.05 V.O., 0.02 ZrO. = 0.43. Bull. 419, U. S. G. S., p. 179, 1910.
  IV. Melilite-basalt. Hochbohl, by Owen, Würtemberg. Anal.,
- IV. Melilite-basalt. Hochbohl, by Owen, Würtemberg. Anal., Meyer, in Stelzner, N. Jahrb. Min., Beil. Bd. ii, p. 398, 1882.
- V. Ouachitite, near Hot Springs, Arkansas. Anal., L. G. Eakins, in J. F. Kemp, Basic Dikes in Arkansas. Ann. Rep. Geol., Surv. Ark., 1890, vol. ii, p. 399.
- Rep. Geol., Surv. Ark., 1890, vol. ii, p. 399.
  VI. Fourchite, Fourche Mt., Ark. Anals., Noyes and Brackett, in J. F. Williams, Igneous Rocks of Ark., Ann. Rep. Geol. Surv. of Ark., 1890, vol. ii, p. 108 includes FeS<sub>2</sub>, 0.56.
- VII. Alnoite, Ste. Anne de Bellevue, by Montreal. Anal., P. H. Le Rossignol, in F. D. Adams, Melilite-bearing Rock, etc. This Journal, vol. xliii, p. 271, 1892.
- VIII. Molecular ratios of No. I.

most modern and best analyses I have been able to find are given in Nos. II and III; they are both not pure melilitebasalts, but contain nephelite and are thus transitional to nephelite-basalt. Rosenbusch remarks that the nephelitemelilite-basalts are characterized, in contrast to the nephelitebasalts, in that the silica is less than 39 per cent, and by the higher content in magnesia, while the lime is about equal or even exceeds.<sup>\*</sup> The more pure melilite types, judging from No. IV and from No. VII, which is that of the intrusive rock, alnöite, and from other analyses as well, are distinctly lower in silica than those which are melilite-nephelite basalts, though not otherwise essentially different. The Bermuda analysis is more like II and III than IV, but differs from these in the higher alumina and lower magnesia. The former explains the considerable amount of analcite present, which in this rock represents the nephelite without regard to whether the analcite be considered original or secondary, while the lower magnesia helps to account for the rather small amount of olivine. The lime of the Bermuda rock, as mentioned later, is considered essentially original.

Two analyses, Nos. V and VI, of those rocks of the monchiquite group, which are most like the type found in the samples, are also included in the table. It will be seen that they have much the general characters of the Bermuda sample, the most marked difference being that one has higher magnesia and that they are somewhat lower in alkalies, especially potash. It may also be noticed that they are much like the nephelite-melilite-basalts, the most notable feature being the higher alumina.

The inference to be drawn from the analysis of the Bermuda sample is, then, that it is what we should normally expect from a mixture of the two determined types; but the table shows also that it does not give data from which one can judge as to the relative quantities of them present.

#### Quantitative classification and Norm.

It was thought that it might be of some interest to calculate the norm of the above analysis and the determination of its position in the Quantitative System; it is understood, of course, that since the rock material is altered, composed of two types, and the analysis a partial one, too much importance must not be attached to any facts or relations yielded by this procedure. In making the calculation it is necessary to consider the lime, which is in combination with calcite, a secondary mineral. Soellner + argues that the lime in the secondary calcite in melilite-basalts has not been brought in from outside, but has come from the alteration of the melilite, and should, therefore, be considered as original, and the writer believes that this is true in the case of the Bermuda lava. The norm has, therefore, been calculated; A, on the assumption that sufficient lime to satisfy CO, should be deducted; and B, that it is all original, and TiO, is turned into perovskite.

> \* Elemente der Gesteinslehre, 3d edit., p. 465, 1910. † Loc. cit.

A	Ł				В
Or,	6.12 )	Sal			
An,	19.46	Sai	An,	19.46)	$\mathbf{Sal}$
Lc,	6.98	45.34	Ne,	12.78	
Ne,	12·78 j		Lc,	11.77)	44.01
Di,	24.68		Di,	16.46)	
Ol,	9.97	44.52	Ol,	13.80	$\mathbf{Fem}$
Mt,	8.35		Am,	10.37	50.34
Il,	1·52 j		Mt,	8.35	00.04
1 Contraction of the second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second se	-		Pf,	1∙36 j	
CaCO,	, 8.08		Н,О,	$2.66^{-1}$	
H <sub>2</sub> O,	2.66		$CO_2$ ,	3.56	
			•		
	100.60			100.57	

Both of these norms lead to the same sub-rang position III, 7, 3, (3) 4, etindose. The ratio of salic  $K_aO'$  to salic  $Na_aO' = 0.60$ so that it is on the exact line between sub-rangs 3 and 4; subrang 3 has not yet, so far as the writer is aware, been named, and the proper double name cannot, therefore, be given. In calculating B the formula 3CaO, 2SiO, recently established by the Geophysical Laboratory of the Carnegie Institution, for akermanite has been used. Akermanite is, of course, the essential basis of the melilite molecule, and in B it appears, due to the presence of the full amount of lime, diopside being correspondingly reduced in amount on account of the deficiency in silica. In neither the basalt nor the monchiquite has the anorthite been seen in the form of feldspar; it is, therefore, in the augite, not, of course, as CaAl<sub>2</sub>Si<sub>2</sub>O<sub>2</sub>, but as CaAl<sub>2</sub>-SiO, Tschermak's augite molecule, and this helps to explain the larger amount of this latter mineral actually in the mode than is shown in the norms.

In regard to the leucite in the norms this is actually, in part at least, embodied in biotite in the mode of the monchiquite, with some of the olivine aiding it. It cannot be positively stated that there is no leucite modally present in these rocks, for lacking the usual twinning striations and characteristic inclusions it could scarcely be distinguished from analcite. None, however, has been observed.

#### THE ALTERED ZONE OF SOILS AND GRAVELS.

The material of the samples of the well from 700 feet upward has been to some extent also studied in thin section, but without affording any additional information of especial interest, partly because of the more or less profound alteration it has undergone and partly because it appears, certainly for the most part, composed of the same types of rocks as the underlying lavas in place. This of course is what should be expected from geological considerations, since the sedimentary deposits represent those portions of the island which projected above sea-level, as described in the foregoing paper, and it is evident that the submarine lavas must have had an upward landward extension. The trachytic keratophyre mentioned by Dr. Thomas was not found by the writer; on the other hand, fragments of a brown glass were observed, in some cases filled with indeterminable microlites.

### ALTERATION OF THE BASALTS.

From what has been said in the foregoing account of the petrography of these basaltic lavas it is clear that their situation under sea-water has not preserved them from alteration. We find that water and carbonic acid have been the chief reagents, and carbonates, chlorite, serpentine, titanite, and other secondary minerals are present. Feldspathic minerals, together with melilite and olivine, have been the original ones most attacked and, while biotite, iron ore, and augite in some cases are altered, it is remarkable how often they appear unchanged, especially the augite. The noticeable thing compared with weathering is the lack of oxidation and the accompanying change of ferrous compounds to ferric ones.

But a certain degree of caution must be observed in ascribing these changes to the action of sea-water alone, for it is conceivable that when a lava flow is blanketed by a later superincumbent one, the latter while hot and cooling may exert, especially beneath the sea, a hydrothermal action upon the lower older rock. A similar effect might be caused by vapors from the volcanic conduits passing outward through the lavas.

Thus the alteration observed may result from a combination of causes, and it is difficult to assign to each its proper value.

#### SUMMARY.

It has been shown in the foregoing that the lavas of Bermuda, in the area penetrated by the well, consist mainly of melilite-basalt and types related to the monchiquite group, with a small amount of trachyte. They are, therefore, of alkalic character and consequently correspond with the lavas of many of the great volcanoes that rise from the floors of the abyssal ocean basins, and especially with those of the Atlantic, such as the Azores, Cape Verde Islands, etc. Bermuda stands in such an isolated position that we are unable here to bring it into relation with any great tectonic lines of the earth, and thus use it for testing those theories which correlate the appearance of certain kinds of magmas with definite types of lithospheric disturbance. The only hint we have in this connection is the elongate shape of the Bermuda mass, which, with its various vents in line, seems to point to their appearance over a fissure, and the eruptions, in most cases, which have taken place from great fissures are of basaltic character.

Sheffield Scientific School of Yale University, New Haven, Conn., June 1914.

# ART. XXVIII.—A Moraine of Kansan or Nebraskan Age at Jackson, New Hampshire; by P. MAXWELL FOSHAY.

In the summer of 1913 I noted and casually studied a drift deposit at Jackson, New Hampshire, whose real significance did not fully impress me until very recently when I read Professor Goldthwait's paper\* on local glaciers on and about Mt. Washington, together with Fuller's masterly report<sup>+</sup> on the Pleistocene of Long Island.

Professor Goldthwait presents the unmistakable evidence of local glaciers around the northern peaks of the Presidential Range, which was not so surprising as his discovery that the local glaciation preceded the last general ice invasion. He found no local moraines, nor any till certainly referable to the local glaciers, but he did find that the ice erosional forms of cirques and valleys are very definite.<sup>‡</sup> On Long Island Fuller has been able to differentiate the

deposits of four major ice invasions, correlating them with the pre-Kansan (Nebraskan), Kansan, Illinoian and Wisconsinthe latter divisible into two substages each with a strong terminal moraine. To reach Long Island these ice sheets of course had to cross the New England states in whole or in part, consequently in each invasion it is safe to predicate that the White Mountains were either covered or surrounded with ice. Leaving aside as apart from the present purpose all other data, particular note is drawn to the degree of decomposition of the rock bowlders and pebbles in the Long Island drift of each age. The granitic materials in the lowest and oldest glacial deposit are described by Fuller as "rotten", crumbling under hand pressure. In none of the succeeding glacial deposits were the granitic bowlders nearly so decomposed.

Lying easterly from Mt. Washington and separated from it by Pinkham Notch lies Wildcat Mountain, which again is divided from Carter Dome further east by Carter Notch, as shown on the sketch map herewith. Wildcat Mountain is roughly wedge-shaped with the base of the wedge to the north and the long tapering point to the south, the terminal portions being named Spruce Mountain and Eagle Mountain. Ellis River rises in the Pinkham Notch and forms the westerly boundary of the Wildcat mass, while Wildcat river rises in

<sup>\*</sup> Following the Trail of Ice Sheet and Valley Glacier on the Presidential Range, by James Walter Goldthwait, in *Appalachia* for June 1913. † The Geology of Long Island, Myron L. Fuller, U. S. Geol. Survey, Prof.

Paper 82, Washington, 1914.

<sup>‡</sup> See also this Journal, (4), vol. xxxvii, p. 460 (May 1914).



FIG. 1.

FIG. 1. A-Spruce Mountain. B-Eagle Mountain. C-Moraine.

Perkins Notch and marks the easterly limit. Ellis and Wildcat rivers join in the village of Jackson, being separated in their lower courses by only a narrow ridge, though above Jackson Falls Wildcat flows at a level 150' higher than Ellis.

Eagle Mountain proper terminates southerly in abrupt cliffs of gneiss 300 feet high. At their foot begins a rough wooded narrow ridge 400 feet above Ellis river and 250 feet above Wildcat. This ridge is 4/5 mile long and curving a little easterly terminates at the top of Jackson Falls, though there is some indication that it once completely crossed the Wildcat Valley. This ridge undoubtedly in large part has a gneissic ridge core, but it has an irregular morainic surface with shallow kettles, and sections show it to be made up of unassorted drift. One major interruption in this ridge must be noted about onefourth mile above Jackson Falls at the "Flume", a narrow, sharply-inclined, parallel-sided, trench in rock. The "Flume" is 1/4 mile long and no doubt represents primarily a depression due to the decay and removal of a stratum of rock softer than that in the bounding walls, but very likely secondarily a stream outlet from the Wildcat Valley to the Ellis Valley at some stage of glaciation. As the "Flume" contains little or no drift its fluviatile history probably was a Wisconsin episode.

The road from Jackson toward Carter Notch follows along Wildcat river, and at Jackson Falls at the north limit of Jackson village there are several fresh cross sections of the drift ridge. The upper two to four feet are composed of the ordinary till of Wisconsin age, the lower ten feet being made up of large and small bowlders unassorted in a matrix of till and sand. The gneissic bowlders in the moraine are somewhat weathered, but the granitic bowlders are "rotten". In the cross section at the road cut the granitic bowlders present a surface cut to match that of the matrix, that is in the process of digging away the bank the thoroughly decomposed bowlders are sliced across at any angle just as easily as the matrix. The bank therefore is studded with numerous bowlders in cross section, and a stick can be pushed into them as easily as into the matrix.

All over the fields on the sloping sides of the moraine are similar decayed bowlders, the residual coarse quartz sand of which has in many instances been shoveled out to repair the road. These ancient bowlders were well-rounded before they were incorporated in the moraine. I saw no faceted specimens, though they should be expected, all seen appearing to have been picked up from deep well-weathered residual earth. The contrast between these crumbling rocks and the hard fresh bowlders in the later till overlying the moraine is most striking, and can only be explained by recognizing that the moraine is

AM. JOUR. Sci.—Fourth Series, Vol. XXXVIII, No. 226.—October, 1914. 24 much older than the thin sheet of till that overlies it. This later till is probably of Wisconsin age, though of course the possibility that it may be of Illinoian age must not be overlooked.\*

The advanced stage of decomposition of the granite bowlders demonstrates the great antiquity of the moraine. The horizon on Long Island containing the thoroughly rotted granites, according to Fuller, is the Mannetto gravel which he places as of "pre-Kansan" age.<sup>+</sup> It is true that Fuller finds that on Long Island, as well as in eastern and southern New England, the Manhasset (Illinoian) glacial invasion left the greatest deposits of drift, and the Eagle Mountain moraine may be of Illinoian age in its present form, though made up in considerable part of materials of Nebraskan age. As it seems possible that at some stage the Eagle Mountain moraine blocked the Wildcat Valley at the crest of Jackson Falls, although its major portion forms the southern end of the ridge dividing the Ellis and Wildcat valleys, it appears that the Ellis glacier was the most powerful, or else persisted the longest. Later persistence of the Ellis glacier might perhaps be due to the much lower level of the valley bottom. However so far as topography indicates, there is more reason to call the Wildcat valley glaciated than there is the Ellis, as the latter is not so wide as the Wildcat, although Ellis valley heads in Pinkham Notch right on the flank of Mt. Washington itself. The position of the main portion of the moraine, forming as it does the southerly continuation of the Wildcat-Eagle Mountain ridge, indicates quite likely that it was a mesial moraine between the local Ellis and Wildcat glaciers.

Finally the very great difference in age between the moraine and the overlying coat of Wisconsin till confirms Professor Goldthwait's conclusion that the local glaciers of the Presidential Range existed before the last glaciation.

Montclair, N. J., May 20, 1914.

\* Fuller, loc. cit., p. 150. † Loc. cit. p. 85.

# ART. XXIX.—A Rheostat of Variable Range, Suitable for Large Currents; by R. G. VAN NAME.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxii.]

In experiments involving the accurate regulation of currents of one hundred amperes and above, it is often a matter of some difficulty to provide a suitable rheostat. The commercial types are expensive, and substitutes operating on the metallic resistance and sliding contact principle are not easy to make, on account of the necessity for very substantial construction of the contacts. Electrolytic resistances (iron plates in sodium carbonate solution, and the like), though very easily constructed, are not always satisfactory. When used with direct current their resistance cannot, on account of the polarization, be gradually reduced to zero as with the other types of rheostat, and this is often a disadvantage, especially with lowvoltage currents, and in general when economy of energy is a consideration.

Below is described a form of rheostat which may be employed under a wide range of conditions, but is especially suitable for large currents, including those of low voltage for which an electrolytic rheostat is nearly or wholly useless. It was devised and used by the writer for the control of a 25-volt current of about 200 amperes, in studying the electrolysis of fused calcium chloride. This rheostat possesses the advantage that the resistance element can be quickly removed and another of different dimensions inserted, thus altering the range. Extra resistors are easily made, at trifling cost, and may be used indefinitely.

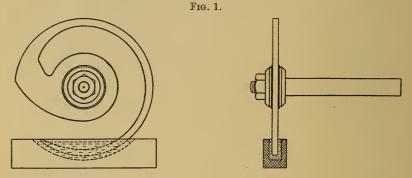
Essentially, the rheostat consists of a curved rod of graphite, submerged in water and so mounted that its effective length is varied by rotating an axle which serves at the same time as one of the current leads. The graphite resistor, which has the general form shown in figure 1, is sawed out of a plate of Acheson graphite, conveniently  $\frac{1}{4}$  inch thick. It is centrally mounted on a stout horizontal axle, so that its rim runs with liberal clearance in a suitably shaped hollow milled in a block of copper. This hollow is filled with mercury, thus providing electric contact between the copper and graphite. Cooling is effected by enclosing the whole in a wooden box through which water circulates.

It is evident that by rotating the axle the resistance interposed between the axle and the copper block may be varied from practically zero up to a maximum determined by the shape and dimensions of the graphite resistor, in particular by the thinness of its "tail." Since this part of the resistor is not subject to any mechanical strain, it may, if desired, be

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given a very small cross section. The axle may conveniently consist of a small steel circular saw arbor, which can be purchased ready-made for two or three dollars, and comes fitted with a suitable device for holding the resistor. It is desirable, though not essential, to electroplate the arbor at the outset as a protection against rusting.

Further details of construction are given by the following description and figure of the rheostat used by the writer in the work above mentioned. Figure 2 is a side view of the

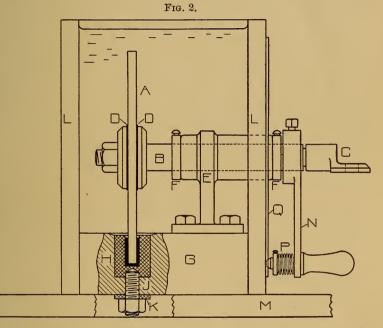


apparatus, and except for a small part drawn in section, shows it as it would appear if one end of the enclosing box were removed. The resistor A was of Acheson graphite, 6 inches in diameter and  $\frac{1}{4}$  inch thick; the steel axle B a  $\frac{3}{4}$ -inch circular saw arbor, threaded at one end to receive the copper terminal lug C, but otherwise used just as purchased. Washers of sheet copper D D were inserted between the arbor and the resistor to improve the electrical contact. The axle was supported by the bearing E, a stout brass casting, and kept from longitudinal motion by the two brass collars FF, held by set screws. The bearing E was mounted on the wooden base block G, as was also the copper block H which contained the mercury contact, the copper block imbedded in the wood slightly below its surface, and connected by copper bolts J, passing through the wooden base, to the copper strip K below, which served as one of the current terminals.\* Wooden sides LL, and end pieces, attached to the base block G, formed a box about 12 by 5 inches and 6 inches deep, inside measurment. When the rheostat was in use a stream of water, sufficiently rapid to keep the box full and to prevent excessive heating of the resistor, was admitted by a tube inserted into the box from above, and passed off by an overflow. The box did not need to be watertight, since the apparatus, mounted on

\* Direct currents may be connected to flow through the rheostat in either direction, but it is better, when practicable, to connect the axle with the negative pole, as a protection against corrosion by the working current.

wooden cross-pieces M, was always placed over a sink when in use.

The device for turning the resistor and holding it in any desired position was attached to the portion of the axle which projected outside the box. It consisted of a radial arm N, carrying a spring catch P which engaged in a series of holes arranged in a circle in a brass plate Q attached to the outside of the box. No stress is laid upon the construction of this



part of the apparatus, since it is immaterial what device is used for the purpose, so long as it permits quick adjustment and holds securely. Since the lug C turned with the axle, a flexible cable was needed for the current connection at this point.

The resistance of the rheostat, when fitted with the resistor generally employed, covered the range from 0.22 ohm down to 0.015 ohm, measured between terminals. This resistor was shaped almost exactly as shown in figure 1, the narrow portion having a cross-section of about  $\frac{1}{4}$  by  $\frac{1}{4}$  inch for the greater part of its length. So far as was observed, prolonged use produced no deterioration or change in this graphite resistor, but it was finally broken by accident. Another resistor of the same dimensions was subjected as a test to a load of over 4000 watts (170 amperes  $\times$  24 volts) for thirty minutes without the slightest injury, and could, apparently, have safely carried a considerably heavier load.

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# ART. XXX.—On a Possibility of Detecting Contractions of the Order of the Fitzgerald-Lorentz Effect; by CARL BARUS.

In my experiments on the application of the displacement interferometer to the horizontal pendulum,<sup>\*</sup> I came across a method for measuring the linear elongation of rods, of exceptional precision and interest. In fig. 1, h, v, b, is a triangular metal bracket, right-angled at a, with a vertical angle,  $\theta$ . The pivots, etc., of the horizontal pendulum, PP, are attached to the standard v, at p and p', the plane of the pendulum being normal to the diagram, the frame extending outward to g, about a meter forward. The grating of the displacement interferometer is placed at g and observed along the line between the concave mirrors m, n. The interferometer is linear in type; i. e. the interferometer beams mg and gn are approximately in the same straight line with the frame of the apparatus. A micrometer screw actuates the mirror m. Rotations are to take place at the angles of the triangle.

If a changes, owing to the unequal expansion of v, b, h, we may write

$$da = \psi \Delta N / 2R \tag{1}$$

where  $\psi$  is the inclination of the axis, PP, of the horizontal pendulum to the vertical, R (normal to the diagram) the distance of the grating g from the axis and  $\Delta N$ , the excursion of the mirror n, which restores the elliptic interference pattern to its fiducial position. In my apparatus  $\psi$  was usually of the order of  $10^{-2}$ , R of the order  $10^2$  cm.

The change of the angle, da, resulting from the elongation of b, v, h, may be independently written, since a is nearly 90°,

$$da = \tan \theta (dh/h - db/b) + \cot \theta (dh/h - dv/v)$$
(2)

If  $a = 45^{\circ}$ 

$$da = 2dh/h - db/b - dv/v \tag{3}$$

One should notice that the equation is numerical, the quantities being of dimension zero.

To take an example illustrating equation (2), suppose b, h have the same coefficient of expansion,  $\gamma$ , differing from that,  $\epsilon$ , of the post v. Then incorporating equation (1)

$$da = (\epsilon - \gamma) / \tan \theta$$
, or  $\epsilon - \gamma \equiv \psi \tan \theta \Delta N / 2R$ 

 $\Delta N$  is larger and the apparatus more sensitive as  $\theta$  is smaller. If  $\Delta N = 10^{-4}$  cm., R and  $\psi$  as above,  $\theta = 14^{\circ}$  (as in my apparatus)

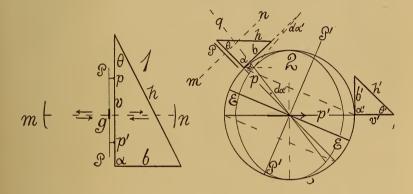
\* This Journal, xxxvii, 501, June, 1914.

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$$\epsilon - \gamma = \frac{10^{-3} \times \cdot 25 \times \cdot 10^{-4}}{2 \times 10^2} = 1.25 \times 10^{-9},$$

so that per vanishing interference ring, a differential expansion of  $4 \times 10^{-10}$  would be registered. Similar relations hold if any one of the rods v, b, h, expand. Since an ordinary coefficient of expansion is of the order of  $10^{-6}$ , the precision of the method, apart from instrumental considerations (which are experimental questions), is manifest. As a second example, such small apparent elongations as occur in the Michelson-Morley experiment may be considered.

The problem may be stated with reference to fig. 2, where PP is the polar EE, an equatorial diameter of the earth, p and



p' diameters of 23.5° of latitude. The earth moves along the diameter p' with the speed of  $3 \times 10^{-6}$  cm./sec. Hence the h, v, b triangle with  $\theta = 47^{\circ}$  is placed with the side v vertical in latitude 23.5°, the base, b, horizontal and the plane in the meridian as shown. The horizontal pendulum is carried by the post v, with its plane normal to the meridian and observed along mn in it, as mentioned above.

Twelve hours of rotation bring the triangle h, v, b into the position h', v', b' and it is required to find the change of angle da, seeing that the motion is now along v' instead of h. For convenience in computation let the angle  $\theta$  be taken as 45° in place of  $2 \times 23.5^{\circ}$ . Let  $\beta = 10^{-4}$  be the velocity of the earth in terms of that of light, so that  $\sqrt{1-\beta^2}$  is the longitudinal contraction coefficient. Hence the lengths h, v, b, for the earth at rest, are to be multiplied respectively by  $\sqrt{1-\beta^2}$ ,  $\sqrt{1-\beta^2/2}$ ,  $\sqrt{1-\beta^2/2}$ ; h', v', b' by  $\sqrt{1-\beta^2/2}$ ,  $\sqrt{1-\beta^2}$ , 1; and on expanding

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 $dh/h = -\beta^2/4, \quad dv/v = +\beta^2/4, \quad db/b = -\beta^2/4$ 

These in equation (3) give, apart from signs,

$$da = -\beta^2/2, \quad \Delta N = \beta^2 R/\psi$$

Using the constants of the apparatus specified,

$$\Delta N = \frac{10^{-8} \times 10^{-2}}{10^{-2}} = 10^{-4} \text{ cm.}$$

Hence even in the case of the above only moderately sensitive pendulum about three interference rings should vanish between the positions h, v, b and h', v', b'.

Contractions of the pendulum itself are negligible, as these merely displace the center of gravity in its own plane and are otherwise not amplified. All contractions of the linear interferometers are compensated. Tidal forces have approximately the same value in the two positions and may be allowed for. Unfortunately the earth (radius r) itself contracts under the same relations, to an oblate spheroid with its minor axis  $r\sqrt{1-\beta^2}$  in the direction of motion; and as the direction of gravity will probably follow the displacement,  $d\theta$ , of the radius in latitude 23.5°, the effect on the pendulum will be neutralized. The h, v, b triangle, in other words, is a part of the earth. Specifically in fig. 2, the triangle h, v, b moves inward a distance s and it is easily shown that the angle between p and q, the new radius vector, is  $da^i = d\theta = \beta^i/4$ . Similarly the angle between two tangents is here also  $d\theta = \beta^2/4$ , both being decrements. Hence since nothing is changed at a' in the h', v', b' triangle,  $da = 2d\theta = \beta^2/2$ , agreeing with the above value. Thus the center of gravity of the horizontal pendulum lies in the normal plane whose trace is q and the displacement from p to q would not be recognized. Similarly if the horizontal pendulum were attached to a massive vertical pendulum (rigid plumb line) the displacement  $d\theta = \beta^2/4$  would entirely escape detection.

Nevertheless it has seemed to me worth while to develop a method which, potentially at least, would be able to measure the small displacements in question, as there are other noncompensated micro-displacements of the earth's diameter, in relation to which the method would be applicable.

Brown University, Providence, R. I.

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# ART. XXXI—The Simultaneous Crystallization of Calcite and Certain Sulphides of Iron, Copper and Zinc. A Crystallographic Study; by H. E. MERWIN.

THROUGH the kindness of Mr. C. E. Siebenthal I have been able to study some specimens in which marcasite, pyrite and chalcopyrite are enclosed within large crystals of calcite.

In one occurrence from Roach's Crystal Cave, Joplin, Missouri, within a group of large crystals of calcite smaller crystals are outlined by included marcasite and chalcopyrite, and also by slight color differences. The outer zones contain little or no sulphides and are differently colored by included matter. The middle zones contain sulphides and are nearly colorless; the inner zones contain a little sulphide and are tinted red.

The crystal forms represented during the various stages of growth are different. The unit rhombohedron is the dominant form outlined by the earliest sulphides. In the pink zone  $-\frac{1}{2}R$  is present, and in the colorless zone the scalenohedron (2130). The latter is dominant to the exclusion of the others in the outer part of the crystal. During one period the rates of growth of the unit rhombohedron and (2130) are clearly outlined by the marcasite. The rhombohedron grew from 2 to 20 times as fast as the scalenohedron (fig. 1, A).

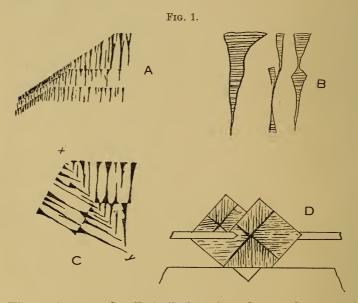
The marcasite developed in very thin branching blades and spicules having forms represented in fig. 1, B. The long axes of the blades are very nearly normal to the faces of the rhombohedron, which they outline, but the blades are flattened in not nearly parallel planes. On the scalenohedron faces also the orientation is normal to the unit rhombohedron (fig. 1, A). The maximum dimensions of the blades are  $5 \times 1 \times 0.1^{\text{mm}}$ .

A small amount of chalcopyrite was identified only after dissolving the calcite. It is spicular to pyramidal in habit and coarser than the marcasite.

The presence of the structure along xy shown in fig. 1, C is conclusive proof of the simultaneous deposition of the calcite and the marcasite. The successive broadening and narrowing of the blades of marcasite indicates changes in the relative rates of deposition of the two minerals. Also, while at certain periods marcasite formed at nearly equal rates on both rhombohedral and scalenohedral faces the calcite was precipitated much more rapidly on rhombohedral faces, thus producing differences in the relative amounts of the two minerals in unit volumes. The form of the chalcopyrite is evidence that it also was deposited simultaneously with the calcite.

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The second specimen is a calcareous geode about 9 inches in diameter, from central Missouri. The geode was first lined with dark brown calcite containing bituminous (?) matter. With this is associated a very little marcasite in free spaces amongst the calcite. A second generation of clear calcite is accompanied by considerable marcasite and some pyrite. The marcasite appears in slender blades, or reticulate structure due to twinning. It is partly free and partly enclosed in calcite. Much of it appears to have formed since the clear calcite began growing, but conclusive evidence is lacking.



The pyrite crystals, all similarly oriented upon the marcasite blades, appear like knots or encircling beads. The marcasite has not grown perceptibly since the pyrite began depositing, but it is still bright. Some pyrite crystals have been enclosed in calcite. Others after being partly enclosed grew out over the calcite, indicating a halt in the growth of the calcite (fig. 1, D).

There is no evidence that during any interruption in its growth the calcite was etched. After etching, there would be a strong tendency for any renewed growth to start irregularly upon the old, giving rise to a parallel aggregate of small crystals rather than to the single symmetrical crystals found on the specimen.

A thin section shown me by Mr. J. B. Umpleby contains a minutely-branching crystal or a parallel aggregate of wurtzite

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crystals enclosed in calcite. There are enlargements upon the slender filaments which could scarcely have been sustained in a free space. Such a structure would not be likely to result from replacement. Therefore, it seems extremely probable that the wurtzite and calcite were deposited simultaneously.

While at temperature above the ordinary, slight or decided acidity is a dominating factor in determining that marcasite and wurtzite rather than pyrite and sphalerite come out of their solutions,\* there are conditions, of which the specimens just described are representative, under which the first named minerals are produced from solutions which are practically neutral. In case of the marcasite one of the conditions, as indicated by geological relations, must have been ordinary temperature. Recent laboratory studies<sup>†</sup> have shown that a little above ordinary temperatures much less acidity is necessary in solutions from which these minerals are depositing to permit the appearance of marcasite and wurtzite than is necessary at higher temperatures.

Crystallographic study of the pyrite and marcasite.-The pyrite in the geode above described appears in crystals 1 to 3<sup>mm</sup> in diameter, having the form of both the rhombic dodecahedron with faces striated strongly parallel to the long diagonal, and rarely of the octahedron striated parallel to the edge. None of the dodecahedral faces give reflections, but from positions corresponding to the octahedron, cube, and the pyritohedrons (230) and (210), reflections with accompanying light figures are obtained. The character of the light figures is shown in fig. 2, A. They are almost identical with those from the diamond having similar striations. Fersmann and Goldschmidt<sup>‡</sup> have shown that such striations on the diamond accompany growth.

The dodecahedron is not a common form on pyrite, yet a few cases are known in which it is the dominant form.§

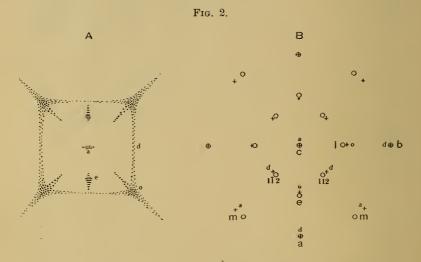
It has been observed both bright and dull.§ but I have found no definite statement as to the character of its striation except that given by Boeris.§ He says the faces are grooved and striated parallel to the edge of the cube, and that they vary from bright to dull. The crystals occur in nodules of calcite. The striation on these faces parallel to the cube is in marked contrast to those on the crystals here described.

The pyrite began growing on the flat sides of the blades of marcasite, c(001). All stages between this and single crystals

\* This Journal, xxxiii, 193, 1912. † Ibid., xxxiv, 358-359, 1912. ‡ A. von Fersmann and V. Goldschmidt, Der Diamant, figs. 30, 35 and

others, 1911. §E. F. Ayres, this Journal, xxxvii, 236, 1880. A. Lacroix, Minéralogie, 2, 540. G. Boeris, Zs. Kryst. (abs.), xxxv, 504.

of pyrite completely encircling marcasite were found. An intermediate stage is shown in fig. 1, D. The orientation of the two minerals is such that the vertical axis of the marcasite coincides with one of the cubic axes of the pyrite, and the lateral axes are turned counter-clockwise nearly 53° from the other cubic axes so that the prism face 110 nearly coincides with the cube face 010. This orientation has been observed in



two other occurrences of these minerals.\* Either mineral may be the later. Sadebeck\* has observed another orientation in which the turning of the lateral axes is 45°. In the first orientation, sections of the two minerals parallel to the faces upon which common growth began, show similar outlines, but crystals of the two minerals having faces of the dominant forms or forms with simple indices can not be made to come very near to coincidence. In the second orientation there would be more nearly coincidence between the crystals. The stereographic projection, fig. 2, B, shows the arrangement of the faces of some forms in the second orientation. The circles, larger letters, and numerals are used for marcasite. The two minerals approach closely to an intermediate tetragonal or orthorhombic mineral having axial ratios about equal to those of the octahedron set up as the tetragonal pyramid (101). Apparently no great change in the distribution of crystallographic forces would be required to cause the transformation from one of these forms of iron disulphide to the other. In

\*A. Sadebeck, Zs. Kryst., iii, 628 (abs.); and C. O. Trechmann, Min. Mag., ix, 209.

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fact, the observed monotropic transformation of marcasite to pyrite is accompanied by only a small evolution of heat and a slight increase in density.<sup>\*</sup> Yet experiments in this connection by Dr. E. T. Allen show that crumbling of the crystals accompanies the change.

The microscope shows that the faces of the dodecahedron represent the edges of minute steps made up of octahedral planes. Oblique planes of the cube and pyritohedron interrupt the steps somewhat. The steps are sufficiently close together to produce the semi-diffuse reflection noticed in the light figures (fig. 2, A). Still closer spacing would lead to increased brilliance of the light figures in the vicinity of the dodecahedron, and very close spacing—closer than the length of waves of light—would produce brilliant faces.

The octahedral crystals have faces more or less convex owing to the same step-structure present on dodecahedral faces. If the steps on the octahedral faces were fine enough to make the faces mirrors the slopes of the faces on different crystals would be different and apparently would not lead to simple symbols.

The chain of signals usually seen in the goniometer telescope between the cube and pyritohedron (210) comes from a series of small faces made up of closely spaced steps. These faces correspond not only to well recognized crystal forms but to forms which have very complex symbols.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., July 13, 1914.

\* See this Journal, xxxiii, 188, 1912.

### SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. The Atomic Weight of Lead of Radioactive Origin.—The facts connected with the spontaneous transformation of the radioactive elements have led to the theory that some of the elements, among which is lead, may consist of several individuals differing considerably in atomic weight but not separable by chemical means. According to this theory the lead found in different kinds of radioactive minerals should show variations in atomic weight from that of ordinary lead, as well as differences in the various minerals.

MAURICE CURIE has purified the lead from a number of minerals and has determined the atomic weights by converting the metal into the nitrate with the following results:

			Mean
Pitchblende	206.60,	206.68	206.64
Carnotite	206.38,	206.34	206.36
Yttrotantalite	206.49,	206.59, 206.55	206.54
Monazite	207.06,	207.10	207.08
Galena	206.98,	207.04	207.01

The atomic weight obtained from the lead of galena agrees well with that at present accepted, but the atomic weight of lead from uranium minerals is decidedly lower, and the lead from monazite is slightly higher.

A more elaborate and more anthoritative investigation of the same subject has been made by RICHARDS and LEMBERT, who have obtained as many samples of radioactive lead as possible, have purified the samples with the greatest care, and have determined the atomic weight of the lead in comparison with ordinary lead with the high degree of skill that has been developed by Professor Richards. The method used was the comparison of lead chloride with silver and with silver chloride. The final values found for the atomic weight of lead from different sources were as follows :

North Carolina uraninite	206.40
Joachimsthal pitchblende (2 samples)	206.57
Colorado carnotite (2 samples)	206.59
Cevlonese thorianite (2 samples)	206.82
English pitchblende	206.86
Common lead	

It is to be observed that these results agree with those of Curie in showing the atomic weight of the lead from the uranium minerals to be much lower than that of ordinary lead. The authors say that the result is amazing. Previous atomic weight determinations made in Professor Richards's laboratory upon ordinary elements from different sources have never shown differences in atomic weight. The samples of lead chloride from the radioactive minerals showed no spectroscopic differences from ordinary lead chloride except the presence of a trace of copper, too minute to have any effect upon the atomic weight, but the samples showed radioactivity, which was very slight in the freshly crystallized lead chloride, but increased with time and reached a maximum in about 30 days.

Attention should be called to the work of Soddy and Hyman, noticed on page 91 of this volume, according to which the lead from Ceylon thorite gave an atomic weight of 208.4. According to the calculations, the lead derived from uranium should have an atomic weight of about 206, and that from thorium about 208. Therefore, the results mentioned in this notice appear to confirm the theory in regard to the radioactive transformations.— *Comptes Rendus*, clviii, 1676; *Jour. Amer. Chem. Soc.*, xxxvi, 1329. H. L. W.

2. Two New Modifications of Phosphorus.-P. W. BRIDGEMAN has obtained two new modifications of phosphorus during an investigation of the effect of high pressure upon the melting point of ordinary white phosphorus. The new modification of white phosphorus, which is called "white phosphorus II," was first produced by increasing the pressure on ordinary white phosphorus to 11,000 kg. per cm<sup>2</sup> at 60° C. Its existence was shown by a discontinuous change in the volume at this pressure, and the transition, which is reversible, was found to take place at lower pressures as the temperature was lowered, until it occurred at atmospheric pressure at about  $-80^\circ$ . The appearance of this new form in bulk is much like that of ordinary white phosphorus, but it may be a triffe yellower, and there are liable to be cracks formed, as there is a volume contraction of about 2 per cent when the transition occurs. Evidence was obtained that this new form probably crystallizes in the hexagonal system, the usual form being regular in its crystallization. The other new form of phosphorus, called "black phosphorus," is more interesting than the first one on account of its color and other properties, and also on account of the fact that it is stable when once formed. It was discovered when an attempt was made to force white phosphorus to change to red phosphorus by the application of a high pressure at a temperature below that at which the change takes place with appreciable velocity at atmospheric pressure. At a temperature of 200° C. and a pressure of 12,000 to 13,000 kg. the change takes place in from 5 to 20 minutes. The black substance formed has a very much smaller volume than the original white phosphorus. Attempts to produce the black phosphorus from red phosphorus were unsuccessful. The fracture of the black phosphorus is sometimes granular, sometimes fibrous with a metallic luster, very much like graphite in appearance. It was found by analysis to be practically pure phosphorus, not a com-pound. The most striking difference between the new black phosphorus and the previously known modifications is its high density, which is 2.691, while that of white phosphorus is 1.83, and that of red phosphorus varies according to the method of preparation from 2.05 to a maximum of 2.34 for Hittorf's "metallic" crystallized red phosphorus. The black phosphorus is ignited with difficulty, is stable in the air, and while almost opaque, shows a translucence of an olive-brown color when very minute particles are observed under the microscope. These minute particles show action upon polarized light, so that it is evident that the substance is crystalline. The black phosphorus is remarkable in possessing a fair amount of electrical conductivity.—Jour. Amer. Chem. Soc., xxxvi, 1344.

3. The Detection of Cyanides in the Presence of Ferrocyanides. Ferricyanides and Thiocyanates.-For this qualitative test O. C. BARNEBEY uses the well-known reaction of copper sulphide with The reagent is a dilute ammoniacal solution of copper evanides. To a little of this liquid a little hydrogen sulphide is sulphate. added, which gives a black precipitate of copper sulphide. Upon adding this black liquid to an ammoniacal solution of the substance to be tested, or making a vice versa addition, in the presence of a cyanide the black color of the copper sulphide is discharged. The other cyanogen derivatives do not have this effect, and by using a copper solution of known strength and volume an idea of the amount of cyanide present can be formed. The reaction was found to be capable of detecting 0.5 mg. of HCN in the presence, in 50°, of 2 g. either of potassium ferrocyanide, ferricyanide or thiocyanate, and in the presence of small quantities of these substances the test is reliable down to 0.1 mg. of HCN.-Jour. Amer. Chem. Soc., xxxvi, 1092. H. L. W.

4. Colorimetric Determinations.--C. HUTTNER recommends the use of the well-known colors produced by the chlorides of cobalt, nickel, iron, and copper in solutions of fuming hydrochloric acid for the quantitative determination of these metals, particularly when they are present in small amounts. He uses solutions of known strength for comparison and states that the error in matching the colors is usually not more than onetwentieth of the whole amount, so that the method may be applied without serious error in cases where the metal amounts to several units per cent. For minute amounts, particularly of iron and of copper, the method is exceedingly accurate. It is important that the solutions compared, especially in the cases of iron and copper, should be made up of hydrochloric acid of the same strength, since the colors vary greatly with the strength of the acid.--Zeitschr. anorgan. Chem., lxxxvi, 341. H. L. W.

5. The Origin of the Cyanogen Bands.—In the aniline and soda factories of Germany nitrogen is obtained from air by the aid of alternating current arc lights, some of which attain as great a length as 8 meters. The flame is made stable by introducing the gas into the main tube through a smaller tangential tube. In this way an ascending, helical vortex of gas is maintained and the arc burns quietly along the common axis of the tube and helix. The light emitted by such arcs in various gases has been investigated spectroscopically by W. GROTEIAN and C. RUNGE, and a very important result has been obtained. These scientists found that the emission bands which have had their origin referred to a compound of carbon and nitrogen (commonly called cyanogen for brevity), by all other spectroscopists, are really due to *nitrogen alone*. The importance of the result justifies the presentation of the details given below.

The arc lamps actually used in this investigation were of smaller dimensions than the ones employed in the technical furnaces and they were run on direct instead of alternating current. The uni-directional current has the obvious advantage of differentiating the radiations from the anode and cathode. With 5,000 volts and 3 amperes an arc in air one meter long was obtained. The success of the work depended primarily upon the following essential difference between the ordinary low potential arcs with relatively large amperage and the high potential arcs with small current values. In the former the current is carried by the ions of the metallic vapors as well as by the gaseous medium in which the electrodes are placed, so that the metallic and other "impurity" lines usually stretch across the entire gap between the poles. On the other hand, in the case of the high potential arcs the spectral lines pertaining to the constituent elements of the electrodes only jut out a short distance from the anode and cathode, while the lines of the gaseous atmosphere span the entire length of the arc. That the current in the center of the arc is carried only by the ions of the atmosphere used is also shown by the experimental fact that the form of the "characteristic curve" of The the arc is independent of the nature of the solid electrodes. authors state that under certain conditions (not specified) they have obtained pure glow discharges, at atmospheric pressure and "high" amperage, which did not show a trace of the spectrum of either electrode. Furthermore, the high potential arcs have a distinct advantage over the ordinary discharges in partially evacuated tubes in that small traces of impurities have a negligible influence on the spectrum of the gas under investigation because this gas is let into the lamp at high pressure, from a bomb, and the impurities are swept out immediately by the vortex.

As stated above, the spectroscopic investigation of the nitrogen arc showed that the four groups of bands, whose wavelengths, expressed in round numbers, are 3360, 3590, 3884, and 4216, are due to nitrogen alone and not to cyanogen. The nitrogen arc attained a length of  $30^{\rm cms}$  with a current of 1 ampere. The discharge starts with a bright rose color at a point-like spot of the anode and then passes over to the arc proper, which consists of a reddish-violet band. When the current of gas is strong no aureole or "glory" can be distinguished. A broader, bluish spot is formed at the cathode which is analogous to the negative glow in a vacuum tube and which radiates the so-called negative

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 226.—October, 1914. 25 bands of nitrogen. The bands, whose approximate wave-lengths are given above, extend over the whole length of the arc. In order to show conclusively that these bands are due to nitrogen alone it was necessary to prove, (a) that cyanogen was not present in the gas used, and (b) that carbon and carbon compounds were not present in the arc proper. Chemical analysis gave 99.5 per cent pure nitrogen and 0.5 per cent for the remaining constituents of ordinary air, but no cyanogen. Furthermore, since the nitrogen was obtained from liquid air, and since cyanogen does not ordinarily occur in air, it is extremely improbable that cyanogen was present in the nitrogen as an impurity which had escaped detection by chemical tests. Also, the direct combination of carbon with nitrogen only takes place at very high temperatures.

That carbon was not involved in the radiation of the bands in question is demonstrated by the following experimental evidence. When the gas was driven through a wad or plug the spectrum was not altered in intensity. Hence, the hypothesis that the bands owed their origin, in part, to fine particles of carbon which were torn from the bomb by the rushing gas is not tenable. When small amounts of carbon dioxide were mixed with the nitrogen no appreciable effect on the bands could be observed. When, however, larger quantities of carbon dioxide were introduced with the nitrogen, the bands were noticeably weakened. The strongest evidence in favor of the nitrogen origin of the bands is the fact that the spectrum of the center of the arc was precisely the same when the electrodes were made of the following metals : aluminium, copper, iron, magnesium, and platinum. It would be very extraordinary to find the same per cent of carbon in all of these elements. Besides, if carbon had been present, even in extremely minute quantities, the carbon bands at  $\lambda$  4382, 4737, 5165, and 5635, and above all the carbon line at  $\lambda$  2478, would have shown on the negatives. Not the slightest suggestion of these radiations was detected. Finally when carbon electrodes were used the carbon bands appeared close to the poles while the so-called cyanogen bands persisted throughout the entire length of the arc with the same intensity as when metallic terminals were employed.

For the sake of completeness, the authors show how the hypothesis of the nitrogen origin of the "cyanogen" bands accounts for all the phenomena observed by earlier investigators who erroneously ascribed these bands to a nitro-carbon compound. —*Phys. Zeitschr.*, June 1, 1914, p. 545. H. s. U.

6. The Influence of Magnetic Fields on Explosions.—It has been suggested by Sir J. J. Thomson and other physicists that combustion is concerned not only with atoms and molecules but also with rapidly moving electrons. In particular, it was thought that the great rapidity of combustion in an explosion-wave might be due to the molecules at the instant of combustion sending out electrons having very high speeds. These may precede the explosion-wave and prepare the way for it by ionizing the gas. This problem has been investigated experimentally by HAROLD B. DIXON, C. CAMPBELL and W. E. SLATER.

The explosive mixtures were detonated by an electric spark in a long tube placed between the pole-pieces of a powerful electromagnet, which was specially designed for deflecting high-speed electrons. This magnet was loaned to the experimenters by Sir Ernest Rutherford. The explosion-waves characteristic of a given mixture of gases were photographed when the electromagnet was and was not excited, all other conditions being kept invariable. Preliminary experiments showed that the  $\beta$ -rays from radium bromide were completely deflected. The explosive mixtures tested consisted of (a) cyanogen and oxygen with different proportions of nitrogen, (b) hydrogen and oxygen in varying relative amounts, (c) acetylene and oxygen, (d) carbon bisulphide and oxygen, and (e) carbon monoxide and oxygen. In all cases, no difference between the explosion-waves with the magnetic field on and off could be detected. At the end of the article the authors say : "Since the powerful magnetic field employed produced no visible effect with any gas mixture, and since the mechanism of a compression-wave (liberating the chemical energy as it goes along) accounts in a reasonable way for the phenomena of gas explosions, we see no evidence that convinces us that the velocity of the explosion-wave is due to the ionizing action of electrons." In addition to its theoretical value the paper is of interest because of the inclusion in it of excellent reproductions of clear photographs of eight pairs of explosionwaves.-Proc. Roy. Soc., vol. xc (A), p. 506. H. S. U.

7. The Spectrum of Silicon.-For more than eleven years SIR WILLIAM CROOKES has been making observations on the spark spectrum of elementary silicon, the primary objects of the investigation being (a) to determine precisely what lines pertain to silicon alone, and (b) to determine the wave-lengths of all the lines on a consistent and accurate basis. The spectrum of silicon is of considerable importance in physical astronomy. Great difficulty was encountered in the attempt to obtain perfectly pure silicon. The best specimens were furnished by the Carborundum Company of Niagara Falls. The impurities of these samples were aluminium, iron, and titanium. The apparatus used was a five-prism spectrograph. In order to obtain a photographic record of some of the fainter lines exposures as long as seven hours were necessary. In the visible spectrum the photographic processes were supplemented by eve-observations. The table of wave-lengths contains 43 values and, with two exceptions, each number comprises seven significant figures. In spite of the fact that this piece of work is undoubtedly the most thorough that has been done on the spark spectrum of silicon there is a noteworthy lack of agreement between the wave-lengths of three lines given both by Crookes and by Fabry and Buisson. The interferometer values for silicon, as a carbon-arc impurity, are

2435.159, 2506.904, and 2528.516. The spark data exceed these numbers by 0.053, 0.151, and 0.069 Å respectively. Whether these differences are due to the manner of excitation (arc versus spark) of the radiations or to instrumental errors is a question which needs further consideration.—*Proc. Roy. Soc.*, vol. xc (A), p. 512. H. S. U.

8. Solar Oxygen.—Attention has already been called to the investigation of Runge and Paschen which showed that a certain triplet in the spectrum of the iron arc in air is due to oxygen. (See vol. xxxvii, page 195.) This triplet at about  $\lambda$  7774 and the doublet at  $\lambda$  8446 match lines in the solar spectrum and hence they may be either of solar or of telluric origin. From considerations of intensity Jewell concluded that the triplet is caused by solar absorption but he was unable to detect the Doppler effect. At the suggestion of Paschen the problem was taken up by K. W. MEISSNER. By using a plane-grating spectrograph of high resolving power in conjunction with plates specially sensitized with dicyanin it was possible to record photographically, and to determine the magnitude of, the Doppler displacement of the lines in question from the opposite limbs of the sun. There remains, therefore, no doubt concerning the evidence that oxygen is present in the solar atmosphere. - Phys. Zeitschr., July 1, 1914, p. 668. H. S. U.

9. X-Rays; G. W. C. KAYE. Pp. xx, 252, with 97 figures. London, 1914 (Longmans, Green and Co.).—This book covers the ground very well from the time of Röntgen's discovery in 1895 down to the end of the year 1913. "The author trusts that the form of the book will be acceptable, not only to the student of physics, but to the man of general scientific interests, and particularly to the members of the medical profession, . . .

. ." Consequently the treatment is non-mathematical. The successive chapters deal respectively with :--the phenomena of a discharge tube, cathode rays, positive rays, X-rays, an X-ray bulb, high-potential generators, the "hardness" of an X-ray bulb, the blackening of an X-ray bulb, the measurement of X-rays, secondary rays, further properties of the X-rays, practical applications of X-rays, interference and reflection of X-rays, and the nature of the X-rays. The practical value of the text is increased by the inclusion of five appendices, twenty-eight tables and an index. The material is presented in a very clear and pleasing style, the number of errors is small, and the reading of the volume leaves one with the impression of time well and profitably spent. H. S. U.

10. A First Book of Experimental Science; arranged by W. A. WHITTON. Pp. vii, 137, with 77 figures. London, 1913 (Macmillan and Co.).—"The scope of this book has been determined largely by the syllabus prescribed by the Civil Service Commissioners for Boy Artificers who wish to enter the Royal Navy as Engineroom Artificers." The experiments suggested pertain to statics, hydrostatics, heat, combustion, and the elemen-

# Geology.

tary chemical properties of hydrogen, nitrogen, oxygen, water, etc. These experiments can be performed in a short time with simple, inexpensive apparatus. At the end of each chapter a number of questions taken from recent examination papers are collected. The figures and typography are good, and the material is interesting and well-selected. H. S. U.

# II. GEOLOGY.

1. Early Cambrian stratigraphy in the North American Cordillera, with discussion of the Albertella and related faunas ; by LANCASTER D. BURLING. Geol. Surv. Canada, Museum Bull. No. 2, 1914, pp. 93-129.-The writer presents here a good summary of the Lower Cambrian sections, with a view to learning the true position of the Albertella fauna of Canada. Walcott had assigned this to the Lower Cambrian, but Burling, after analyzing the Pioche fauna, finds that, as the latter is made up of two biotas of which the great part is of Middle Cambrian age, the Albertella horizon clearly falls into the Middle Cambrian. Then, too, but a single brachiopod passes from the Lower Cambrian into the higher division, showing that the two faunas are clearly distinct. Burling is, however, inclined to the view that there is no time break in the best sections, but the evidence as recited by him, especially on page 124, shows that great changes had taken place and that the sections are irregular in character between the Olenellus Pioche fauna and the Albertella biota.

c. s.

2. Notes on the Lorraine faunas of New York and the Province of Quebec; by AUG. F. FOERSTE. Bull. Denison Univ., vol. xvii, pp. 247-340, pls. I-V, 1914.—This important paper describes a long Upper Ordovician section (over 2500 feet) on Nicolet River, Quebec, and compares it with the strata of the New York Lorraine and equivalent sections on Lake Huron. Fifty-three species are described, of which many are new. Glyptorthis is a new brachiopod genus, Pholadomorpha a new bivalve genus, and Ruedemannia a new genus of univalves.

c. s.

3. Fauna of the Martinez Eocene of California; by Rox ERNEST DICKERSON. Bull. Dept. Geol., Univ. California, vol. viii, No. 6, pp. 61-180, pls. 6-18, 1914.—In this clearly wrought out paper the author attains the following conclusions:

"That the Martinez is separated from the Chico (Cretaceous) below and from the Tejon (upper Eocene) above by well-marked unconformities are the principal conclusions from stratigraphic studies. Faunal studies prove that the Martinez fauna of approximately two hundred species is quite distinct from the Chico and the Tejon faunas. The great increase in the fauna makes correlation with the lowermost Eocene of the Gulf and Atlantic states more certain. The proposed correlation made in this paper fixes a portion of the Martinez as the equivalent of the lowermost Eocene of the Gulf States, the Midway, and the rest as the representative of an earlier Eocene time than has been recognized elsewhere in the United States" (64).

"The mixture of subtropical and boreal forms indicates a warm temperate climate. . . Tejon climate, however, was decidedly warmer than that of the Martinez (111). . . . The faunal differences between Chico and Martinez and between the Martinez and the Tejon are very great" (120). c. s.

4. West Virginia Geological Survey, I. C. WHITE, Director. —The following publications have recently been issued by the West Virginia Geological Survey, under the direction of I. C. White, the State Geologist: Kanawha County, by Charles E. Krebs and D. D. Teets, Jr., Part IV, Paleontology, by W. Armstrong Price. Pp. 679, pls. I–XXXI and I–II (in Pt. IV), figs. 14, atlas maps (3) in separate case; and a Map of West Virginia, on scale of 8 miles to 1 inch, showing Coal, Oil, Gas, Iron Ore, and Limestone Areas, compiled by I. C. White, R. V. Hennen, C. E. Krebs, and D. B. Reger. Kanawha ranks first among the counties of West Virginia in wealth based on coal, oil and gas. The present volume, therefore, has a wide economic interest. On the maps accompanying the report, topography, soils, and structural contours on the Pittsburg coal bed, as well as the areal distribution of stratigraphic limits are indicated. H. E. G.

5. Mining Practice.—The State of Illinois has established two commissions for the investigation and improvement of coal mining practice. To the Illinois Miners and Mechanics Institutes, R. Y. WILLIAMS, Director, is assigned the duty of preventing accidents and conserving the resources of the state. Bulletin No. 1, Education of Mine Employees, by H. H. Stoek (pp. 1-136, 1914), and Bulletin No. 2, Outline of Proposed Methods (pp. 1-27, 1914) have just appeared.

The Illinois Coal Mining Investigations, working under a coöperative agreement between the State Geological Survey, the United States Bureau of Mines, and the State University, has issued the following: Coal Mining Practice in District VIII (Danville), Bull. 2, 1914, by S. O. Andros, pp. 47, figs. 32; and Coal Mining Practice in District VII (southwest Illinois), Bull. 4, 1914, by S. O. Andros, pp. 43, figs. 34. H. E. G.

6. Western Australia Geological Survey.—Two bulletins have recently been issued: Bull. 44, A Geological Reconnaissance of a portion of the South-West Division of Western Australia, by E. C. SAINT-SMITH, 1912. Pp. 80, 1 geological map, 1 locality plan, 18 figs. Granite, gneiss and pegmatite of unknown age form the western and eastern boundaries of the Geographic Bay region. Sandstones of Mesozoic age are exposed in small patches along the Darling Fault. The other sediments represented are of post-Tertiary age and include coastal limestone (buff colored sea sand firmly cemented by carbonate of lime), an enormous expanse of laterite and the sands, clays and gravel forming the coastal plain. The Swan Coastal Plain has experienced three stages : downfaulting which submerged the area and permitted the deposition of river-borne material on the sea floor ; a widespread uplift which restored the sea floor to the land ; and a later slight uplift still in progress. An interesting physiographic feature is the fresh Darling fault scarp not appreciably modified by stream dissection. Bull. 49, Geology and Mineral Resources of the Yilgarn Gold

Bull. 49, Geology and Mineral Resources of the Yilgarn Gold Field. Part I, Southern Cross, by E. C. SAINT-SMITH and R. A. FARQUHARSON, 1913. Pp. 193, 10 pls., 52 figs. This report deals exclusively with the Southern Cross Mining center, and is the first of a series designed to cover the Yilgarn Gold Field. Petrology and economic geology, including microscopic and chemical analyses, are given the chief attention. H. E. G.

chemical analyses, are given the chief attention. H. E. G. 7. Geology of the Titanium and Apatite Deposits of Virginia; by Thomas L. Watson and Stephen Taber; Virginia Geol. Sur. Bull. III-A; 1913. Pp. 308; 37 pls., 22 figs.—The districts here described lie in Amherst-Nelson, Roanoke, and Goochland-Hanover counties. The rocks of the Amherst-Nelson area have close genetic relationships and are all characterized by the presence of apatite and the titanium minerals, rutile and ilmenite. They consist of monzonite-gneiss, syenite, gabbro, diabase and the rock called nelsonite made up chiefly of apatite with ilmenite, rutile or magnetite. They are all intrusive and holocrystalline in texture. Gradations occur between the gabbro and the syenite and the gabbro and nelsonite. The nelsonite occurs in the form of dikes varying in length of strike up to 2000 feet and in width up to 65 feet. These dikes vary considerably in the proportions of the different minerals present, all of which at times become dominant in amount. The rutile deposits in this district were first mined in 1902.

In general the geology of the Roanoke area is similar to that described above. Similar dikes of nelsonite occur in syenite and pegmatite. The rocks have suffered intense metamorphism. There are some striking differences in the secondary minerals of the two districts.

The Goochland-Hanover area shows a different series of rocks. The chief types are a granitic gneiss cut by granitic pegmatite and a variety of basic igneous rocks. The rutile occurs in the pegmatites. The surface rocks in all these areas are badly weathered. W. E. F.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Conférences de Radiumbiologie, fuites à l'Université de Gand en 1913; par MM. JACQUES DANNE, PAUL GIRAUD, HENRI COUTARD, GASTON DANNE. Pp. 214. Brussels, 1914 (L. Severeyns, 34 rue Botanique).—This set of lectures delivered by specialists in radioactivity cannot fail to be of value to those interested in the application of radium in the field of medicine. The authors are all connected with the Laboratory of Radioactivity at Gif.

The lecture by M. Paul Giraud on the medical technique and results of the successful treatment of various malignant growths, together with some of the theories of the mode of action of radium, are well worth the perusal of both physician or physiologist. The next lecture by M. Jacques Danne, at one time an assistant to M. Curie, and a man who took a great part in the discovery of radium, gives an excellent résumé of the properties, production and medical technique of the use of radium emanation. This lecture treats of the work up to the latest times. M. Gaston Danne, Chief of the Laboratory at Gif, describes the various means of utilizing radium and the apparatus employed. The final lecture by M. Henri Coutard treats of the action of radio-active substances other than radium, their medical application and the technique of their use. A very important part of the publication is a complete bibliography of radium literature, particularly as applied to medicine. S. G.

#### OBITUARY.

REV. OSMOND FISHER, of Graveley, Huntingdon, England, well-known for his important papers on the geological history of the earth, died on July 12 at the advanced age of ninety-six years. A communication from his pen was published in the number for February last.

MR. ALFRED JOHN JUKES-BROWN, formerly connected with the Geological Survey of England, died on August 14 at the age of sixty-three years.

DR. EDUARD REVER, professor of Geology at the University of Vienna, died recently at the age of sixty six years.

PROFESSOR HERMANN KLEIN of Cologue, astronomer and meteorologist, died recently at the age of seventy years.

DR. FRANCIS HUMPHREYS STORER, the eminent chemist, died recently at the age of eighty-two years. He was professor of general and industrial chemistry at the Massachusetts Institute of Technology from 1867–1870 and professor of agricultural chemistry in Harvard University from 1870–1907. He was the author of numerous books and papers upon chemical subjects.

DR. FREDERICK WILLIAM TRUE, the zoologist and assistant secretary of the Smithsonian Institution in charge of the library and exchanges, died on June 25 in his fifty-sixth year.

DR. SETH EUGENE MEEK, the zoologist and assistant curator in the Field Museum of Natural History at Chicago, died on June 6 at the age of fifty-five years.

MR. CARL FUCHS, the entomologist, died at his home in Alameda, California, on June 11 at the age of seventy-four years.

DR. ALBERT SMITH BICKMORE, naturalist and educator, died on August 12 at the age of seventy-five years.

PROFESSOR FRANKLIN WILLIAM HOOPKR, director of the Brooklyn Institute of Arts and Sciences, died on August 1 at the age of sixty-three years.

REV. HORACE CARTER HOVEY, known for his papers on caverns and their fauna and flora, died recently in his eighty-second year.

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# AMERICAN JOURNAL OF SCIENCE

# [FOURTH SERIES.]

ART. XXXII.-The Stokes Method for the Determination of Pyrite and Marcasite; by E. T. Allen and J. L. CRENSHAW.

SYLLABUS.

I. DEMAND FOR THE METHOD.

II. THE STOKES METHOD.

- A. Formula for the percentage of sulphur oxidized.
- B. Relation of the iron dissolved to the composition of the mixture.
  - 1. Cause of the deviation of the values of x from a straight line.
    - (a) Explanation of the low results with pure marcasite.(b) The necessary excess of the sulphide.
  - 2. Results on mixtures of the natural minerals.
  - 3. Other sources of error in the Stokes method.
    - (a) The ratio of the surface of the two minerals in weight percentage mixtures.
    - (b) Loss of water during the oxidation process.
    - (c) Reduction of the ferric solution during the blank test.

    - (d) Errors in the determination of the iron. (e) Oxidation of either ferrous solution or finely divided sulphides by atmospheric oxygen.
  - 4. Accuracy of the method.
  - 5. Linear relation between any pyrite and any marcasite.
    - (a) Independence of the chemical action of the two sulphides.
      - (b) Electrolytic effect in the Stokes reaction.
      - (c) Stokes' curve.
        - Summary.

#### I. DEMAND FOR THE METHOD.

THE question whether a given specimen is pyrite or marcasite, in the case of well-crystallized natural material, will seldom arise; color and crystal form are generally sufficient criteria. For doubtful cases, which are more liable to be met with in synthetic products, few reliable tests exist, and for estimating either in mixtures with the other, the Stokes method is the only one known.

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In a recent investigation by the authors, on the genetic conditions of certain allotropic forms, such a method became essential. We had already made some use of the Stokes method for identifying synthetic products, but had never carefully tested its accuracy. This has now been done; two serious sources of error have been detected and obviated, and some facts and relations of much more general interest have been discovered and worked out, in connection with it.

#### II. THE STOKES METHOD.\*

The Stokes method depends on the difference in the behavior of the two minerals when boiled with a standard solution of ferric sulphate. The reaction takes place in two stages, thus:

(a) 
$$\operatorname{FeS}_2 + \operatorname{Fe}_2(\operatorname{SO}_4)_3 = 3\operatorname{FeSO}_4 + 2S.$$
  
(b)  $\operatorname{S} + 3\operatorname{Fe}_2(\operatorname{SO}_4)_3 + 4\operatorname{H}_2O = 6\operatorname{FeSO}_4 + 4\operatorname{H}_2\operatorname{SO}_4.$ 

Both minerals give the same products, viz., ferrous salt, sulphur and sulphuric acid; their difference is manifested in the relative quantities of the products, for experiment shows that about 52 per cent<sup>+</sup> of the sulphur in pyrite is oxidized to sulphuric acid, while only about 12 per cent of the sulphur in marcasite is oxidized. This behavior is not entirely unique. Penfield<sup>‡</sup> found that concentrated nitric acid dissolved pyrite completely (i. e., all the sulphur is oxidized), while it leaves with marcasite a copious residue of sulphur. More recently, Arbeiter§ has made a long series of careful experiments with hydrogen peroxide and hydrochloric acid, in which he finds that marcasite always gives more free sulphur than pyrite under the same conditions. As the reagents are diluted the relation between the sulphur oxidized and the sulphur liberated approaches a simple constant ratio characteristic for each mineral. Arbeiter very plausibly infers that these phenomena are dependent on a difference in constitution between pyrite and marcasite.

To identify either pyrite or marcasite, Stokes determined the percentage of sulphur which was oxidized by a standard ferric sulphate solution. Before proceeding to show how the composition of a mixture of the two is determined, it will be best to explain the chemistry of the process in greater detail. The standard ferric alum solution, which contains close to 1 g.

\* H. N. Stokes, Bull. U. S. Geol. Survey, 186.

\* H. N. Stokes, Bull. U. S. Geol. Survey, 186. † The numbers vary somewhat in different natural specimens. The numerical data here and in the sequel belong to a pyrite from Roxbury, Connecticut. Stokes' values were 60.5 and 16.5-18.0 for pyrite and mar-casite respectively. These variations will be discussed farther on. ‡ Brush and Penfield, Determinative Mineralogy, 15th ed., p. 252. § Min. Chem. Untersuch. an Markasit, Pyrit und Magnetkies. Inaugural Discussive and the second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second se

Dissertation, Breslau, 1913.

of iron and 5 g. free sulphuric acid per liter, is always used in the same quantity, 250<sup>cc</sup> in each experiment. The sulphide, finely ground and purified, is used in large excess (about 1 g.). The water of the solution is kept constant by a reflux condenser, while the influence of atmospheric oxygen is prevented by a stream of moist carbon dioxide which traverses the apparatus during the process. At the end of the test the ferric iron of the solution should be entirely reduced, partly by iron and partly by sulphur. A quantity of iron in the ferrous state which is constant for each mineral has passed into solution and a constant percentage of the sulphur has been oxidized. From the iron dissolved in our own experiments, we calculate that about 155 milligrams of marcasite are required in the reduction of 250<sup>cc</sup> of the standard solution, while only about 65 milligrams of pyrite are required for the same work. This of course is due to the fact that far less of the sulphur in marcasite is effective in reduction, nearly 90 per cent of it being precipitated in the free state. The complete data are given in the footnote.\*

A. Formula for the percentage of sulphur oxidized.— Stokes determined directly the iron dissolved by the ferric salt, and calculated stochiometrically the percentage of sulphur which was oxidized. Similarly, the percentage of sulphur oxidized in unknown mixtures of the two sulphides was estimated by him experimentally and a curve plotted which was used to determine their composition. The formula for the precentage of sulphur oxidized or the "oxidation coefficient" of either sulphide or of any mixture of the two was derived

directly from equations a and b, viz. (1)  $p = \frac{8 \cdot 33b}{c-a} - 25$ , where

* I.	
	was equivalent to $4.46$ g. KMnO <sub>4</sub> solution per 100 <sup>cc</sup> , or for $250^{cc}$ .
	$2.5 \times 4.46 \times .001544$ (value of KMnO <sub>4</sub> solution) = KMnO <sub>4</sub> 0.0172 g.
	1000000000000000000000000000000000000
	Equivalent to Fe
	Equivalent to $\operatorname{FeS}_2$
	Total sulphur in $.0652$ g. FeS <sub>2</sub>
	Fe reduced by Fe (see equation $a$ )
	Fe reduced by S, 0.2500 - 0608 1892 g.
	S reducing Fe, or S oxidized (see equation $b$ )
	.0181
	Percentage of S oxidized $\frac{101}{0348}$
II.	Marcasite. The increase of iron in solution after reduction with
	marcasite was equivalent to $10.57$ g. KMnO <sub>4</sub> solution per $100^{\circ\circ}$ .
	Hence $2.5 \times 10.57 \times .001544 = \text{KMnO}_4$
	$\frac{1}{2} = \frac{1}{2} = \frac{1}$
	Equivalent to Fe
	Equivalent to $FeS_2$
	Total sulphur in $0.1546$ g. FeS <sub>2</sub>
	Fe reduced by Fe (see equation $a$ )
	Fe reduced by S, 0.2500-1441
	S reducing Fe, or S oxidized (see equation $b$ )
	Percentage of S oxidized $\frac{.0101}{.0825}$ 12.3%
	Percentage of S oxidized 12.3%

p = the percentage of sulphur in the decomposed sulphide which is converted into sulphuric acid; b is the ferrous iron at the end of the experiment originating both from the reduction of the ferric salt and from the decomposition of the iron disulphide; c is the total iron, ferrous and ferric,\* at the end of the experiment; while a is the iron originally present in the standard solution. Our experiments soon showed that the reaction normally proceeds to the complete reduction of the ferric salt; b and c are therefore identical. Hence  $p = \frac{8 \cdot 33b}{b-a} - 25$ ,

or better written, since b is variable, (2)  $p = \frac{8 \cdot 33x}{x-a} - 25$ .

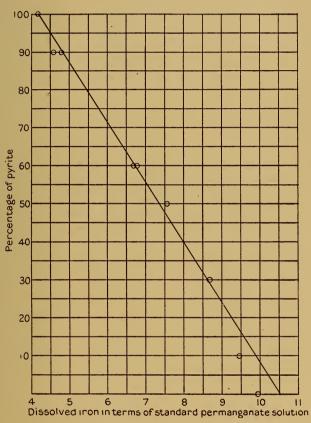
Relation of the iron dissolved to the composition of the В. mixture.—A simpler relation than this and one more satisfactory in estimating the quantities of pyrite and marcasite in a mixture of the two is obtained by comparing directly x, the total quantity of iron in solution at the end of the test, with y, the percentage of pyrite in the sulphide mixture. Some results obtained by us before any such relation was suspected, indicated, when plotted in this way, a rectilinear relation; only the mixtures lowest in pyrite deviated much from a straight line (see fig. 1). Stokes concerned himself only with the relation between the composition of the sulphide mixture and the percentage of sulphur oxidized, but when his results are put into the same form they confirm our own. Table 1 gives the values of x, the total iron in solution at the end of the test, calculated by means of equation (2) from Stokes' published values of p. Our own value for a was used. a is the concentration in iron of the standard ferric solution. Both x and aare given in terms of a standard permanganate solution, 1 g. of which contained 001544 g. KMnO<sub>4</sub>; and 100<sup>cc</sup> of the ferric solution, measured at 25°, required 36.71 g. of this solution to oxidize it after reduction by sulphur dioxide. In fig. 2, Stokes' values for (x - a), the iron dissolved by 100<sup>cc</sup> of the standard ferric solution from pyrite-marcasite mixtures, are plotted against y, the percentage of pyrite which they contained. Here also the points fall into a nearly straight line, excepting those which stand for mixtures low in pyrite.

1. Cause of the deviation of the values of x from a straight line.—It seems decidedly probable that the low values for xin mixtures which contained 75%-100% marcasite were due to some disturbance in the reaction. This hypothesis would simply mean that the chemical action of the ferric solution on each sulphide in the mixture was proportional to its surface; that each sulphide acted independently of the other; and that the

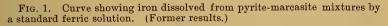
\* Stokes did not get a complete reduction of the standard ferric solution.

# Determination of Pyrite and Marcasite.

deviation in the line indicated that, in those mixtures where it occurred, the surfaces of the two minerals were no longer proportional to their weights. There was in fact some positive ground for this view, since it had already been noted by Stokes that marcasite was inclined to *flocculate* during the oxidation







tests. Flocculation would of course reduce the surface of the finely powdered marcasite, and if the pyrite were unaffected, the results would indicate too much pyrite, which as the reader may see, is exactly the direction of the errors in figs. 1 and 2. Many ways were tried to obviate the difficulty, but the only

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### TABLE I.

Percent Pyrite	p = percentage of sulphur oxidized (experimentally determined)	$\begin{array}{c} x \text{ cal. from } p \\ \text{by equation} \\ (2) \end{array}$	(x - a)  (the iron dissolved) a = 36.71
100	60.2	40.68	3.97
95	52.9	41.11	4.40
90	48.9	41.38	4.67
80	40.3	42.08	5.37
60	29.0	43.41	6.70
40	22.3	44.58	7.87
20	17.1	45.78	9.07
10	15.2	46.33	9.62
5	16.0	49.09	9.38
0	18.0	45.54	8.83

Stokes' values for x, the total iron in solution, and (x-a), the iron dissolved from pyrite-marcasite mixtures by ferric sulphate solution.

one which proved of any value was to shake the ferric solution and sulphide together with coarsely powdered quartz\* and beads by means of which the lumps of sulphides were thoroughly ground up. Some details may make the operation clearer to the reader. The 500° boiling flask used in the oxidation experiments was fitted to a rubber stopper through which passed the reflux condenser (the cooling jacket of which was 20<sup>cm</sup> in length) and a glass tube reaching to the bottom of the flask through which the carbon dioxide entered. 250<sup>cc</sup> standard ferric alum solution with 2 g. quartz and about fifty beads of Jena glass were then added. The solution was now freed from air by boiling for ten minutes in the stream of carbon dioxide, and then cooled for fifteen minutes while the gas was still passing. Stokes' device for introducing the sulphide was used, viz., a small glass bucket suspended above the liquid by a platinum wire which passed up through the condenser. After the sulphide had been purified and dried for an hour in a vacuum desiccator, as shown farther on, it was quickly removed and poured into the bucket, the bucket attached to the platinum wire, and the flask again closed. The solution was now brought to boiling, while the bucket remained suspended above the liquid. Finally the bucket was dropped by drawing out the wire and the flask vigorously rotated for five or ten minutes, or until the powder seemed to fill the liquid and so remained, neither floating on the surface nor sinking to the bottom. The boiling was continued for two hours, when the ferric iron should be entirely reduced.

\* This quartz contained only 0.04 per cent of oxides other than silica.

In some instances, for some unknown reason, the solution would fail to wet the sulphide satisfactorily, and the results would then be unsatisfactory.

(a) Explanation of the low results with pure marcasite.— The abnormal results for the sulphide mixtures low in pyrite

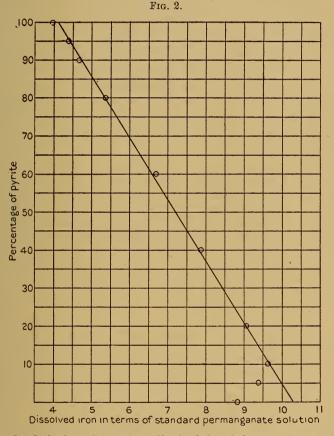


FIG. 2. Stokes' results on iron dissolved (x-a) from pyrite-marcasite mixtures by a standard ferric sulphate solution. The values for x are calculated from Stokes' published values for p, the percentage of sulphur oxidized.

are very well accounted for, as we have seen, on the supposition that the reactive surface of the marcasite is reduced by flocculation. In mixtures which contain 25 per cent or more of pyrite, flocculation rarely if ever occurs. Marcasite alone, however, gives somewhat too low results for the iron dissolved (x-a) unless it is shaken with quartz. Here, to be sure, there is no pyrite to compete with the marcasite in the reduction of the ferric salt, but it is not improbable that the sulphur which is set free might act as a competitor to the marcasite, so that less iron would dissolve in case the marcasite surface were diminished by flocculation. Stokes found, it is true, that ordinary powdered sulphur had scarcely any effect on the ferric solution and we have confirmed his results. From this it appears that such oxidation of the sulphur as normally occurs in the Stokes reaction is probably contemporaneous with the solution of the iron (see equations a and b, p. 372). Still the particles of separated sulphur are doubtless at first very small, and if the surface of the marcasite should become much reduced by flocculation, the slow reducing action of the sulphur might cease to be negligible. At any rate, our value for (x-a), the quantity of iron dissolved, was only 10.30 without quartz, and this value rose to 10.57 and 10.58 when quartz was used.

(b) The necessary excess of the sulphide.—We have found one other important source of error in the application of the Stokes' reaction which must be discussed before our final results are presented, viz., the quantity of sulphide which must be used. It will be recalled that 250<sup>cc</sup> standard ferric solution is taken in each test, and that the quantity of the sulphide must be such as to reduce completely all the iron (250 mg.) present. If reproducible results are to be obtained, the excess of sulphide must be considerable. 0.75 g. gives virtually the same results as 1.0 g. for all mixtures containing 25 per cent of pyrite or more, but for other mixtures and for pure marcasite as much as 1 g, should be used. It will be noted on p. 373 that it takes much more marcasite than pyrite to reduce a given quantity of ferric iron. The ratio as determined by us is 2.37:1.\* while Stokes found 2.26:1. The discussion of the relation between weight per cent and surface per cent given on p. 381 shows why the use of weights of the sulphides which are but little in excess of the quantity actually decomposed by the solution, would result in error, for in that case the surface percentage, which is the all important matter, would vary decidedly during the reaction, while in the ideal case it should be constant. It may be seen from the table (Table II) that the same results were obtained whether 1.5 g. or 1.0 g. marcasite was taken, and the same is also nearly true for pyrite. Stokes states that the fineness of the sulphide makes no appreciable difference in the results. We have never found any systematic

\* This is the ratio between the constants for marcasite from Joplin, Mo., and pyrite from Roxbury, Conn.; the ratio for the *purest* natural minerals is about 2.5:1.

difference due to the time of grinding, though marcasite was repeatedly tested after grinding from 2 to  $5\frac{1}{2}$  h., pyrite from 1 to 2 h., and synthetic products from 1 to 2 h. It seems, therefore, to be true that after a sufficient excess of the sulphide is reached the results are unchanged by increasing the surface further, though more work would have to be done before this statement could be made unqualifiedly.

	-
'I' A DT	E II.
TUDT	IL II.

Showing the relation between the composition of the sulphide mixture,\* the iron dissolved, and the sulphur oxidized.

Per cent	(x-a) = iron dissolved				p = per cent
pyrite	0.75 g. sulphide	1.0 g. sulphide	1.5 g. sulphide	x	of sulphur oxidized
100	4.40	4.46	4.59	41.17	51.9
85	5.35			42.06	40 5
75	6.08			42.79	33.6
60		7.04		43.75	26.8
50	7.67			44.38	23.2
45		7.94		44.65	21.9
35		8.48		45.19	19.5
25	9.06	9.07		45.77	17.1
17		9.54		46.31	15.5
$\cdot 10$		9.95		46.66	14.1
5	9.40	10.27		46.98	13.1
0	10.30	10.28	10.57	47.28	12.2

For all our work on either natural or synthetic products we have taken 1.05 to 1.1 g. and ground with water for 2 h. The sulphide is then removed from the mortar with a "policeman," filtered in a porcelain Gooch crucible on a hardened filter disc and kept in a vacuum desiccator till the next morning, when 1 g. of it is weighed out, boiled with dilute hydrochloric acid, poured on to a new hardened filter and finally washed, first with dilute hydrochloric acid and then with boiled water cooled in carbon dioxide. The washing is done in a special apparatus in which an atmosphere of carbon dioxide free from oxygen is maintained, for the details of which a former paper should be consulted.<sup>+</sup> In these operations the total loss of material should be only a few centigrams. If it is considerable

\* The pyrite used was from Roxbury, Conn., and the marcasite was from Joplin, Mo.

<sup>+</sup> Allen, Crenshaw and Johnston, this Journal, (4), xxxiii, 169, 1912; Zs. anorg. Chem., lxvi, 201, 1912.

from any cause, the results will be unsatisfactory for mixtures containing less than 25 per cent pyrite. Ignorance of this fact cost us much time in one stage of our work.

2. Results on mixtures of the natural minerals.-When the above precautions were carefully followed, we obtained the

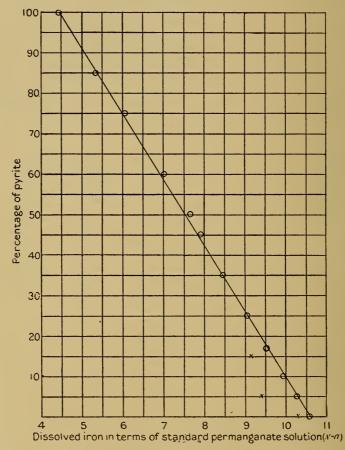


Fig. 3.

FIG. 3. Iron dissolved (x - a) from pyrite-marcasite mixtures by a standard ferric sulphate solution. Revised results. oo Results obtained by shaking with quartz. xx Results obtained without quartz. The pyrite was from Roxbury, Conn.; the marcasite from Joplin, Mo.

results given in Table II and graphically presented in fig. 3. It is evident that we have here a sensibly linear relation between the iron dissolved and the composition of the mixtures

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reckoned in weight per cent, but before we consider in detail the meaning and accuracy of the results, it will be best to put the method on a safer footing by examining all other possible sources of error which we could discover.

3. Other sources of error in the Stokes method.

(a) The ratio of the surfaces of the two minerals in weight percentage mixtures.—In the first place if the active mass of each sulphide depends on its surface rather than its weight, as it should for solids, it will be obvious to the reader that the relation between (x-a) the iron dissolved in the Stokes reaction, and y, the percentage of pyrite in the sulphide mixture, cannot be strictly linear in weight percentage mixtures, because the minerals naturally differ a little in density. They are of nearly the same hardness, and assuming that both are brought to the same degree of fineness when they are ground together, the percentage of surface of the marcasite, the lighter mineral, would be somewhat greater than its percentage by weight. Suppose that a mixture containing 50 per cent of each mineral by weight when ground in water,\* x = 5 + 5 + 02

 $\frac{n_1}{n_2} = \frac{S_m}{S_p} = \frac{5.03}{4.89}$ , where  $n_1$  = the number of particles of mar-

casite,  $n_2$  = the number of particles of pyrite, and  $S_m$  and  $S_p$ the total surface of the two minerals respectively. The ground mixture of the minerals in equal quantities would therefore contain only 49.3 per cent instead of 50 per cent pyrite surface. This error, however, is approximately compensated, under the conditions described, by the more rapid action of the ferric solution on the marcasite particles. If all the particles are of the same size, those of each mineral must be uniformly attacked, and assuming the action of each is independent of the other, the *final surface of the marcasite* would be  $s_m = n_1 4 \pi R_1^2$ , and the *final surface of the pyrite* would be  $s_p = n_2 4 \pi R_2^2$ , where  $R_1$  and  $R_2$  are the radii of the particles of the two minerals at the end of the oxidation. It follows from the above that the final weights of the two minerals in a 50 per cent mixture where 1 g. was taken would be :

$$0.500 - \frac{0.155}{2} = 0.423$$
 for the marcasite, and  
 $0.500 - \frac{0.065}{2} = 0.468$  for the pyrite. (See also p. 373.)

\* To insure a more uniform size of grain as well as a more uniform mixture, each mineral was screened within similar limits before mixing, after which the mixture was ground in water. Then  $n_1 4 \cdot 89 \frac{4}{3} \frac{\pi}{8} \mathbf{R}_1^{\ s} = 0.423$  and  $n_2 5 \cdot 03 \frac{4}{3} \frac{\pi}{8} \mathbf{R}_2^{\ s} = 0.468$ .  $\frac{n_1 4 \cdot 89 \frac{4}{3} \frac{\pi}{8} \mathbf{R}_1^{\ s}}{n_2 5 \cdot 03 \frac{4}{3} \mathbf{R}_2^{\ s}} = \frac{.423}{.468} \therefore \frac{n_1 4 \pi \mathbf{R}_1^{\ 2}}{n_2 4 \pi \mathbf{R}_2^{\ 2}} = \frac{2 \cdot 832}{2 \cdot 946} = \frac{49 \cdot 0}{51 \cdot 0}$ 

So while the pyrite in a 50 per cent mixture by weight would possess only about 49 per cent of the surface; *after the oxidation* by ferric sulphate, it would possess about 51 per cent. The average variation of the surface percentage from the weight percentage in the course of the reaction is therefore slight. By the same mode of reasoning we find that in a mixture of the sulphides containing 90 per cent by weight of marcasite, the surface of the latter would be 90.2 per cent before, and 89.7 per cent after the oxidation. Here also the average variation of the surface per cent from the weight per cent would be small. In a mixture containing 90 per cent by weight of pyrite, the pyrite surface would vary from 89.8 per cent to 91 per cent. Here the average variation of the surface from the weight per cent is also comparatively small, viz. 0.4 per cent.

The assumptions regarding the size, shape and uniformity of the particles are of course only approximations; still no other error has been found which could compensate any considerable error here and the conclusions deduced from the assumptions are in accord with the experimental results.

The plan naturally suggests itself, of taking the density of the two minerals into account in making the mixtures, and then increasing the quantity of the sulphide to be oxidized, so that the ratio of the surfaces of the two at the beginning should remain sensibly constant throughout the process of oxidation. Small quantities, however, are far more readily purified and otherwise handled, and it should also be noted respecting the application of the method to synthetic products that the latter are troublesome to prepare in quantity.

Although a careful study of other sources of error was made before the disturbance caused by flocculation was entirely understood, none of them proved of any great importance. It may be wise, however, to discuss them as briefly as possible.

(b) Loss of water during the oxidation process.—Stokes asserts that if the reaction flask is provided with a reflux condenser, and if the carbon dioxide which passes through the liquid during the process is first bubbled through water, there is no appreciable change in the concentration when a blank test is made with the standard solution. We can confirm this assertion as far as the water is concerned, but find a slight pre-

### Determination of Pyrite and Marcasite.

cipitation of iron even when 5 g. sulphuric acid instead of 4 g.\* per liter is contained in the standard solution. If correction is made for the precipitated iron, no change in concentration has taken place, i. e., there is no loss of water. It should be stated that in an actual oxidation experiment no iron is precipitated, since the ferric iron is pretty rapidly reduced to the ferrous state. The following results prove these statements:

 $C_1$  is the original concentration of the iron solution in grams of KMnO<sub>4</sub> solution per 100<sup>cc</sup> of the standard.

 $C_2$  is the concentration after the blank test, to determine which  $100^{\circ\circ}$  solution is then reduced with SO<sub>2</sub> and titrated.

	I	II	III
C,	37.06	37.06	36.54
C <sub>2</sub>	∫ 37.09	37.08	36.52
U <sub>2</sub>	37.03	37.04	36.44

(c) Reduction of the ferric solution during the blank test.— Stokes states that no reduction occurred during a blank determination. We found a small reduction due perhaps to some organic matter associated with the ammonium salt. It amounted to only 0.1 g. of the very dilute standard  $\text{KMnO}_4$ solution per 100<sup>cc</sup>. In actual oxidations it is probable that the error would be less on account of the presence of a competing reducing agent.

(d) Errors in the determination of the iron.—These are very slight as previous results would indicate. In standardizing the ferric solution,  $100^{\circ\circ}$  are measured in a calibrated flask at 25°. The solution is washed into a  $500^{\circ\circ}$  flask, reduced in a stream of washed sulphur dioxide, the excess of which is boiled out in a stream of carbon dioxide in which the solution is finally cooled. The titration is then made with a weight burette, using a permanganate solution containing 1.5 g. of the salt per liter. The following determinations<sup>+</sup> of the concentration of four different solutions show the accuracy of the method:

I	II	III	IV
36.60	36.51	36.20	36.69
3662	36.60	36.51	36.69
36.63	36.28	36.46	
	36.58	36.46	

Sulphur dioxide seems to carry with it mechanically some non-volatile reducing agent. This occasions a relatively large blank, but a very constant one. Blank tests were made as fol-

\* The quantity prescribed by Stokes.

+ The unit in these determinations is the gram of the above standard permanganate solution. lows: A similar quantity of water to that used in the standardization tests was treated in the same way with sulphur dioxide and carbon dioxide successively. To the cooled solution was then added 0.86 g. ferric alum, thus giving practically the same conditions as those which obtain in the standardization itself. The quantity of the permanganate solution required in the blanks varied from 0.12 g. to 0.14 g. of permanganate solution, while 0.86 g. of ferric alum *alone*, with the usual amount of water, required always about 0.04 g. or one drop of permanganate solution. In the titration of an iron solution obtained in the Stokes process, the latter blank was subtracted, since here the ferric iron was reduced by the disulphide of iron and not by sulphur dioxide.

(b) Oxidation of either ferrous solution or finely divided sulphide by atmospheric oxygen.—The oxygen of the air, if not prevented, may affect the results in several particulars. First, when the finely ground sulphide is transferred from the desiccator to the reaction flask. This operation requires only about two minutes. The oxidation of 1-2 mg. of the sulphide would have an appreciable effect, but oxidation during this operation must be negligible, for a moist mixture of sulphides of similar weight to that used in the oxidation experiments exposed in a Gooch crucible to the air for 20 minutes gave an extract with distilled water which reduced only 0.1 g. permanganate solution.

The purification of the sulphide itself has been sufficiently insisted on by Stokes. He boiled it with hydrochloric acid, washed it successively with hydrochloric acid and boiled water cooled in carbon dioxide, in an atmosphere of carbon dioxide gas, and finally dried it in a vacuum desiccator. The apparatus which we employed in the washing has been described in a previous paper.\* Whether necessary or not, we have dried the product more carefully than Stokes did. The washed sulphide in the Gooch crucible was removed from the above mentioned apparatus and put directly into a vacuum desiccator previously filled with carbon dioxide. The desiccator was then evacuated by a May-Nelson pump connected with driers which contained lime and phosphorus pentoxide. Thus any air in the desiccator was practically all removed in a couple of minutes. The sulphide was dried for about one hour, during which time the pump was kept running. It would seem impossible that any oxidation could have occurred during this process.

It may be said further that we assured ourselves by direct experiment with a titrated ferrous solution that no oxidation occurs when it is filtered in the described way. It has been

\* Allen, Crenshaw and Johnston, loc. cit.

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stated more than once by Baskerville and Stevenson<sup>\*</sup> and others that an acid ferrous solution is not readily oxidized by the oxygen of the air, but we have here in addition the possibility of an oxidation of the finely ground sulphide. Since, however, moist sulphide oxidizes so very slowly even when exposed to the direct influence of the air, oxidation should be negligible when the filtration is done in our apparatus.

4. Accuracy of the method.—The systematic study of this problem has revealed only two considerable sources of error and means for obviating them have been explained. The results in fig. 3 involve errors of one per cent to two per cent. While this is a large error in ordinary analytical operations, it must be borne in mind that the two minerals are very similar and the method is very delicate. The total difference between the quantities of iron which the two minerals yield to the standard solution is, in terms of a dilute permanganate solution, only 6·1 to 6·4 g., according to the sample of pyrite taken, i. e., only 0·06 g. for every per cent. This amounts to about 1·5 drops of the permanganate solution, containing about 0·1 mg. of KMnO<sub>4</sub> and equivalent to only about 0·2 mg. of iron dissolved.

While the results are very constant for the same specimens of pyrite and marcasite, different natural specimens may show considerable differences.

Table III gives the results in tabular form. The only marcasites not of questionable purity which we have ever had in our hands, gave results which were almost identical. The results on the Joplin marcasite also served to show the constancy of the method; the first two results were obtained about a year later than the third with different standard solutions. The two determinations on Elba pyrite No. 1 were also made a year apart. The determinations for synthetic pyrite were made on two different preparations.

The variations on different occurrences of the same mineral species are due in part, if not entirely, to impurities. Thus the Leadville pyrite contains copper probably as chalcopyrite which Stokes found to give low results. Elba pyrite No. 1 is the purest we have ever found; the quantity at our disposal was unfortunately insufficient for this investigation. Elba pyrite No. 2 contained a little cobalt, but hardly sufficient to cause the irregularity noticed. It was selected from a large sample which contained considerable hematite, traces of which were probably retained by the sulphide even after purification. That the suspicion was well founded was proved by the fact that after the ground mineral had been treated for two days at 200° with two per cent sulphuric acid saturated with hydrogen

\* J. Am. Chem. Soc., xxxiii, 1104, 1911.

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Showing the Stokes Constant for Different Pyrites and Marcasites.			
Mineral.	Locality.	x-a	Impurities.
Pyrite	Leadville, Col.	3.95	0.1 per cent of copper.
"	Elba, No. 1	$4.17 \\ 4.20$	
"	Elba, No. 2	4.35	0.04 nickel and cobalt- mostly the latter, ferric
" "	" ' after heating with sulphuric acid at 200°	4.18	oxide suspected.
"	Roxbury, Conn.	4.46	1.4 per cent arsenic.
"	Synthetic, prepared by heat- ing synthetic marcasite	4·14 4·11	
Marcasite	Joplin, Mo.	$10.57 \\ 10.58 \\ 10.52$	only quartz found
• •	Galena, Ill.	10.57	
" "	* Synthetic at 25°	$10.20 \\ 10.34$	may contain pyrite
	·· ·· 200°	10.27 10.42	
	.: ., <b>3</b> 00.	$10 \cdot 42$ $10 \cdot 20$ $10 \cdot 34$	

#### TARLE III.

\* See this Journal, The effect of temperature and acidity in the formation of marcasite and wurtzite, (4), xxviii, 411, 1914.

sulphide, the value of the Stokes constant agreed with the purest pyrite. The hematite had evidently been removed by the treatment. The Roxbury pyrite which was used for the most part in the present work was selected on its macroscopic appearance, the higher results being at first regarded as more accurate. Later, when the lower results with synthetic pyrite had thrown them under suspicion, an analysis showed the presence of arsenic. Stokes found that arsenopyrite gave high results; 1 per cent arsenic in that form having the same effect in the Stokes test as 2 per cent marcasite, while it may be seen from the table that 1.4 per cent arsenic in the Roxbury pyrite has the same influence as 4 per cent marcasite.

5. Linear relation between any pyrite and any marcasite. It is important to note in this connection that the constants of any pyrite and marcasite are additive in their mixtures. Thus a number of tests showed this to be true of the Elba pyrite No. 2 and the Joplin marcasite, while more numerous experiments (see fig 4) show the same thing for the Joplin marcasite and Elba pyrite No. 1. This is a fact of importance in the application of the method to synthetic mixtures, which has been the object of the present investigation.

(a) Independence of the chemical action of the two sulphides. —Since the quantity of iron which dissolves in the Stokes reaction is approximately a linear function of the composition of the sulphide mixtures, each sulphide in the mixture behaves

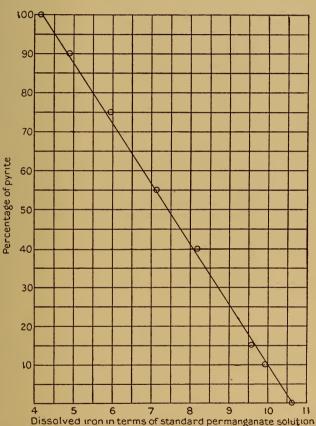


FIG. 4.

FIG. 4. Iron dissolved from pyrite-marcasite mixtures by a standard ferric solution. Pyrite from Elba; marcasite from Joplin, Mo.

with the solution practically as it does when alone. The iron which dissolves comes only from decomposed sulphide, consequently in a sulphide mixture the quantity of each decomposed is directly proportional to its percentage in the mixture. Thus in a 50 per cent mixture, one half as much of each mineral is decomposed as when each reacts alone with the solution. AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXVIII, NO. 227.—NOVEMBER, 1914. 27 Further, each sulphide in the mixture must reduce only its proportional fraction of the solution; in a 50 per cent mixture the pyrite must reduce one half of the ferric solution and the two sulphides must reduce the two portions at the same rate, otherwise the one which worked faster would encroach on the province of the other and the results would not be linearly related. In other words, the results are the same as if one should first separate the two minerals, divide the solution between them in proportion to their percentages, and allow each constituent to reduce its own portion separately.

The rate at which the solution is reduced by the two sulphides must then be the same for each mineral, but the rate at which each mineral is decomposed is quite different; that is proportional to the quantity of iron (x-a) which each yields to the solution. This quantity, in terms of the standard permanganate solution, is 4.20 for pyrite (Elba No. 1) and 10.57 for marcasite. Marcasite is therefore decomposed 2.5 times as rapidly as pyrite, while the solution is reduced at the same rate by each.

(b) *Electrolytic effect in the Stokes reaction.*—From the findings of Gottschalk and Buehler,\* and of R. C. Wells,† one would expect an electrolytic effect here. If there is one, it must be very small. The results in fig. 3 do indeed appear to form a slightly convex curve which means of course that the marcasite seems to have a little more than its proportionate effect. Possibly this may be attributed to electrolytic influence.

(c) Stokes' curve.—If the relation between x and y is linear, x = by + c. By substituting in this equation the values  $x_0$  and  $x_{100}$  for x, when y = 0 and y = 100 respectively, i. e., when we have pure marcasite and pure pyrite, we obtain

(3) 
$$x = \frac{x_{100} - x_0}{100} y + x_0$$
.

Now substituting this value for x in equation (2) (page 374) the latter becomes

(4) 
$$y = \frac{(p+25)a - (p+16.66)x_0}{(p+16.66)\left(\frac{x_{100}-x_0}{100}\right)}$$

or if we replace  $x_0$ ,  $x_{100}$  and a by their experimental values, viz., 47.28, 41.17 and 36.71, we have  $y = \frac{10.57 \ p - 129.8}{.0611 \ p + 1.018}$ . This curve, which is evidently a hyperbola, is plotted in fig. 5. The *plotted curve* is a true hyperbola *calculated* from the values which fall on the line drawn between the values of (x-a) for pyrite and marcasite respectively; the *points plotted* are the values of p calculated directly from experimental values of x.

\* Gottschalk and Buehler, Econ. Geol., vii, 28, 1912.

† R. C. Wells, ibid., vii, 571, 1913.

These are the figures for Roxbury pyrite and Joplin marcasite. We have seen above that these results are affected by the presence of arsenic in the Roxbury pyrite. In fig. 6 are graphically shown the Stokes constants (x-a), for the purest natural pyrite and marcasite (Curve 1, 1) and also for the synthetic minerals (Curve 2, 2). It must be admitted that the

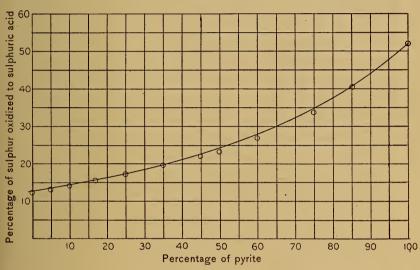


FIG. 5.

FIG. 5. Curve showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. Roxbury pyrite. Joplin marcasite.

value 10.3 for synthetic marcasite is open to the suspicion that the products may have contained a little pyrite.\* Fig. 7 shows the hyperbolas calculated from these results, the assumption being made that the constants are exactly additive in their mixtures, while the points plotted are, as in fig. 5, calculated from the experimental values as given in fig. 4.

Fig. 8 shows Stokes' published values for p plotted against y. The plotted curve is again a true hyperbola calculated from the values of x which fall on the line in fig. 1. The minimum in his curve which Stokes obtained at 10 per cent pyrite seems therefore to have no real existence.

### Summary.

1. The Stokes method for determining pyrite and mar casite, alone or in mixtures, depends on the estimation of the \*This Journal (4), xxxviii, 411, 1914.

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iron dissolved when the finely ground and purified sulphide is treated with a boiling standard solution of ferric alum. The *same* pyrite or marcasite gives very constant values and the influence of each in mixtures is additive, i. e., there exists a linear relation between the iron dissolved and the composition of the mixture. The sum of the errors usually amounts to

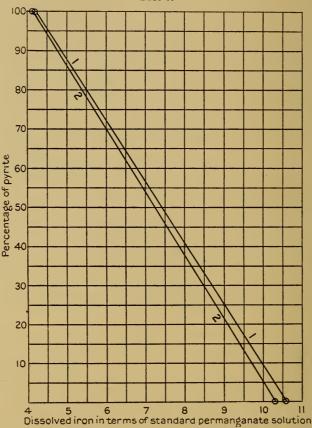


FIG. 6.

FIG. 6. 1, 1. Values of the Stokes' constant  $(x-\alpha)$  for the purest natural pyrite and marcasite, and their mixtures. 2, 2. Values of the Stokes' constant for synthetic pyrite, synthetic marcasite and their mixtures.

about 1 per cent, reaching a maximum of 2 per cent. There are two important sources of error. First there must be a sufficient excess of the sulphide, which is many times greater

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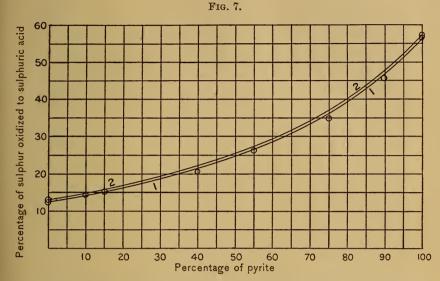


FIG. 7. Curves showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. 1, 1. Curve for purest natural pyrite and marcasite. 2, 2. Curve for the synthetic minerals.

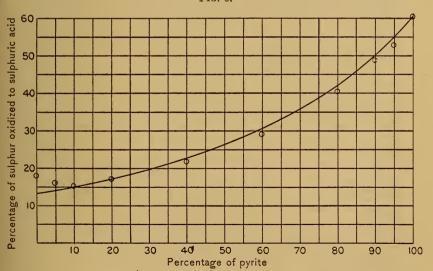


FIG. 8.

FIG. 8. Curve showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. Stokes' results. The curve is a true hyperbola.

(7-15) than the amount required by theory. With such an excess the percentage of the surfaces remains on the average nearly the same as the percentage by weight, the basis on which the mixtures are made up. About 1 g. is sufficient for 250° of the standard solution. Secondly, the marcasite has a characteristic tendency to flocculate and thus reduce its reacting surface. This difficulty may be avoided by shaking the reaction mixture with pure quartz and beads until the lumps of the powder are thoroughly disintegrated. Different specimens of pyrite and marcasite give with the Stokes reaction values which differ somewhat. The differences are due in some cases, if not in all, to the presence of impurities. It is unfortunate that small quantities of impurities which will reduce ferric iron or give up iron to the solution exercise a serious influence. It is therefore not always possible to decide between a natural pyrite and a pyrite containing several per cent of marcasite by the Stokes reaction alone, nor to determine accurately the percentage of each in a natural mixture. In an investigation on the conditions of formation of pyrite and marcasite, this method has been very useful.

2. The results with the Stokes method plainly indicate that each mineral behaves in a mixture of the two just as it does alone; each appears to reduce a quantity of solution which is proportional to its surface; and each appears to reduce the solution at practically the same rate. The rates at which the sulphides are decomposed is quite different for the two minerals, because more of marcasite than of pyrite is required to reduce a given quantity of ferric iron. The ratio of these rates is not far from 1:2.5.

3. That ferric sulphate dissolves from pyrite a smaller quantity of iron than it does from marcasite means simply that more reduction is effected by sulphur in the case of pyrite, in other words that more of the sulphur in pyrite is oxidized. Stokes considered only the relation of p, the percentage of sulphur oxidized, to y, the percentage of pyrite in the sulphide mixture. We have shown that this curve is a hyperbola. This characteristic behavior of pyrite and marcasite towards oxidizing agents is probably general. It has been found by other observers that nitric acid and hydrogen peroxide both oxidize more of the sulphur in pyrite under the same conditions.

The authors wish to thank Prof. E. S. Dana of Yale University and Drs. Geo. P. Merrill and Edgar T. Wherry of the National Museum for specimens of pyrite and marcasite used in this work.

Geophysical Laboratory,

Carnegie Institution of Washington.

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ART. XXXIII.—Effect of Temperature and Acidity in the Formation of Marcasite (FeS<sub>2</sub>) and Wurtzite (ZnS); A Contribution to the Genesis of Unstable Forms; by E. T. ALLEN and J. L. CRENSHAW. Microscopic Study; by H. E. MERWIN.

#### SYLLABUS.

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2. The conditions necessary for the genesis of either form alone. IV. Natural genesis of the sulphides of iron and zinc.

- A. Pyrite from cold alkaline solutions.B. Paragenesis of marcasite and wurtzite with calcite.
- C. Paragenesis of pyrite with calcite. Summary.

# I. INTRODUCTION.—DETERMINATIVE INFLUENCE OF ALKALINITY AND ACIDITY ON CRYSTALLINE FORM.

In the course of an investigation of the disulphides of iron, it was found by the authors that the stable form, pyrite,\* is the only crystalline form which is obtained by the action of alkali polysulphides on ferrous salts. The first product of this reaction at room temperature is a mixture of amorphous ferrous sulphide and sulphur, from which the disulphide gradually forms. The formation is very slow at low temperatures, and, even at 100°, the product appears to be at first amorphous, but it crystallizes in time to pyrite with excess of reagent-a transformation which could not be effected with natural marcasite under similar conditions. From acid ferrous solutions, on the other hand, by the action of sulphur and hydrogen sulphide the unstable form marcasite is obtained. The marcasite is commonly admixed with pyrite, the quantity of which may be reduced by raising the initial concentration of the free acid; or increased by raising the temperature.

The same regularity was observed to hold good for the sulphides of zinc and mercury, + i. e. only the stable forms, sphalerite and cinnabar, were obtained from alkaline solutions; while only from *acid* solutions could the corresponding unstable forms, wurtzite and metacinnabar, be obtained. This peculiar regularity seemed to us of sufficient interest to form the subject of a separate investigation. There has never been any doubt about the products of the alkaline solutions, but a more thorough study of the products of the acid solutions seemed desirable, more especially as so little is known about the genesis of unstable forms. We have been obliged to confine ourselves to the investigation of marcasite and wurtzite, for, while our synthetic black sulphide of mercury is an unstable crystalline form and conforms to the above rule in crystallizing from acid solutions, it could not be absolutely identified with the natural metacinnabar, and its formation has thus far been brought about only within a very limited range of conditions.

#### II. MARCASITE AND PYRITE.

A. *Preparation*.—The marcasite-pyrite mixtures were prepared by heating in sealed tubes, a 5 per cent solution of hydrous ferrous sulphate,<sup>‡</sup> containing a measured quantity of sulphuric acid, sulphur and hydrogen sulphide. A Jena glass tube of about 17-18<sup>mm</sup> internal diameter and closed at one end

\* This Journal, xxxiii, 169, 1912; Zs. anorg. Chem., lxxii, 201, 1912. † This Journal, xxxiv, 341, 1912; Zs. anorg. Chem., lxxix, 125, 1912.

‡ In one series of experiments ferrous chloride and hydrochloric acid were taken.

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# Effect of Temperature, Acidity, etc.

was first constricted at a point about 50<sup>cm</sup> from the closed end. to a diameter of 6 or 8 millimeters. The ferrous sulphate and sulphur were then dropped in through a long funnel; a sufficient quantity of a titrated sulphuric acid (30 per cent con.) was measured out from a burette into a graduated cylinder, enough water added to make 75<sup>cc</sup> and the resulting solution poured into the tube. The tube was then packed in ice, saturated with hydrogen sulphide and quickly sealed at the constriction, after which it was placed in a steel bomb surrounded by water and closed up. The bomb was finally put into a suitable furnace already heated to a degree such as to bring the bomb to the desired maximum temperature. For details of bomb and furnace construction a former paper\* should be consulted. At the end of a period of from 1-4 days, depending on the temperature of the experiment, the bomb was withdrawn from the furnace, cooled and opened, and the tube then removed. The glass tube should never be so long that it cannot be entirely covered by water; partially covered tubes are very apt to break.

B. Purification of the synthetic products.—The glass tube is opened and the contents quantitatively transferred to a suitable beaker. The sulphide is then filtered out while the filtrate is caught in a measuring flask of 250<sup>cc</sup> capacity and, after adding the washings, diluted up to the mark.

In the solution the acid is determined by titrating with a standard sodium carbonate solution using methyl orange as indicator. The excess of hydrogen sulphide, or of sulphur dioxide, which forms when the temperature and acidity are sufficiently high, should first be removed by boiling in a current of carbon dioxide. The sulphide needs to be carefully freed from sulphur in all cases, and it was thought best to get rid of the siliceous matter originating from the glass when the products were formed at the highest temperatures. To this end the wet sulphide is first dried by washing with alcohol and ether and sucking off with the pump. Most of the sulphur is then dissolved out by carbon bisulphide, but the film which commonly persists and coats the sulphide as the last portions of the volatile solvent evaporate, should be removed by concentrated colorless ammonium sulphide, after the excess of carbon disulphide has been washed out by ether. The excess of ammonium sulphide is then removed by water and the product finally dried with alcohol and ether; or if siliceous material is present the product should be warmed with a mixture of hydrofluoric and hydrochloric acids for half an hour on the steam-bath. The sulphides should be kept in a vacuum desiccator. When they are to be tested by the Stokes reaction

\* Loc. cit.

1.05 to 1.1 g. is ground for 1 h. with water in a McKenna oregrinder and further purified as described in the preceding paper.\*

Disulphide of iron was formed by the above method at 25°, 100°, 200° and 300°. All the products with the possible exception of those obtained at 100° were evidently crystalline to the naked eye, and those obtained at the higher temperatures, especially the products formed from solutions which contained 2 per cent to 3 per cent of sulphuric acid consisted of crystals of relatively large size. The finest were crystallized from hydrochloric acid solutions; these formed beautiful aggregates of splendid lustre the individuals of which were not infrequently  $0.7^{\text{mm}}$  in length  $\times 0.2-0.3^{\text{mm}}$  in width.

C. Chemistry of the formation of iron disulphide.—The chemical reaction which is involved in the formation of iron disulphide is expressed by the equation :

$$H_sS + S + FeSO_s = H_sSO_s + FeS_s$$
.

Table I may be put in evidence on this point. The figures there given show that the increase in acidity and the weight of the sulphide formed are in practically the ratio which the equation demands. This is strictly true within the limits of error at the lower temperatures, 25° and 100°. To be sure the errors are greater than they are in ordinary gravimetric operations because we are under the necessity of recovering the sulphide in pure condition; what clings to the filter can not be saved by burning and this fact entails an appreciable loss.

At the higher temperature and the higher acid concentrations a side reaction becomes manifest, viz: the reduction of the sulphuric acid to sulphur by the hydrogen sulphide, followed in turn by the interaction of the sulphur with the sulphuric acid and the appearance of sulphur dioxide. This reaction is pretty slow at 200°. The first series of results at this temperature (see Table I) show very little reduction; the second series more. The cause of this difference is not clear. At first it was ascribed to differences in the glass tubes, which were taken from two different lots. The glass of the second lot was believed to have neutralized more acid than the other. Blank experiments made by heating dilute sulphuric acid in sealed tubes at 200° show that the suspicion was incorrect, but the results are given because the behavior of "Jena combustion" glass with aqueous solutions at 200° is a matter of some interest (see Table II). At 300° the reduction of sulphuric acid by hydrogen sulphide and sulphur is considerably greater in the same time than it is at 200° (see Table I).

\* This number, p. 384.

Thus after one day's heating sulphur dioxide is formed if the initial acid concentration reaches 1 per cent, and it appears after a longer time where the acid is weaker. At no temperature, however, do these side reactions appear to have any connection with the crystalline form of the product.

Tempera- ture	FeS <sub>2</sub> found	Gain in wt. of acid calc. from FeS <sub>2</sub>		Final acid in wt. % calc.	Final acid in wt. % found	Initial acid in wt. %
25°	2.46	2.01	2.23	0.115	0.127	0.012
66	3.67	<b>3</b> .00	3.18	$\cdot 165$	·173	.015
"	4.31	3.52	3.51	$\cdot 235$	$\cdot 234$	.059
100°	1.32	1.08	1.11	1.54	1.58	0.10
66	•93	•76	•73	1.26	1.22	.25
66	.68	:55	•55	1.23	1.20	.50
66	•43	•35	$\cdot 37$	1.47	1.50	1.00
"	1.03	•84	•86	2.62	2.65	1.50
200°	0.71	0.28	0.60	1.27	1.30	0.20
66	•96	•78	.74	2.04	2.00	1.00
66	•96	.78	•75	2.54	2.49	1.50
66	.93	•76	•70	3.01	2.90	2.50
"	•68	•55	•52	3.24	3.19	2.50
$200^{\circ}$	1.02	0.83	0.68	2.10	1.91	1.00
66	.82	.67	•49	2.14	1.90	1.25
"	•81	•66	•47	2.64	2.37	1.75
66	•74	•61	•34	2.81	2.45	2.00
"	•73	•60	•33	3 <b>·3</b> 0	2.94	2.50
300°	<b>1</b> ·18	0.92	0.74	1.36	1.08	0.10
"	1.04	·85	·61	2.13	1.82	1.00
"	·81	•66	•30	2.89	2.40	2.00
"	•29	•24	•17	3.32	2.78	3.00

#### TABLE I.

TABLE II.

Neutralization of H<sub>2</sub>SO<sub>4</sub> by Jena combustion glass\* at 200°

Time = 3 days.

Grams H₂SO₄ taken	Grams H₂SO₄ found after heating	Grams H <sub>2</sub> SO <sub>4</sub> neutralized	Concentration H <sub>2</sub> SO <sub>4</sub> in wt. % before heating	Concentration $H_2SO_4$ in wt. % after heating
0.1937	0.1859	0.0078	0.97%	0.93%
0.3874	0.3752	0.0122	1.94	1.88
0.2949	0.2875	0.0074	2.95	2.88

\* The surface exposed to the action of the acid was about 30cm<sup>2</sup>.

The relation between the sulphide formed and the acid set free.

Analysis of the products.-The molecular ratio between D. the two products of the interaction of hydrogen sulphide, sulphur and a ferrous salt is strong evidence of the composition of the precipitate. This had already been directly proved by chemical analysis to be the disulphide,\* while the color, luster and chemical behavior agreed with pyrite or marcasite. The purposes of the present investigation necessitated a method for determining whether we had one or the other, or both. In the preceding paper<sup>†</sup> we have shown how the Stokes method may be utilized for this purpose. The method is founded on the difference in the chemical behavior of the two crystalline forms toward oxidizing agents. A boiling standard solution of ferric alum dissolves a characteristic and constant quantity of iron from each of the minerals pyrite and marcasite, and these constants are additive for mixtures of the two; i. e., the quantity of iron dissolved by ferric alum is a linear function of the composition of the mixture. We may anticipate the results so far as to say that the Stokes method indicates in all cases, with the possible exception of the products formed at 100°, that the sulphides are either pure marcasite or mixtures of marcasite and pyrite.

E. Other evidence on the nature of the products.—Certain objections to exclusive reliance on the Stokes method will occur to the chemist. The products are all crystallized from solutions containing an excess of ferrous salt as well as hydrogen sulphide. Sulphur dioxide also is a final product in many instances. Any of these impurities if occluded by the precipitate would disturb the Stokes test; the ferrous salt by directly increasing the iron in solution; the sulphur dioxide or hydrogen sulphide by reducing the standard solution and thus decreasing the iron which should normally dissolve.

Many instances are known of occlusions which are impossible to remove by ordinary washing. But the purification of these sulphides was out of the ordinary in that the substance was ground in a mortar for two hours before boiling with hydrochloric acid and washing with water. Such drastic treatment might be expected to remove these occlusions if any are present. Still we have positive evidence that the products which we infer to be mixtures of pyrite and marcasite from the Stokes tests are really such, rather than marcasite containing reducing impurities.

1. *Microscopic evidence.*—The identification of opaque minerals as compared with the transparent minerals is much less fully worked out. In default of optical constants, one must rely on crystal form, color, cleavage and on microchem-

<sup>\*</sup> This Journal (4), xxxiii, 173, 1912; Zs. anorg. Chem., lxvi, 206, 1912.

<sup>†</sup> This number, p. 371.

ical tests where they are available. Synthetic sulphides, prepared as above described, except where hydrochloric acid is used, consist of crystals which are usually not sufficiently developed to make microscopic diagnosis certain. Apart from any other evidence, color and crystal habit in most of the preparations make the presence of marcasite almost certain, but that of pyrite doubtful. When the preparations are made in *double tubes* (see p. 412), however, the crystals are well developed, and Larsen\* found pyrite in many of them; the marcasite was always better developed, in fact, the crystals were often measurable, though some crystals of pyrite were  $0.5^{mm}$  across. The pyrite crystals usually showed a combination of the cube and octahedron.

Color.-Pyrite is distinctly yellower than marcasite, 2.though in making comparisons care should be taken that the specimens are untarnished. Synthetic products which consist of very small crystals can not be satisfactorily compared for color differences by simply placing small portions side by side; but by grinding a few tenths of a gram to a rather fine powder and then boiling in a small beaker with dilute hydrochloric acid (to remove tarnish), a considerable amount can be made to float on the surface of the liquid in the form of a metallic mirror. When examined in this way, the products which were determined by the Stokes reaction to be either pure marcasite, or very near it, showed the same color as a mirror of the natural marcasite obtained in the same manner, while products found by the Stokes reaction to contain 28 per cent and 35 per cent pyrite respectively, formed mirrors of decidedly yellower color, identical with that of pyrite-marcasite mixtures, as three observers all agreed. This test, while purely qualitative, gave evidence which may be regarded of considerable weight.

3. Evidence concerning inclusions.—It has already been admitted that the synthetic sulphides might possibly have occluded ferrous sulphate, hydrogen sulphide, or in some cases sulphur dioxide, and that any of these substances would interfere with the Stokes test and the conclusions drawn from its use. The absence of hydrogen sulphide was pretty conclusively shown by a series of experiments in which the synthetic sulphides were heated in vacuo. These experiments were made on products formed at 200° under conditions where sulphur dioxide never formed.

À vertical glass tube about  $1^{cm}$  in diameter, closed at the lower end, was used for heating the sulphide. About  $15^{cm}$ from the lower end a side tube  $5^{mm}$  in diameter was sealed on. Above the side tube the vertical tube was constricted and left

\* This Journal (4), xxxiii, 215, 1912; Zs. anorg. Chem., lxvi, 251, 1912.

open at the top. The side tube was sealed direct to one arm of a U-tube of the same diameter  $(5^{mm})$  stuffed with glass wool. The U-tube was about 18<sup>cm</sup> high and during the experiments was surrounded by ice to condense any free sulphur. The other arm of the U-tube was sealed to the absorption tube. This was about 1<sup>cm</sup> in diameter drawn down to 5<sup>mm</sup> at either end and contained a layer of pure solid caustic soda about 6cm in length, which was kept in place by plugs of glass wool. The free end of the absorption tube was sealed to a May-Nelson vacuum pump. When the apparatus was made ready the sulphide was dropped through a small funnel into the vertical tube, which was then sealed off at the constriction.

The sulphide was heated by a small resistance furnace by which the vertical tube was surrounded. The apparatus was, of course, evacuated before the heating began and the pump was kept running during the experiment.\* The temperature in all the experiments, where not otherwise stated, was carried to 600° measured by a thermoelement, the hot junction of which touched the glass on the outside of the tube close to the sulphide. The time required to reach this temperature was about three-quarters of an hour. The current was then turned off, for under these conditions considerable decomposition of the disulphide into pyrrhotite and sulphur always took place, thus leaving no reasonable room for doubt that all the gas was driven off.

After the heating was over, the furnace was removed and the tube quickly cooled, air was admitted to the apparatus, the absorption tube cut out, the soda dissolved in water and freed from glass wool by filtering. The solution was then tested with cadmium chloride and if yellow cadmium sulphide came down, a sufficient excess of the reagent was added, the precipitate filtered and washed, and finally dissolved in ammonia and perhydrol. The solution was then just acidified and precipitated hot with barium chloride. After the nature of the sulphur compound had been sufficiently well established the use of the cadmium salt was omitted and the soda solution directly oxidized by perhydrol.

The results are shown in Table III. All the synthetic sulphides gave off hydrogen sulphide when heated, but the facts plainly indicate that this was not present originally in the sulphide, but was formed by the action of water, during the heating, on the pyrrhotite, one of the decomposition products of the disulphide; + for when pure natural marcasite was ground

\*None of the gas escapes by this method. In the last experiment in Table III, the apparatus was isolated from the pump by a stopcock after evacuation and before heating. The results were practically the same. †When the maximum temperature was only 350°, much less pyrrhotite

was formed and far less sulphur was obtained.

## TABLE III.

Showing the hydrogen sulphide obtained by heating natural and synthetic iron disulphide to 600° in vacuo.

Sulphide tested 1 g. in all cases	Quantity of pyrite in the product determined by the Stokes test.	Quan ob	tity of H₂S tained in s of BaSO₄	Quantity of H <sub>2</sub> S calculated in milligrams
Joplin marcasite, ground in water	none	7•6 r	nilligrams	1.1
Joplin marcasite, ground in water	none	8.1	66	1.2
Joplin marcasite, ground dry	none	0.0	66	0.0
†Joplin marcasite, heated in 2% H <sub>2</sub> SO <sub>4</sub> 2 days at 2	<b>30-40%</b> 00°	8.1	"	1.2
Synthetic FeS <sub>2</sub> at 200° from 0·1% HS <sub>2</sub> O <sub>4</sub> , groun in water	- /0	12.2	66	1.8
Synthetic $\text{FeS}_2$ at 200° from $0.1\% \text{ H}_2\text{SO}_4$ , groun in water	45% 1d	9.7	66	1.4
Synthetic FeS <sub>2</sub> at 200° from 1% H <sub>2</sub> SO <sub>4</sub> , ground in water	28%	5.7	"	0.8
Synthetic $\text{FeS}_2$ at 200° from 2% $H_2\text{SO}_4$ , ground in water	3-5%	20.0	<b></b>	2.9
Synthetic $\text{FeS}_{2}$ at 200° from 2.5% $\text{H}_{2}\text{SO}_{4}$ , ground in water	26%	17.1	"	2.2
Synthetic FeS <sub>2</sub> at 200° from 2.5% H <sub>2</sub> SO <sub>4</sub> , ground in water	26%	16.2	"	2.4

for 2 h. in water and purified like the synthetic products for the Stokes test, it gave off hydrogen sulphide on heating in vacuo; whereas the same mineral ground dry for 2 h. gave off none. It is also certain that the water could not have come

+ Ground in water before heating.

from any other source than the moist sulphide itself; it could not have come from the soda, since pyrrhotite crystallized from a fusion and ground dry, gave off no hydrogen sulphide even when heated for an hour or more at 700° under similar conditions.

A careful study of the table (Table III) proves that the quantity of hydrogen sulphide given off by the products bears no relation whatever to the quantity of pyrite indicated by the Stokes test. Thus a preparation which, according to the Stokes test, contained 28 per cent pyrite, gave off less hydrogen sulphide than the natural marcasite; and the preparation which contained the least pyrite (3%-5%) gave off more hydrogen sulphide than the one which contained the most pyrite (45 per cent). True, the synthetic preparations usually gave off more gas than the natural mineral, but we attributed this difference to the greater fineness and hence larger surface of the former, a condition which is well known to favor the retention of water. That the synthetic products are finer-grained appears from the fact that they are more readily transformed into pyrite. Thus products which contained originally 5 per cent and 45 per cent pyrite, after heating in vacuo for about 1 h. at 300° to 350° showed 21 per cent and 62 per cent respectively, while pure natural marcasite after the same treatment had changed only to the extent of 6 per cent. Previous experience in this laboratory shows that fine powders are transformed into polymorphic modifications more readily than coarse materials.

Though no direct experiments for the detection of any possible sulphur dioxide or ferrous sulphate in the synthetic sulphides were made, there was no indication of the presence of either. Only the products formed at a maximum temperature of 300° could have contained sulphur dioxide, because none was formed under other conditions. If we accept the conclusion that at 200° the products occluded no reducing impurities, there is no reason to believe that occlusion occurred at 300°. The composition of the three-hundred-degree products as determined by the Stokes reaction shows a similar dependence on the acid concentration as that of the twohundred-degree products; both curves are smooth and the relation between them is rational (see fig. 1).

In regard to the occlusion of ferrous sulphate in the products, we can simply say that its presence would increase the quantity of iron dissolved in the Stokes reaction, which would then indicate too much marcasite, while, on the contrary, in the products obtained at three different temperatures (25°, 200° and 300°) the maximum percentage of marcasite indicated was always the same—not far from 100 per cent as compared with Joplin marcasite—never more than 100 per cent as would be expected if ferrous salt was occluded.

Thus, while it would be difficult, if not impossible, to prove that the synthetic products contained no inclusions, everything indicates that they do contain pyrite, and that the quantity of it is regularly influenced by increasing acid concentration and by temperature, as we shall see farther on.

4. Analogous behavior of zinc salts.—Further light is thrown on the nature of the synthetic iron disulphides by the

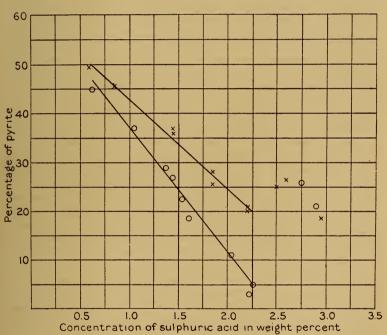
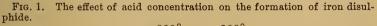


Fig. 1.



 $o = 200^{\circ}$ ;  $x = 300^{\circ}$ 

similar behavior of the zinc sulphides. We shall find in the next chapter that acid exerts the same specific influence on the sulphide of zinc that it does on the disulphide of iron, i. e., it causes that substance to crystallize in an unstable crystalline form—wurtzite. But there also the unstable form is commonly mixed with the stable form sphalerite. Now the method employed to identify the zinc sulphides is entirely different from that used for the iron sulphides. Because of

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 227.—November, 1914. 28 the transparency of the former, optical tests are the most practical. Yet we arrive at the same general conclusion in both cases: viz, that the product of hydrogen sulphide on acid solutions very commonly gives *both* crystalline forms.

F. Effect of temperature and acidity on the crystalline form of the products.—The two variables of prime importance in their effect on the crystalline form of iron disulphide are temperature and acid concentration. Experiments were made at several temperatures, as follows:

The products at 25°.-In bottles of about 2.5 liters 1. capacity were put a 5 per cent solution of hydrous ferrous sulphate, several grams of powdered sulphur and a variable quantity of sulphuric acid. The bottles were packed in ice and their contents saturated with hydrogen sulphide. Several series of these bottles were tightly stoppered and left to stand at room temperature for periods of many months. Excepting a single instance no precipitate was ever obtained where the initial concentration was as high as 0.03 per cent by weight of sulphuric acid even when the time was lengthened to a year. Precipitation always resulted when the initial acid was as low as 0.015 per cent.\* As Table I shows, precipitation started in one instance where the initial acid was  $\overline{0.059}$  per cent. This bottle had been used before for the same purpose, so that one might suspect some crystal nuclei had been left behind; yet in other cases crystals intentionally added had no effect when the original acid was '03 per cent. Whatever the cause, there can be no doubt of the fact, for the data in Table I show a close equivalency between the acid and the sulphide formed. This is not a solubility phenomenon, for again the table shows that the precipitation once started will proceed in a concentration far beyond the above figure.

A few data on the rate of formation may be of some interest. The first two experiments in the table required about one month, the third 80 days. The products in all cases were crystalline powders and microscopic examination indicated that crystallinity was complete.

The results of the Stokes method were in good accord. In Experiment 3 (Table I), where the final acid concentration was 0.23 per cent, the value obtained for (x - a), the dissolved iron, was 10.20, corresponding to 94 per cent of marcasite. Where the final acid was 0.17 per cent, (x - a) was 10.34, equivalent to 96 per cent of marcasite. These figures depend on results obtained with the purest natural marcasite we have yet found, but not all natural marcasites show exactly the same value for (x - a), and farther on we shall give a reason for believing that this product is pure synthetic marcasite.

\* Wrongly given 0.15 per cent in a previous paper, loc. cit.

Below the concentration 0.015 per cent  $H_sSO_4$  we have made no effort to experiment; we were deterred by the fear of getting amorphous products except possibly from solutions of very low iron concentration, and these on account of the small yield would be impractical to work with. Alkali sulphide solutions at this temperature unquestionably give pyrite, but what may happen in the narrow field between these two classes of solutions, i. e., in neutral or barely acid solutions, has not yet been experimentally proven. (For further considerations on the significance of these experiments for the formation of marcasite in nature, see pp. 427-429.)

2. The products at 100°.—The results obtained on the sulphides precipitated at 100° were unsatisfactory. Not only was no regular relation between the composition and conditions of formation of the products found, but the results were not reproducible. The products at all other temperatures gave results consistent with one another, and the peculiar behavior of these has not been fully explained. In general it was found that the products contained more marcasite for a given acidity than at higher temperatures, and the products all seemed to be preponderantly marcasite; apparently none contained more than 25 per cent pyrite. This was as it should be, but none of the products seemed to be pure synthetic marcasite, as we should expect from the results at other temperatures. Their anomalous behavior is possibly due to the presence of some amorphous disulphide. The products are for the most part crystalline; but most if not all contained a variable quantity of a fine, black powder which did not show any crystalline form or luster under the microscope. The occurrence of amorphous zinc sulphide of low refractive index was common in the zinc sulphides and if any amorphous material was present in the iron sulphides it would doubtless affect the results. One would expect, however, that the Stokes constant (x - a) would be higher for the amorphous substance than for marcasite, since it is higher for marcasite than pyrite, and the amorphous sulphide is less stable and more soluble than marcasite, as marcasite is less stable and therefore more soluble than pyrite. As a matter of fact, the constant (x - a) was always lower for these products than for marcasite. It may also be stated that the color of the films floated on water (p. 339) were somewhat different from those of marcasite-pyrite mixtures. Judging from the Stokes method, the products ranged from 15 per cent to 25 per cent pyrite.

3. Products at 200° and 300°.—Most of the investigation of the iron disulphides centers on the products formed at 200° and 300°. Probably because these were better crystallized, the results were always reproducible and the relations between them were regular. Of course, ideal conditions of formation would include precipitation at constant temperature and constant acidity, but even though these can not as yet be completely controlled, we have been able to determine the direction and regularity of the influence of each factor on the crystal form of the product. To keep the acidity constant would be a well-nigh impossible task, for it will be borne in mind that the formation of every molecule of sulphide is necessarily accompanied by the generation of a molecule of acid, and to keep the volume so great that the acidity would remain sensibly constant while enough sulphide is obtained for experimental purposes would be practically out of the question.

(a) Method of plotting.—It is obvious that if the acid exerts a specific influence on the composition of the product, the latter should be changing from moment to moment so long as precipitation continues. Two different products formed from the same initial acid could only contain the same percentage of the two crystalline forms when the weight of each product was the same. If the latter varied by a chance variation in the quantity of hydrogen sulphide, or by a variation in the time of reaction, the composition of the sulphide would also change. The abscissa used in the figure is therefore the average acidity (fig. 1). The results are tabulated in Table IV.

(b) Significance of the curves.—The curves show clearly that the greater the acidity up to a certain point, the greater is the percentage of marcasite formed at either temperature; and the higher the temperature for a given acidity the greater is the percentage of pyrite formed.

percentage of pyrite formed. The sensibility of the product to the influence of acid is extraordinary; even a difference of 0.1 per cent in the average acid concentration makes a difference of about 2.5 per cent of pyrite. The decrease in the acidity with falling temperature required in the formation of pure marcasite is also notable, and, when taken together with the results at the lowest temperature, 25°, this fact throws interesting light on the natural genesis of the mineral. The highest percentage of marcasite we have been able to get at 300° from sulphuric acid solution is about 80 per cent; at 200° the quantity increases to 95 per cent—the same percentage as was obtained at 25° and at 300° from hydrochloric acid solutions.

(c) Irregularity at high acid concentrations.—The plot shows further that when a product is formed in an acid of more than about 2.25 per cent average acidity, there is a sudden and somewhat irregular increase in the percentage of pyrite. We supposed at first that marcasite would be found to change when heated in acids of this concentration and higher, and experiment seemed to confirm this; for pure

#### TABLE IV.

Temper- ature	Initial acid concentration in wt. %	Final acid concentration in wt. %	Average acid concentration in wt. %	(x-a) iron dissolved in the Stokes reaction	Percent- age of pyrite
200°	0.10	1.14	0.65	7.77	45
	.75	1.35	1.05	8.23	37
	1.00	1.88	1.44	8.84	27
	1.00	1.73	1.38	8.75	29
	1.25	1.83	1.54	9.15	22.5
	1.50	1.78	1.64	9.41	18.5
	1.75	2.32	2.03	9.89	11
	2.00	2.20	2.25	10.27	5
	2.00	2.42	2.21	10.42	3
	2.50	3.00	2.75	8.94	<b>26</b>
	2.75	3.02	2.90	9.22	21
$300^{\circ}$	_ 0.10	1.08	0.29	7.43	49.5
	0.20	1.20	0.82	7.71	45.5
	1.00	1.90	1.45	8.26	37
	1.00	1.90	1.45	8.30	36
	1.50	2.22	1.86	8.97	25.5*
	1.20	2.20	1.85	8.78	28.0
	2.00	2.38	2.19	9.31	2 <b>0·0</b>
	2.00	2.40	2.20	9.24	21.0
	2.50	2.50	2.50	8.96	25.0
	2.50	2.60	2.60	8.89	26.5
	3.00	2.84	2.92	9.42	18.5

Showing the percentage of pyrite obtained in synthetic products at observed temperatures and acid concentrations.

\* The time in this experiment was 7 days; in all other experiments at this temperature it was 1 day.

natural marcasite when ground 1 h.† and heated at  $300^{\circ}$  in acid of 2.5 per cent saturated with hydrogen sulphide appeared to contain 30 per cent to 40 per cent pyrite, judged by the Stokes test. But further experiments showed that when marcasite was heated at 200° instead of 300°, or when the concentration of the acid was changed from 2.5 per cent to 2 per cent, a similar change in the marcasite took place. Thus under conditions (2 per cent H<sub>2</sub>SO<sub>4</sub> at 200°) where pure or nearly pure synthetic marcasite was formed, natural marcasite appeared to change, judging from the Stokes test alone. No corresponding change in color was seen. Such products always flocculated decidedly, a behavior which is probably accountable

+ Coarsely ground marcasite was unchanged when treated in this way.

for the results with the Stokes test.<sup>\*</sup> When marcasite which had been subjected to the above treatment was heated in vacuo, it gave off no more gas than marcasite which had never been subjected to such treatment (Table III). The former, therefore, could hardly have contained occlusions which affected the Stokes test. Some change in the marcasite, probably some change in its surface, has doubtless taken place, but when all the facts are considered it seems impossible that there should be any change to pyrite. Equally puzzling is the irregular increase in pyrite from the highest acid concentrations; some unknown condition, perhaps the greater solvent power of strong acid, enables the difference in potential between the two forms to assert itself.

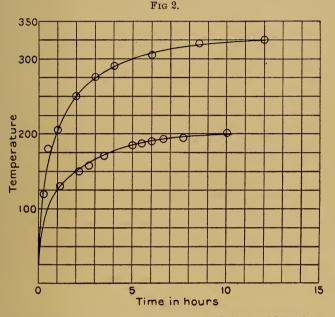
(d) The contemporaneous precipitation of pyrite and marcasite.-The simplest explanation one can offer for the relation found between the acidity and the percentage of marcasite in the synthetic disulphides formed from acid solutions. is that the pyrite and marcasite crystallize simultaneously. Our general knowledge of the subject of unstable forms is quite limited, but many cases are known where the unstable form appears first and is followed by a stabler form. In the case we are considering, the stable form is found in larger quantity in the products from low acid concentration and we know the acid increases with the progress of precipitation; the obvious inference is, therefore, that less pyrite is precipitated in the later stages of the process. It might be supposed that pyrite alone is precipitated until a certain limiting acid concentration is reached, when pure marcasite appears, but this hypothesis is easily disproved, for if the percentage of pyrite in any product is known, as well as the initial and final acid concentrations which prevailed during its formation, the limiting concentration can be easily calculated and yet a different calculated value is found for every product.

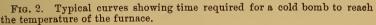
If precipitation occurred entirely at any given temperature, we could say without reserve that the percentage of marcasite in the product was a linear function of the acid concentration, at least within the errors of experiment, and then there would apparently be no escape from the conclusion that both crystalline forms of the disulphide come down together, the relative proportions at any temperature depending on the average acid concentration.

This conclusion cannot be hard and fast, however, because, owing to the considerable heat capacity of the bomb and its contents, several hours are required before the maximum temperature is reached, and consequently some of the product is precipitated while the temperature is rising (see fig. 2). It

\* See p. 375 of this number.

was at first believed that the quantity of sulphide precipitated below the maximum temperature would decrease regularly with the increase in acidity, since the total quantity of product obtained at different temperatures diminished with the acid concentration. But experiment has shown that the relation is not so simple as that, and the question arises: Why are the final products at these maximum temperatures so simply





related to the acidity? The most plausible explanation is that the influence of temperature is comparatively small in the interval in which precipitation occurs. We can get no adequate measure of this by comparing the curves for 200° and 300°, for experiment shows that when the furnace is set for 300° most of the product is precipitated (i. e., the hydrogen sulphide is nearly used up) by the time the maximum temperature is reached. Until we have more knowledge or can bring about precipitation at a constant temperature we can not state quantitatively the influence of either temperature or acidity. What we do know is the direction and regularity of both influences. It will be noticed in the figure (fig. 1) that the two lines representing the composition of sulphides from various acids at  $200^{\circ}$  and  $300^{\circ}$  respectively, should intersect at an average acidity of about .05 per cent. For the reason given above, the only meaning which attaches to this is that in a furnace set for  $300^{\circ}$ , all the product would be precipitated when  $200^{\circ}$  was reached in an acid of this concentration.

The main conclusions in this paragraph are confirmed by the results obtained with hydrochloric acid solutions.

4. Influence of hydrochloric acid.—The influence of hydrochloric acid on the crystalline form of iron disulphide was regarded with much interest, not only because side reactions due to the oxidizing effect of sulphuric acid could thus be entirely avoided, but also because in this way any peculiar effect due to *sulphuric* acid could be eliminated and the specific influence of the hydrogen ion concentration could be put to test.

The same experimental methods were followed as before, only ferrous chloride was substituted for ferrous sulphate. The ferrous chloride solution was prepared by partially dissolving a quantity of powdered iron in hot hydrochloric acid. pouring the mixture on to a filter, so that the excess of iron would keep the solution from oxidation, and catching the filtrate in a flask which was kept full of carbon dioxide by the passage of a continuous stream. After the excess of acid had been neutralized by sodium carbonate, the iron was determined and the solution then diluted with air-free water. The concentration actually taken in the experiments was equivalent to the ferrous sulphate solutions in previous experiments, and all the work was done at a maximum temperature of 300°. The products were better crystallized than any others.

#### TABLE V.

Initial acid in wt. %	Final acid in wt. %	Average acid in wt. %	(x - a)	Percent pyrite
0.10	0.60	0.35	9.63	15.
•10	•82	•46	9.77	13.
.05	•69	•37	9.81	12.
.05	•25	•15	9.94	10.
•50	•90	.70	10.20	6.
•50	•90	•70	10.31	5.
•25	.93	59	10.34	4.
.50	•86	·68	9.12	28.
.75	1.00	•88	9.13	28.

Showing the influence of hydrochloric acid in the formation of marcasite at 300°.

The numerical data are presented in Table V.\* The first point to be noted here is that the range of acidity within which it is possible to work is very limited, for a comparatively low concentration, about 1 per cent, inhibits precipitation entirely. Such products as one can obtain within this range vary comparatively little in composition also. However, excepting in the highest concentrations, the percentage of pyrite is seen to diminish as the acid concentration increases. While the results are too limited in range to determine accurately the slope of the curve, it appears to be nearly the same as that for sulphuric acid solutions at 200°. The fact that any given quantity of hydrochloric acid exercises a greater specific influence on the crystalline form of iron disulphide than the chemically equivalent quantity of sulphuric acid may be explained by the greater hydrogen ion concentration in solutions of the former. Still, we should logically conclude also that the slope of the curve ought to be steeper from the same cause. This appears not to be true, but perhaps the numerical values are, as suggested above, too limited in range to make sure of it.

Hydrochloric acid solutions unquestionably give results which are analogous to sulphuric acid solutions in the following particulars: they give products containing marcasite which increases in quantity with increasing acid concentration; the highest acid concentrations give results abnormally high in pyrite; an acid concentration is found which inhibits precipitation entirely, and finally, the *product highest in marcasite is* of the same composition as that highest in marcasite obtained from sulphuric acid solutions at 200° and 25°.

Synthetic marcasite.—These facts lead to the suspicion G. that the above product may be pure marcasite. This suspicion is strengthened by the fact that acids of 0.6 per cent and 0.7 per cent average hydrochloric acid concentration give the same product. Measured by the Stokes constant for natural marcasite, the composition should be 95 per cent marcasite. We know that this constant varies somewhat in different natural specimens of marcasite, as well as pyrite, and that impurities affect it. The purest natural marcasite from Joplin, Missouri, contained no foreign metals, but it is possible it may have contained a little oxide of iron, which would certainly have raised the value of the constant. We have no positive evidence of this, but it is strange that under three different sets of conditions the same product should be obtained, unless that product were a chemical compound. There is another explana-

\* It is interesting to note that with 0.05 per cent HCl solutions a precipitate of FeS<sub>2</sub> was obtained when no  $H_2S$  was introduced, due to the formation of  $H_2S$  by the interaction of sulphur and water at 300°. When the initial acid was greater the formation of  $H_2S$  in this way was not observed.

tion possible. The results in Table III do not prove that very small quantities of hydrogen sulphide might not be occluded by the products, and it may be that this apparent 5 per cent of pyrite is due to a slight occlusion, though there is no proof of it.

### III. WURTZITE.

It has been shown in a previous paper\* that crystalline zinc sulphide may be obtained by the action of hydrogen sulphide on acid solutions of zinc salts at sufficiently high temperatures. Nearly all our work was done on sulphate solutions, since chloride solutions for some unknown reason gave no crystalline products. Many of the products contained both the stable form sphalerite and the unstable form wurtzite,<sup>†</sup> and the experiments indicated that the more acid was the solution for any given temperature, the greater was the proportion of wurtzite; and the higher the temperature for any given acidity, the greater was the proportion of sphalerite.

It was hoped that a more thorough investigation would not only establish these points, but would also decide whether temperature and acidity were the sole determining influences on the crystalline form or whether other conditions, such as the pressure of the hydrogen sulphide, the time and the concentration of the zinc salt had any effect.

A. Method for preparing wurtzite.—Zinc sulphide is very difficult to crystallize-a fact which complicates the process of its formation and makes the conditions difficult to study. First, it needs a higher temperature than marcasite, not less than 250°, and secondly, it must be precipitated slowly; consequently a *double* tube was required in its preparation, for when an acidified solution of a zinc salt was saturated with hydrogen sulphide and heated in a *single* tube at 300°, only an amorphous precipitate was obtained. The procedure in our experiments was as follows: 20<sup>cc</sup> of a solution containing measured quantities of zinc sulphate and sulphuric acid were dropped into a platinum tube 1.5cm in diameter and 25cm long, closed at the lower end. This was supported by a piece of glass tubing of convenient size, inside a larger glass tube 1.8<sup>cm</sup> inside diameter also closed at the lower end. The outside tube, which contained a solution (either sodium thiosulphate or ammonium thiocyanate) yielding hydrogen sulphide when heated, was then sealed, enclosed in a steel bomb with water and heated to the desired temperature. After heating for the necessary time

\* Allen, Crenshaw and Merwin, this Journal (4), xxxiv, 341, 1912; Zs. anorg. Chem., lxxix, 125, 1912.

+Sphalerite undergoes a reversible transformation into wurtzite at about  $1020^{\circ}$ ; wurtzite is therefore unstable at lower temperatures.

the bomb was removed from the furnace and allowed to cool. The glass tube was removed and opened, the volume of solution remaining in the platinum tube was measured, the zinc sulphide filtered off and the final acidity determined as described in the chapter on marcasite. When sulphur was found mixed with the sulphide, it was removed by carbon disulphide before microscopic examination.

The wurtzite from these solutions never appeared in distinct crystals, but in radial parallel or felty aggregates of minute prisms. The sphalerite formed clear faceted crystals which were usually grouped, but rarely in single elongated dodecahedra. Regular groups usually appeared at first sight to be single, deeply cross-striated, hexagonal prisms up to  $0.2^{\text{mm}}$ long, but further study indicated that they were strings of dodecahedra twinned after the spinel law. Some regularly branching groups were observed, made up of such prismatic forms all pointing outward.

Since sulphuric acid, even when dilute, is reduced by hydrogen sulphide at the temperatures of these experiments, an effort was made to use solutions of zinc chloride, acidified with hydrochloric acid. Although many experiments were tried at temperatures as high as 350°, crystalline zinc sulphide was never obtained from chloride solutions.

The necessity of using a double tube and sulphate solutions made it impossible to determine accurately the acid concentration at the time the zinc sulphide was being precipitated; the sulphuric acid was not only reduced by hydrogen sulphide but also distilled in considerable quantity from the inside to the outside tube. It was of course possible, however, to determine with accuracy the acid which remained at the end of the experiments, and this *final* acid concentration proved to be the factor which determined the crystalline forms of the products at any given temperature.

Although a discussion of the distillation and reduction of sulphuric acid is somewhat of a digression from the main purpose of this paper, it is introduced because it was a necessary part of the work and the results obtained are of considerable chemical interest.

B. Reduction of dilute sulphuric acid by hydrogen sulphide.—The reduction of dilute sulphuric acid by hydrogen sulphide was proven by the universal occurrence of sulphur in the products, and the formation of sulphur dioxide in many cases. This sulphur might be regarded as the product of a secondary reaction of sulphuric acid on sodium thiosulphate when that reagent was used, but it also appeared where ammonium thiocyanate was substituted for the thiosulphate, as well as where the sulphuric acid solutions were heated directly with hydrogen sulphide.\* Solutions which contained at the start 2 per cent of sulphuric acid were always partially reduced to sulphur after being heated to 300° for one day, while solutions which contained from 5 per cent to 10 per cent sulphuric acid were further changed to sulphur dioxide under similar conditions.

C. Distillation of dilute sulphuric acid.—The acidity of the solutions was still more seriously affected by the distillation of acid from the inside to the outside tube. The results of

TABLE VI	
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Inside tube					Outside tube			
H₂SO₄ taken	H₂SO₄ from ZnSO₄	Total H₂SO₄	H₂SO₄ found	Loss from inside tube	H <sub>2</sub> SO <sub>4</sub> taken (to decompose NH <sub>4</sub> CNS)	H₂SO₄ found	Gain in outside tube	H2SO4 decomposed by H2S
2·061 g. 1·603 2·061	0·136 g. none 0·118	2·197 g. 1·603 2·179	1·599 g. 1·140 1·516	0·598 g. 0·463 0·663	0.677 g. 0.677 0.677	1·199 g. 0·940 1·086	0.522 g. 0.263 0.409	0.076 g. 0.200 0.254

Showing the distillation of dilute sulphuric acid at 300°.

Table VI will make this plain. The quantities of acid taken (Columns 1 and 6) were determined by measuring out the required volume of acid of known strength. The zinc being practically all precipitated, in the experiments quoted, its equivalent in sulphuric acid is added to 1 (Column 2) to give the total acid taken in the inside tube (Column 3). The acid left in the inside platinum tube was determined by titration of the filtrate from zinc sulphide. It should be stated here that it was ascertained by blank experiment that no sulphuric acid The was formed from the thiocyanate in the outside tube. amount of sulphuric acid in Column 7 was determined by precipitation with barium chloride. A comparison of the results in Column 7, with determinations of the free acid by direct titration, showed that the latter were always lower because presumably the acid had been partly neutralized by the bases in the glass, which is always considerably attacked under these conditions (300°). The figures in the last column refer to the differences between the losses from the inside tube and the gains in the outside tube. Some of the acid, as we have already learned, is reduced to sulphur and sulphurous acid, a fact which accounts for this.

\* See p. 396.

The loss of sulphuric acid from the inside to the outside tube by distillation was found to be fairly constant, other conditions remaining unchanged. Fig. 3 shows that the relation

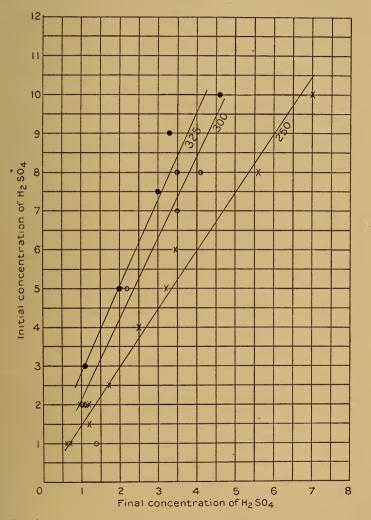


FIG. 3.

FIG. 3. Showing the relation of the initial to the final acid concentration.

between the initial and the final acid concentration is approximately linear. Since it appears from what follows that the final acid concentration is the factor which determines the crystal form of the zinc sulphide at any given temperature, we found this plot useful in ascertaining what initial concentration to choose for any desired final concentration.

D. The precipitation which takes place before the tube reaches its final temperature.—In the case of dilute acids it was impossible to prevent some precipitation of zinc sulphide during the time required for heating the tubes to the desired temperatures, but this was reduced to a minimum by having the furnaces heated to the necessary temperature before the bombs were introduced. The time required for the bomb to reach the temperature of the furnace is graphically shown in fig. 2.

A very small amount of precipitate was formed below 250° since below this temperature H<sub>s</sub>S is not formed very rapidly from the reagents in the outside tube. It is also true that zinc sulphide precipitated below 250° is amorphous and easily recognized by the microscope. In experiments done at 250°, therefore, the time required for heating the bomb may be disregarded since we are concerned only with the crystalline portion of the product. At 300° and 325° however, when the acid concentration is low, a considerable amount of zinc sulphide is precipitated between 250° and the final temperature, and we should therefore find relatively too much wurtzite in the products, since with falling temperature and constant acidity the proportion of this crystalline form increases (see pp. 421-426). Experimental evidence confirms this (see p. 420). If the initial acid concentration is fairly high (over 3 per cent) practically no precipitation occurs before the maximum temperature is reached.

# E. THE EFFECT OF CHANGING CONDITIONS OTHER THAN ACID CONCENTRATION.

1. Hydrogen Sulphide pressure.—Before the above serious variation to which the very important condition—acid concentration—was subjected, was fully realized, some efforts were made to control the pressure of hydrogen sulphide. This was done by varying the quantity of reagent, either sodium thiosulphate\* or ammonium thiocyanate,† which yields the hydrogen sulphide. It proved to be a physical impossibility to vary the pressure greatly without varying the acid concentration greatly; to judge from the pressure manifested when the tubes were opened, it varied a number of atmospheres, but in these experiments there was found no appreciable influence on the crystalline form which could not be directly ascribed to the acid concentration.

> \* Allen, Crenshaw and Johnston, loc. cit., p. 186. † Weinschenk, Zs. Kryst., xvii, 493, 1890.

2. Zinc concentration.—The experiments which were made on this point were all carried out at 300° and lasted 24 hours. The products from the more concentrated zinc solutions usually contained considerable amorphous material while the crystalline portion was generally poorly developed. The microscopic analyses are therefore more difficult and presumably less trustworthy. Nevertheless the study of the analyses of products

LABLE VII.	E VII.
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Initial H2SO4 in wt. %	Final H₂SO₄ in wt. %	ZnSO4.7H2O in wt. %	Percent amorphous	wurtzite	Per cent wurtzite in products from 2% ZnSO <sub>4</sub> .7H <sub>2</sub> O solutions and the same final H <sub>2</sub> SO <sub>4</sub> .
2	2.0	5	50	0	40
2	2.9	5	25	65	90
2	1.6	5	5-10	5	15
2	1.2	5	40	15-20	10
2	2.5	10	?	50	70
2	3.7	10	?	50.	100
2	2.7	10	considerable	50 - 75	70
2	3.0	15	50	100	100
2	3.1	15	25	100	100
2	5.6	15	5-10	0	100
2	8.0	20	25	100	100
$^{2}$	6.7	20	35	100	100
2	6.2	20	25	100	100
2	2.9	20	90	50	100

Influence of zinc concentration on the crystal form of zinc sulphide at 300°. Time 24 hours.

precipitated from solutions containing 5 per cent to 20 per cent of hydrous zinc sulphate (Table VII) brings out a number of interesting points. First, an increase in the zinc concentration increases the percentage of wurtzite in the product, as is shown by a comparison of the results in Table VII, with the product obtained from the same initial acid (2 per cent) and a *dilute* zinc sulphate solution (2 per cent) (Table XI). In the latter, indeed, only sphalerite was obtained. The observer might at first attribute this effect to the influence of the varying zinc concentration. There is a simpler explanation, however. The action of hydrogen sulphide on the zinc salts results in the formation of sulphuric acid as well as zinc sulphide, and, since the sulphide precipitate naturally increases with the zinc concentration, so also does the acidity increase. If we compare products obtained from the same final acid, the initial zinc concentration varying in one series and remaining constant (2 per cent) in the other (Tables VII and XI), we shall find that more than half the results agree within the limits of error of the microscopic determination. In other cases the quantity of sphalerite obtained from concentrated zinc solutions is greater than from dilute zinc solutions. This variation, however, may be explained if we note that in one series of experiments the acid concentration is rising, in the other falling (see pp. 421).

3. Sodium Sulphate.—In the earlier stages of our work in order to prevent the distillation of sulphuric acid from the platinum tubes (see p. 414) sodium sulphate was introduced to lower the vapor pressure. By this means it was possible to keep the acid concentration much more nearly constant during the course of the precipitation of the zinc sulphide, but the products were usually not well crystallized and in many cases

TABLE	VIII
TUDIE	V TTT*

Influence of  $Na_2SO_4$  on the crystalline form of ZnS at 300°.

Initial	Final	N- CO			Crys	talline
H <sub>2</sub> SO <sub>4</sub> in wt. %	H₂SO₄ in wt. %	Na₂SO₄ grams	Time	% Amorphous	% Wurtzite	% Sphalerite
2	2.2	1.0	1 day	60-75	50	50
2	1.9	2.0	2	nearly all	?	?
<b>2</b>	2.1	2.0	1	100		
5	3.4	1.0	1	20	?	nearly all
5	3.5	2.0	$1\frac{3}{4}$	25	67	33
5	4.0	5.0	1	50	50	50
8	6.2	2.0	1	some	?	some
10	6.8	2.0	$1\frac{3}{4}$	15	?	100
10	7.0	2.0	1		no ZnS	
10	6.6	5.0	1	40-50	100	?
10	7.6	5.0	1	25	100	0
10	7.5	5.0	1	5	70-80	20-30
15	10.2	5.0	1	20-30	90-95	5-10
15	11.4	5.0	1	30-40	90-95	5-10
20	12.1	5.0	$1\frac{3}{4}$	0	99	<1

an estimate of the percentage of wurtzite could not be made. The results are shown in Table VIII. Almost without exception the products show more sphalerite than those obtained from solutions of the same *final* acid concentration where sodium sulphate was not used. Although this may be due specifically to the presence of sodium sulphate it seems more probable that the variation is due to the reduction of the

hydrogen ion concentration owing to the formation of sodium acid sulphate. This hypothesis seems to be supported by the fact that the precipitates from 2 per cent initial sulphuric acid solutions were largely amorphous when sodium sulphate was used, whereas when it was not used the products from 2 per cent sulphuric acid were well crystallized, becoming amorphous only when the acid concentration was reduced to less than 1 per cent.

Time.-Since wurtzite is unstable below 1020°\* it was 4. thought that a longer heating of the products with the solution out of which they crystallized would cause the wurtzite to change into sphalerite. It was impossible to obtain conclusive evidence on this point owing to the fact that the time could not be increased without a corresponding decrease in acid concentration due to the reduction of the sulphuric acid by the hydrogen sulphide, which had to be renewed continually to prevent solution of the zinc sulphide. The duration of each experiment is given in the tables (X-XII) and it will be seen that at 250° (Table X) (the reduction of the acid is slow enough to allow a long heating at this temperature) there is no increase in sphalerite in the products when they are heated 5 days instead of 3 days, provided the acid concentration does not fall below a certain limit. The following experiment shows that at 325° wurtzite is not changed to sphalerite in one day if the acid concentration is high but considerable change occurs in one day if the acid concentration is low.

F. Evidence that wurtzite is changed to sphalerite by heating with dilute acid.—A product which had been made from a solution, the final acidity of which was 4.2 per cent, by heating for one day at  $325^{\circ}$ , consisted entirely of wurtzite. This wurtzite was again put into a platinum tube with 3 per cent sulphuric acid saturated with hydrogen sulphide and sealed in a glass tube containing 0.5 g. ammonium thiocyanate and 0.66 g. sulphuric acid dissolved in  $15^{\circ\circ}$  of water in the outside tube. The air in the glass tube was replaced by hydrogen sulphide before sealing. Except for the acid concentration this tube was similar to the one in which the wurtzite had been formed. After heating for one day microscopic examinations showed that the wurtzite had well-formed new crystals of sphalerite growing on it. The acid concentration had fallen to 1.45 per cent owing to distillation and reduction.

Additional evidence on this point is given in Table IX. As has been stated (page 416), some zinc sulphide is precipitated from solutions having an initial acid concentration of 3 per cent or less before the tubes reach the temperature of the furnace. When the furnaces were set for 300°, or higher

\* Allen, Crenshaw and Merwin, loc. cit.

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TA	BLE	IX.	

Showing that wurtzite is changed to sphalerite by heating with dilute acid.

Time in hours	Temperature of furnace	Initial H2SO4 in wt. %	Final H2SO4 in wt. %	Product			
				Composition of Crystalline Part		% Amorphous	
				% wurtzite	% sphalerite		
7	300°	2.0	1.9	100	0	trace	
8	$300^{\circ}$	3.0	2.2	0	100	5-10	
7	$300^{\circ}$	3.0	2.5	95	5	1-2	
$8\frac{1}{2}$	$325^{\circ}$	3.0	1.9	95	5	2-3	
11	$300^{\circ}$	2.0	1.1	33	67	trace	
12	$300^{\circ}$	3.0	2.0	60	40	2-3	
11	$300^{\circ}$	3-0	2.4	100	0	5-10	
12	$325^{\circ}$	3.0	1.7	10	90	5-10	
24	$300^{\circ}$	2.0	1.5	0	100	5-10	
24	$300^{\circ}$	3.0	2.0	0	100	5	
24	300°	3.0	1.9	50	50	0	
25	325°	3.0	1.1	0	100	trace	

temperatures, much of this first precipitate was crystalline and contained a larger percentage of wurtzite than that portion which was precipitated after the final temperature was reached. The products which were obtained (Table IX) at the end of 7 or 8 hours must have been precipitated before the temperature of the furnace (column 2) was reached. With one\* exception they consist largely of wurtzite.

At the end of 11 or 12 hours the percentage of wurtzite is, in general, much less. This is, no doubt, partly due to the fact that more zinc sulphide has been precipitated and this must have been largely sphalerite since it was precipitated after the maximum temperature had been reached. In every case except one, however, the wurtzite had entirely disappeared at the end of 24 hours. It is evident that the wurtzite present at the end of 8 and 12 hours has been changed to sphalerite by further heating with dilute acid.<sup>+</sup> This cannot be explained as a simple case of an unstable form precipitat-

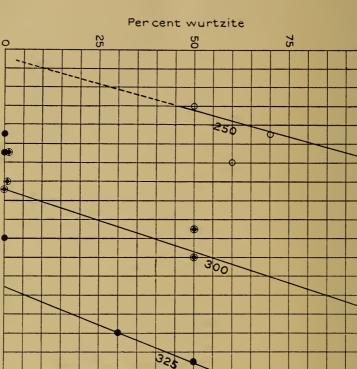
\*We have no explanation for this apparent exception. We have found that the time at which precipitation begins varies considerably in different experiments, and it may be that in this case no precipitation took place until the temperature of the furnace was practically reached.

† It might be objected that the more soluble wurtzite had been dissolved away in these cases, leaving the sphalerite. This could not have occurred since an excess of hydrogen sulphide was always found at the end of the experiments and the weight of the products was always greater at the end of 24 hours. The wurtzite had evidently been transformed and probably by solution and recrystallization, since there is no evidence that the change occurred in the solid state. ing first and changing to the stable form with time, since it is specifically dependent on the acid concentration. In Table XI, it is shown that at 300° even after 48 hours wurtzite is entirely unchanged provided the acid concentration is kept sufficiently high. The evidence given above forces the conclusion that the crystal form of zinc sulphide, under the conditions of our experiments, depends on the final concentration of acid with which it is heated, and not on the concentration out of which it is precipitated. For this reason the final acid concentration has been used in plotting the results.

The above conclusion is valid only when the concentration of the acid falls during an experiment, and this always occurred when 2 per cent zinc sulphate was used. This concentration of zinc sulphate yielded the best developed crystals and was always used except in the series where the influence of the zinc concentration was studied. If the acid increases during an experiment and the initial acid concentration is low enough for the formation of sphalerite, this sphalerite will naturally persist, since it is the stable form, after the acid has increased to the concentration from which wurtzite will form. In such a case the crystalline form depends on the acidity at the time of formation. In the concentrated zinc solutions, Table VII, the acid increased during the experiments, and this accounts for the fact that more sphalerite was found there in some cases than in products from dilute zinc solutions (2 per cent) with the same final acid concentration.

G. The influence of acidity in the formation of wurtzite.— The evidence accumulated by a more complete study of this subject entirely corroborated the earlier indications. It has been shown that, in all probability, the changing of other conditions, such as the pressure of the hydrogen sulphide, the zinc concentration, and the addition of sodium sulphate has no appreciable effect on the crystalline form. The influence of acid, however, is in some ways even more striking than it was in the case of marcasite. At 300° and 325° we were able to obtain crystalline products varying in composition from pure sphalerite, through mixtures of the two forms, to pure wurtzite. In the iron disulphide mixtures, we were not able to obtain from acid solutions a product which contained more than about 50 per cent of the stable form (pyrite).

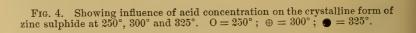
In the investigation of the two sulphides of zinc, however, many difficulties were encountered which were not met with in the case of the disulphides of iron. In the first place the range of temperature was very restricted. As has been said, only amorphous zinc sulphide was obtained below 250°, and, as is shown in Table XIII, only sphalerite was obtained at 350° or higher, though the acid concentration was increased to the point at which no precipitation took place.





100

0



 $\frac{2}{2}$  3 Final percent H<sub>2</sub> SO<sub>4</sub>

4

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The determination of the percentage of wurtzite in the products was done by microscopic estimation, and naturally the accuracy of this method, especially as the wurtzite was usually coated with sphalerite and frequently mixed with amorphous material, can not be compared to that of the Stokes reaction which was used with the disulphides of iron. When the products consisted entirely of one of the two forms, the microscopic estimate was, of course, entirely satisfactory.

The results are given in Tables X to XII, and plotted in fig. 4. The final acid concentrations, instead of the average concentrations, are here taken as abscissas for reasons already given (p. 421).

1. The question of a linear relation between the percentage of wurtzite and the final acid concentration.-Considering the difficulties of the work the results show surprising regularity. When the determinations were made, the microscopist was without knowledge of the experimental conditions under which the different products were formed and the estimates could not have been biased in any way. The results are of more interest, because of the similarity to those obtained in the synthesis of pyrite and marcasite. The reader will bear in mind that in the latter case a linear relation was found between the acidity and the percentage of marcasite, and that the only satisfactory explanation of this relation was that the two crystalline forms were precipitated at the same time, the proportions varying with the acidity. There are some facts about the formation of the zinc sulphides which are not in accord with the supposition of the simultaneous precipitation of the two. The wurtzite is very commonly coated over with sphalerite, which must, of course, have formed later. There are, however, often separate crystals of sphalerite which may have been formed simultaneously with the wurtzite and before the final coating. Simultaneous precipitation of the two forms is, perhaps, in this case, not a necessary consequence of a linear relation between acidity and composition, for the reason that synthetic wurtzite appears to undergo change into sphalerite subsequent to its formation whenever the acidity falls sufficiently, while marcasite never suffers a similar change so far as we know. Still, in view of the difficulties both in following the experimental processes and in estimating the composition of the products, it would be unwise to insist on the existence of a linear relation here, though the parallelism between the results on the synthesis of the zinc sulphides and those on the iron disulphides is remarkable. The results, however, leave no doubt of the specific influence of acid on the crystalline form of zinc sulphide, nor of the conclusion that when wurtzite and sphalerite are formed together, the products precipitated

# Allen, Crenshaw, and Merwin-

### TABLE X.

Influence of acid on the crystalline form of ZnS at 250°. All solutions contained 2% ZnSO<sub>4</sub>.7H<sub>2</sub>O and were precipitated by H<sub>2</sub>S from 0.5 g. NH<sub>4</sub>CNS.

	Final H₂SO₄ in wt. %	Product				
Initial H <sub>2</sub> SO <sub>4</sub>			Composition Pa	% Amorphous		
in wt. %		Time	% wurtzite	% sphalerite		
1.0	0.6	3 days	50	50	60	
1.0	0.7	4 <i>"</i>	?	?	80	
1.5	1.2	3 "	60	40	50	
2.0	0.9	4 "	70	30	15	
2.0	1.1	3 "	5	95	5	
2.0	1.2	5 "	99	1	0	
2.5	1.7	5 "	99	1	5	
4.0	2.5	2 "	100	0	0	
5.0	+	2 "	100	0	5	
6.0	$2\cdot9$	3 "	no	precipitate of	ZnS	
8.0	5.6	3 "	"	· · · · · · · · · · · · · · · · · · ·	"	
10.0	7.0	2 "	66	"	"	

#### TABLE XI.

Influence of acid on the crystalline form of ZnS at  $300^{\circ}$ . All solutions contained 2% ZnSO<sub>4.7</sub>H<sub>2</sub>O and were precipitated by H<sub>2</sub>S from 0.5 g. NH<sub>4</sub>CNS.

		Product				
Initial H₂SO₄	Final H2SO4 in wt. %		Ē	Composition of Crystalline Part		
in wt. %		wt. % in wt. %	Time	% wurtzite	% sphalerite	
0	0.3	$2\frac{1}{2}$ day	7S		100	
1.0	1.4	3 "	2 <b>*</b>	98	75	
1.0	t	4 "	0	100	5	
2.0	+		0	100	0	
2.0	1.1	2 "	2 or 3	97-98	5	
2.0	1.2	1 "	0	100	10	
3.0	1.9	1 "	50	50	0	
5.0	2 <b>·2</b>	$1\frac{1}{2}$ "	50	50	0	
8.0	3.5	$1\frac{1}{2}$ "	99	1	0	
8.0	2.8	1 "	100	0	0	
8.0	3.7	1 "	75	25	0	
10.0	3.4	2 "	100	0	0	
10.0	3.3	2 "	100	0	0	
10.0	3.7	1 "	25	75	0	

\* This wurtzite consisted of only 2 or 3 minute pieces of detached crusts. + Not determined.

#### TABLE XII.

 NH4CNS.

 Product

 Initial
 Final
 Composition of Crystaline

  $H_2SO_4$   $H_2SO_4$  Part
 % Amorphous

in wt. %	Time			
	Time	% wurtzite	% sphalerite	
0.9	1 day	0	100	15
1.1	1 "	0	100	trace
2.0	1 "	0	100	0
2.3	1 "	60	40	0
3.0	1 "	30	70	0
3.3	2 "	50	50	0
4.2	1 "	100	0	0
4.6	1 "	nc	precipitate of	ZnS
	$     \begin{array}{r}       1 \cdot 1 \\       2 \cdot 0 \\       2 \cdot 3 \\       3 \cdot 0 \\       3 \cdot 3 \\       4 \cdot 2     \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Influence of acid on the crystalline form of ZnS at 325°. All solutions contained 2% ZnSO<sub>4</sub>.7 $H_2O$  and were precipitated by  $H_2S$  from 0.5 g. NH<sub>4</sub>CNS.

from higher acid concentrations contain higher percentages of wurtzite.

2. Conditions necessary for the genesis of either form of zinc sulphide alone.—Conclusions drawn from experiments which resulted in products consisting entirely of wurtzite or entirely of sphalerite were much more satisfactory, since the microscopic analyses of such products were naturally more certain. At three of the temperatures investigated,  $250^{\circ}$ ,  $300^{\circ}$  and  $325^{\circ}$ , it was found that when the final acid concentration remained above a certain definite limit, wurtzite\* was the only crystalline form obtained. At two of the temperatures ( $300^{\circ}$  and  $325^{\circ}$ ) a final acid concentration was determined below which sphalerite\* was the only crystalline form obtained. When the final acid concentration lay between these limits, both wurtzite and sphalerite were found in the products.

At 250° (Table X) practically pure wurtzite was obtained whenever the final acid remained as high as 1.2 per cent; if the acidity fell to 0.6 per cent the percentage of wurtzite was reduced to 50 per cent, but further reduction in the quantity of wurtzite was impossible since weaker acids gave only an amorphous product. It seems certain that if a crystalline product could be obtained, a concentration of less than 0.5 per cent sulphuric acid would be necessary for the formation of pure sphalerite at this temperature.

At 300° (Table XI) it was possible to determine the final acid concentrations necessary for the formation of either crystalline form alone. Practically pure sphalerite was obtained

\* Amorphous zinc sulphide was sometimes admixed.

in every case when the final acidity was not higher than 1.5 per cent; pure wurtzite resulted when the final acidity was 2.8 per cent or higher.

At  $325^{\circ}$  (Table XII) pure sphalerite was obtained from final acids of 2 per cent concentration or less; pure wurtzite was not obtained until the final acid rose to 4.2 per cent.

At 350° (Table XIII) sphalerite only was obtained in every experiment. At this temperature the necessary acid concentra-

#### TABLE XIII.

Influence of acid on crystalline form of ZnS at 350°. All solutions contained 2% ZnSO4.7SH2O and are precipitated by H2S from 0.5 g. NH4CnS.

Initial H₂SO₄ in wt. %	Final H <sub>2</sub> SO <sub>4</sub> in wt. %	Time	Product
1	0.4	1 day	Some sphalerite, much amorphous, no wurtzite
5	4.2	1 "	All sphalerite
10	5.1	1 "	Probably all sphalerite
10	4.3	1 "	All sphalerite
10	4.2	1 "	Some sphalerite, much amorphous, no wurtzite
12	4•4	1 "	No precipitate
15	5.9	1"	α <sup>1</sup> <sup>1</sup> α

tion for the formation of any wurtzite at all must be higher than 5.1 per cent, above which no precipitate was obtained.

It is evident from these experiments that the higher the temperature the higher the acid concentration necessary to condition the formation of the unstable form, wurtzite, alone. The same was found to hold true for marcasite.

In fig. 5 are plotted the final acid concentrations necessary for the formation of either form of zinc sulphide alone, against the temperature. Conditions of temperature and acidity represented by the area above the line AB give rise to pure wurtzite. The area below the line CD represents the conditions for the formation of pure sphalerite, while in the area between the two lines mixtures will occur. From this plot the acid concentration necessary for the formation of wurtzite at any given temperature may be determined. It is unfortunately thus far impossible to obtain crystalline zinc sulphide at ordinary temperature, and so great an extrapolation of the curve AB would be unconvincing, but the indications are that only a very slight acidity would be necessary for the formation of pure wurtzite, if the rate of formation could be so controlled as to give a crystalline product at ordinary temperatures.

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IV. NATURAL GENESIS OF THE SULPHIDES OF IRON AND ZINC.

In the beginning of this paper, it was stated that former experiments of the authors showed that only the stable forms of the sulphides of iron (FeS<sub>2</sub>), zinc (ZnS), and mercury (HgS), viz: pyrite, sphalerite, and cinnabar, could be obtained from alkaline solutions, and the corresponding unstable forms, marcasite, wurtzite and meta-cinnabar (?) had only been

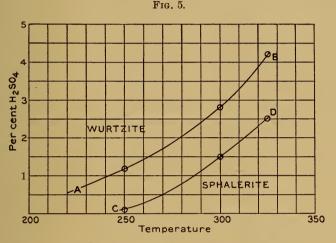


FIG. 5. Fields of precipitation of sphalerite and wurtzite.

obtained from acid solutions. A revision of a portion of that work in the present paper confirms the former results. Some new evidence bearing on the genesis of several of these minerals in nature has recently been brought to our attention. Our experiments on the formation of pyrite from alkaline solutions extended from 300° down to 70°. Pyrite had also been observed as a product of alkaline waters in nature at a temperature of 55°.\* Evidence is now at hand which proves that from *cold alkaline solutions* also, pyrite and not marcasite is obtained.

A. Pyrite from cold alkaline solutions.—Mr. C. E. Siebenthal,† of the U. S. Geological Survey, has made observations on a number of springs in which it can hardly be doubted that pyrite is now forming. These are the "White Sulphur" and "Black Sulphur" occurring in the town of Sulphur Springs, Arkansas. Both contain a dark sediment which has separated

\* In the Carlsbad Springs. See Daubrée, Géologie experimentale, p. 93 (Paris, 1879).

<sup>+</sup> Bull. U. S. Geol. Survey 606, Origin of the Joplin Lead and Zinc Deposits. In preparation.

from the water and which has been shown by analysis to consist largely of ferrous sulphide mixed with much smaller quantities of the sulphides of zinc, lead and copper. Cementing together the sand grains of both springs was also found pyrite in microscopic crystals, on many of which Merwin was able to identify the cube and octahedron. No marcasite was found. The waters of these springs closely resemble that of deep wells in the same geological horizon; they are predominantly alkali chloride and carbonate waters, they smell of hydrogen sulphide and are faintly alkaline.\* Thus it becomes evident that the alkaline nature of the water irrespective of the temperature is sufficient to condition the formation of pyrite. Mr. Siebenthal has kindly placed at our disposal two samples of sediment from deep wells which further correlate natural processes with those of the laboratory. One of these wells is in St. Louis, Missouri, the other in Columbus, Kansas. The waters from both wells are of the same general character as the springs; they are not only decidedly alkaline, but contain a recognizable excess of soluble sulphide. The mud was deposited or settled after the waters had been pumped into storage reservoirs and had stood for an unknown time, probably about a year.+ The sludge consisted of ferrous sulphide, free sulphur, which was dissolved out by carbon disulphide, and a substance having the color of ground pyrite, insoluble in hydrochloric acid, giving tests for both iron and sulphur, and showing no crystal form when examined under the microscope. In addition to these products the sediment from the Kansas well contained also a crystalline substance resembling pyrite but in crystals too small for identification.<sup>‡</sup> Now, we know that a soluble polysulphide gives with a ferrous salt a precipitate of ferrous sulphide and sulphur, and we have observed in the laboratory that they unite at 100° to form amorphous disulphide, which in time crystallizes to pyrite. In the waters of the springs and wells which we have just cited, it is plain that the same processes go on very slowly at ordinary temperature.

B. Paragenesis of marcasite and wurtzite with calcite.—We have stated previously that marcasite is commonly a product of surface waters and have concluded that it may have formed from acid solutions, because the solutions from which it crystallizes are doubtless formed in many cases by the oxidation

\*Both are alkaline toward rosolic acid and the White Sulphur water gives a trace of color with phenolphthalëin. Small recent calcite crystals and recent quartz crystals occur in the Black Sulphur Spring. †Mr. Siebenthal's investigations have brought out the fact that these are not unused by the thete the second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second se

not unusual cases, but that the deep wells of this region in practically all cases yield a sediment of similar nature.

‡ It was impossible to use the Stokes method to identify this substance, for not only was the quantity at our disposal too small but it was mixed with vegetable matter which could not be removed.

of sulphides, including pyrite or marcasite. Mr. Siebenthal has recently submitted some specimens of marcasite imbedded in calcite from Crystal Cave, Joplin, Missouri; and Mr. J. B. Umpleby a specimen of wurtzite also imbedded in calcite. The nature of these crystals indicates that they did not develop in free space, but that they crystallized simultaneously with calcite.\* If so, the marcasite and wurtzite must have crystallized from solutions containing no stronger acid than carbonic acid, and probably at the ordinary temperature. It should be borne in mind that all the solutions used in our experiments, though dilute in some cases, were incontestably acid or incontestably alkaline, so that the specific influence of each is unquestionable. The nearest approach to the above conditions we have been able to employ are given on page 404, where we found that pure marcasite, or at any rate very nearly pure marcasite, was obtained from a solution containing 0.015 per cent sulphuric acid. Between this degree of acidity and very slight alkalinity+ at ordinary temperatures, there exists a narrow field which has not been explored, nor does it present a promising field for exploration. We only know that in solutions containing only hydrogen sulphide, and therefore close to neutrality (reaction with ferric hydroxide suspended in water), pyrite is obtained at 150°.2

We have also shown that wurtzite, in the temperature interval where it could be crystallized, was formed from acid solutions, and the concentration of the acid demanded for the inhibition of sphalerite grows less with descending temperature as it does with pyrite.

С. Paragenesis of pyrite with calcite.-Pyrite also may be contemporaneous with calcite. A specimen of both marcasite and pyrite in calcite was obtained by Mr. Siebenthal and examined by Dr. Merwin.§ The latter believes that we have here two distinct generations of iron disulphide, the marcasite before the pyrite, and each contemporaneous with calcite. It would be unwise to attempt a discussion of the problem here presented without further evidence, but it might be suggested that calcite has been formed in the laboratory by precipitation with alkali carbonate, as well as from carbonic acid solutions, and its occurrence in recent crystals in the slightly alkaline waters of the sulphur springs above cited proves also that pyrite and calcite can form from the same solutions.

It is also possible that in some cases pyrite and marcasite form together in nature, though the specimen in question does not appear to have formed in that way. Our experiments

\* H. E. Merwin, The simultaneous crystallization of calcite and certain sulphides of iron, copper and zinc, this Journal, (4), xxxviii, p. 355, 1914. † The waters of the sulphur springs just cited were almost neutral. ‡ This Journal, (4), xxxiii, 181, 1912; Zs. anorg. Chem., 1xxvi, 215, 1912.

§ Loc. cit.

show conditions of temperature and acidity under which the two minerals may be formed at will together and apparently simultaneously.

#### Summary.

1. Our former results on the genesis of marcasite and wurtzite have been reinvestigated, the former conclusions have been confirmed and new data determined. The specific influence of acidity and alkalinity on the crystalline form of the sulphides investigated has been much more rigorously demonstrated. Only from acid solutions were the unstable forms obtained. The sulphides were prepared by the action of hydrogen sulphide and sulphur on acidic solutions of zinc salts and by hydrogen sulphide and sulphur on acidic solutions of ferrous salts. The unstable forms were usually mixed with the corresponding stable forms, viz.: sphalerite and pyrite, and the composition of the mixtures was determined, approximately for the zinc sulphides, by microscopic estimation; and within 1 to 2 per cent by the Stokes method for the iron disulphides.

2. As previously found, the higher the maximum temperature of experiment, other conditions remaining unchanged, the greater the quantity of the stable form, pyrite or sphalerite, obtained in the product.

3. As previously concluded, the higher the percentage of acid in the solution, other conditions remaining unchanged, the greater in general the quantity of the unstable sulphide, marcasite or wurtzite. The relation between the percentage of marcasite and the average acidity was practically linear for maximum temperatures of 200° and 300.° There are also indications of a similar relation in the case of wurtzite. In the case of wurtzite, however, the final acid was found to be the determining factor, since at 300° and 325° wurtzite appears to change into sphalerite when heated with sufficiently dilute The temperature-acid field in the case of zinc salts may acid. be divided by two boundary curves into three sub-fields, a high acid field in which only wurtzite is obtained, a low acid field where only sphalerite is obtained, and an intermediate field where mixtures of the two are obtained.

4. No crystalline zinc sulphide could be obtained from hydrochloric acid solutions, but the iron disulphides were crystallized from them, and always contained much more marcasite for an equivalent quantity of acid; i. e., hydrochloric acid has a much greater influence on the crystalline form than an equivalent quantity of sulphuric acid, which should be the case if the hydrogen ion concentration were the real determining factor. 5. The acid concentration required to give rise to pure marcasite or pure wurtzite falls with the temperature and is close to neutrality for marcasite at ordinary temperature, and probably so for wurtzite.

6. Several conditions other than acidity and temperature were varied in the formation of wurtzite, where the process was necessarily more complicated; these were zinc concentration, addition of sodium sulphate to the solutions, and hydrogen sulphide pressure. None of these had any influence except as they affected the acidity.

7. At the temperatures of 25° and 200° from sulphuric acid solutions and at 300° from hydrochloric acid solutions, we obtained a product containing 95 per cent of marcasite as compared with the purest natural marcasite we have had in our hands. Since this determination depends on the quantity of iron dissolved from the mineral under definite conditions, and different natural specimens vary somewhat, it may be that this product is pure synthetic marcasite.

8. Some new data on the genesis of the natural minerals are cited.

The authors wish to extend their thanks to Mr. C. E. Siebenthal of U. S. Geological Survey for important field data and mineral specimens, and to Mr. J. B. Umpleby, also of the Geological Survey, for a specimen of wurtzite.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., June 30, 1914.

## ART. XXXIV.—Observations on Craigton Lake ;\* by FRANK LEVERETT.

THE announcement made by Prof. G. D. Hubbard in the May number of this Journal that Lake Craigton, a small glacial lake in north-central Ohio, has tilted shore lines, was received by the writer with considerable distrust; for this lake lies outside the uplifted area of the Great Lakes region and adjoining an area in which the shore lines of the glacial waters occupying the Erie basin are horizontal. The amount of tilting reported, 4 feet per mile, is far greater than that of the southern part of the uplifted Great Lakes area, which shows only a few inches per mile. This region had been examined by the present writer before publishing his report on the Glacial Formations and Drainage Features of the Erie and Ohio Basins,<sup>+</sup> and he had noted no evidence of a tilting of shore lines. Peculiar drift embankments were, however, observed along the valley borders, which occur at lower and lower levels as one passes southward, but which were thought to be due to the presence of an ice tongue in the valley which was subsequently occupied by Craigton Lake and its outlets.<sup>±</sup> Furthermore, such lake action as the writer could discover was confined to lower positions than these drift embankments, and the shore features were found to be very faint and fragmentary. In this valley as well as in others in Ohio and Pennsylvania there seems to have been a very short-lived ponding, and for that reason it hardly seemed worth while to name the ponded waters. Their short duration was due to the slight amount of cutting down in their outlets necessary to effect more or less complete drainage. The statements in Professor Hubbard's paper put the matter in such a different light in reference to Craigton Lake that the present writer took occasion, when passing through Ohio in June, to stop off and examine the field again. Topographic maps are now available which greatly aid in determining the relations of the ponded waters to the outlets, of which two were found to have been operative. No such maps were in existence at the time of the earlier studies, and the map embracing the southern end of the lakes has appeared since Professor Hubbard made his investigations.

\* Published by permission of the Director, U. S. Geological Survey.
† Monograph XLI, U. S. Geological Survey, Washington, 1902.
‡ Op. cit., pp. 390-392.
§ Loudonville topographic sheet.

The accompanying map, fig. 1, is based upon parts of the West Salem and Loudonville topographic sheets, but in order to obtain clearness of representation roads are omitted, and only 100 foot contours are reproduced.

The slopes of the country are such that as the ice border receded from south to north across this area, there were two lines of discharge from it, one directly into Lake Fork valley and the other into an eastern tributary leading past Big Prairie. These two lines of discharge will be referred to as the Lake Fork and the Big Prairie outlets. The position of the southern end of Craigton Lake is such that the waters became ponded in the immediate vicinity of Craigton before the ice had receded from the highlands on the west far enough to allow discharge past Funk into Lake Fork. As a result there was drainage through the Big Prairie outlet down to the beginning of Craigton Lake. By reference to the map it will be seen that the summit in the bed of this outlet, at what may be considered its head, is about  $1\frac{1}{2}$  miles south of Craigton and is There is a very slight fall for two or three miles 959 feet. farther south, and this part of the outlet is included by Professor Hubbard in the lake area; but from Custaloga westward there is a descent of nearly 40 feet in five miles to Lake Fork valley. Professor Hubbard appears not to have recognized the Big Prairie outlet, though the present drainage leads down it from the summit above mentioned, 11 miles south of Craigton. Not having the help of a topographic map, and because of the windings of this outlet between morainic ridges and knolls, it is perhaps not surprising that he did not recognize it.

While this Big Prairie outlet was in operation the level of the water near the head of the outlet appears to have been at times as high as 967 or 968 feet, or eight or nine feet above the bed of the channel, the evidence for this stage of the water being found in sandy bars along the sides of the channel. Near Custaloga, as noted by Professor Hubbard, the highest water level seems to have been only about 960 feet. This slight descent of seven or eight feet in the three miles from Craigton to Custaloga being in the direction of the flow of waters from the southern end of Craigton Lake, seems easily accounted for without bringing in deformation or tilting. Inasmuch as Professor Hubbard was ignorant of the southward discharge through this outlet he accounted for the descent by shore tilting.

As soon as the ice border had receded past the north end of the upland that lies between the two outlets the waters of Craigton Lake were free to take the lower of the two outlets. This, it may be inferred, was Lake Fork channel, from the

The map also shows only such moraines and ice border features as have close relation to the history of Craigton Lake. Inasmuch as Craigton Lake and its outlets occupied what are now the major lines of drainage in nearly the whole extent of this map, and since the contours come out more clearly by omitting the drainage lines this has been done.

mere fact of the abandonment of the Big Prairie channel. There is found, however, direct evidence that the Lake Fork outlet was a little the lower. Between Funk and the hamlet of Lake Fork the highest bar or shore feature that seems referable to Craigton Lake barely catches the 960-foot contour, and seems to mark a high-water stage, just as the one at 967 to 968 feet near the head of the Big Prairie outlet is interpreted to have done. There is likely, therefore, to have been a drop of about seven or eight feet when the Lake Fork outlet was opened, and because of this the discharge through the Big Prairie outlet naturally ceased.

The head of the Lake Fork outlet is about four miles farther north than that of the Big Prairie outlet, and on Professor Hubbard's hypothesis, the shore there should have been about 16 feet higher, yet as indicated above it is really slightly lower, and such difference in altitude as the shore presents is easily explained by the shifting of the outlet. Inasmuch as the real limits of Craigton Lake were only three or four miles north from the head of the Lake Fork outlet, and are, so far as the present writer could detect, nowhere much above 960 feet, it may be stated with confidence that nothing was found to support the idea of differential uplift.

The limits of the lake, shown in the accompanying map, are such as it seems to have had at the highest stage. They are nearly coincident with the 960-foot contour of the topographic sheets, the only notable exception being near Craigton, where the bars reach 967 to 968 feet. Around much of its shore the limits are marked by a sandy strip and by a change from a smooth to a slightly undulating surface. The shore features generally, however, are very faint. The deepest part of the bed of Craigton Lake, under the present conditions of filling, is between 940 and 945 feet. Much of the lake bed has solid ground at a level above 940 feet, the amount of peaty growth being usually, as shown by ditches, only five or six feet. The lake bed was probably filled somewhat by sediment brought in by glacial streams from the receding ice sheet. The volume of water discharged from the lake is likely to have been much greater than that of the present drainage through Lake Fork because of this relation to the melting ice sheet. The persistence of the lake after the diversion to the Lake Fork outlet would be measured by the time involved in cutting the outlet channel about fifteen feet deeper, and this, it is thought, should have been accomplished in a relatively short time, perhaps before the ice had melted away from the headwaters of this drainage system.

On page 448 of Professor Hubbard's paper, attention is directed to a typographical error in an earlier paper that made

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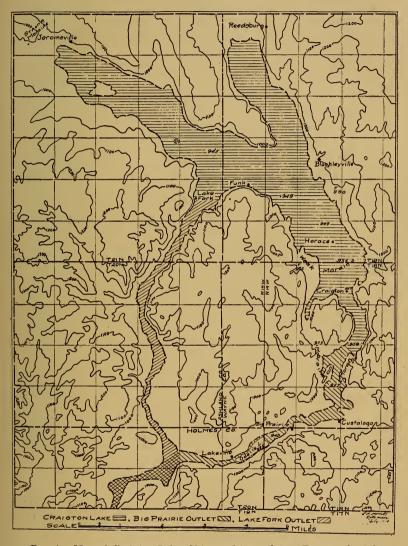


FIG. 1.

FIG. 1. Map of Craigton Lake, Ohio, and its outlets. Topography taken from U, S. Geological Survey topographic sheets (West Salem and Loudon-ville). Numerals indicate altitudes above sea-level.

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the level of the beaches near Funk and Blachleyville 765 feet where it should have been 965 feet. This corrected altitude, it will be observed, is within five feet of the altitude as determined by the present writer with topographic sheets in hand. There is thus, in reality, practical agreement between us as to the features which should be referred to lake action in the greater part of the area of the real Craigton Lake, the only point of disagreement being, as noted above, in the interpretation of the descent between Craigton and Custaloga, which the present writer would refer to the fall of the stream instead of to differential uplift. Our interpretations are, however, widely different as to features farther north beyond the real lake.

It was found that the features along the valley borders to which Professor Hubbard had run lines of precise levels to determine tilting, were, as had been suspected, the same features which the present writer had years before classed as iceborder features. They stand 30 to 50 feet or more above the level of the valley bottom, and are in many cases bordered, on the side toward the valley, by a slope with basins and irregularities, which seem to be the product of the ice edge, and to have been unaffected by subsequent lake action. In some cases these terraces or embankments are expanded into flats or plains one-eighth mile or more in width, but usually they are only a few rods wide, and are subject to frequent interruptions. Two such places on the accompanying map are exceptionally expanded. One about 1<sup>1</sup>/<sub>4</sub> miles northwest of Craigton, marked F 985 (from its altitude), covers an area of about ten acres, while one a mile southeast of Blachleyville, marked F 990, covers fully twenty acres. The former is closely associated with a weak moraine which leads out into the valley north of Craigton and seems likely to be due to the escape of glacial waters while the ice was still occupying the moraine. In the tract southeast of Blachleyville the slope toward Craigton Lake is diversified with basins which seem naturally interpreted as an ice-border product. Now that topographic maps are available it will be possible to work out an interesting detailed history of the recession of small ice tongues from valleys of this sort. Such a full and detailed mapping, however, was not attempted at the time of the writer's recent visit, which was made merely to determine the nature of the evidence in reference to differential uplift.

Ann Arbor, Michigan.

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# ART. XXXV.—Searlesite, a new mineral; by Esper S. LARSEN and W. B. HICKS.\*

#### Introduction.

In the course of the microscopical study of a number of samples from the old Searles deep well at Searles Lake, San Bernardino County, California, by Mr. Larsen, several minerals were found which could not be determined optically. A chemical analysis of one of these showed it to be a hydrous borosilicate of sodium, and the name *Searlesite* is proposed for the new mineral after Mr. John W. Searles, the pioneer who put down the deep well from which the specimen came. The authors wish to express their thanks to Mr. Hoyt S. Gale, of the United States Geological Survey, for his generosity in furnishing the material for this study.

Occurrence and association.—A sample washed from the clay at a depth of 540 feet, according to the label, was made up almost entirely of nearly white spherulites about a millimeter in diameter. From a microscopic examination these were found to be made up chiefly of the new mineral, searlesite, in minute, fairly well-formed, radiating fibers. Small grains of sand were enclosed in some of the spherulites and nearly all contained much calcite in minute grains or crystals. In addition, a little halite was recognized. The sand grains consisted of quartz, orthoclase, microcline, plagioclase, chlorite, and green hornblende. Searlesite was also recognized in a specimen marked 540' "runnings". This specimen is in massive fragments several centimeters across and is made up chiefly of pirssonite, with some halite, trona, searlesite, sand grains, clay-like material, etc.

<sup>6</sup> Physical properties and pyrognostics.—The physical properties of searlesite could not be determined accurately on account of the character of the material. It is known, however, that the mineral is rather soft and fuses below red heat to a nearly clear glass. It is readily decomposed by hydrochloric acid and is appreciably soluble in water apparently without decomposition. Its specific gravity could not be determined.

*Optical properties.*—The optical properties were measured with some difficulty and the following results are only approximate:

 $\alpha = 1.520, \gamma = 1.528.$  Optically — (?) 2E = very large

\*Published with the permission of the Director of the United States Geological Survey.

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#### 438 Larsen and Hicks—Searlesite, a new mineral.

The extinction angles vary from zero to very large. The elongation is positive for fibers showing zero or small extinction angles. The mineral is probably monoclinic in crystal symmetry.

An attempt to dissolve out the calcite with dilute acids revealed the fact that the optical properties of searlesite gradually change on treatment with acids. The indices of refraction decrease, the birefringence remains about the same, the extinction becomes sensibly parallel, and the axial angle smaller. A specimen treated with cold, dilute hydrochloric acid for several hours showed the following optical properties:

#### $\beta = 1.465 \qquad \gamma - a = .01$

Extinction parallel and elongation +.

Another specimen treated for a shorter time showed :

$$\gamma = 1.480$$
 a = 1.470 Optically -. 2E = rather large

Extinction parallel and elongation+. A specimen treated with acetic acid shows  $\beta = 1.50-1.51$ .

Chemical properties.-A sample of nearly 1.5 grams of the spherulitic material was washed with 75<sup>cc</sup> of water to remove the admixed chlorides, dried at 100° C. and preserved for analysis. Inasmuch as the sample contained large quantities of calcite and considerable quartz and feldspar, besides smaller amounts of other impurities, a method of analysis which would eliminate as much of these impurities as possible was planned. The carbon dioxide was determined on a half gram sample by the usual gravimetric method. The material from this determination was digested on the steam bath with strong hydrochloric acid, filtered through a Munroe crucible, and the residue thoroughly washed with water. The amorphous silica was then extracted from the residue by hot ten per cent sodium carbonate solution. The residue still remaining was acidified, thoroughly washed with water, dried at 100° C., and weighed. By microscopic examination this insoluble matter was found to be composed largely of plagioclase with some microcline, chlorite, quartz, hornblende, and clay. After ignition the residue was weighed and reported as insoluble matter. The silica was recovered from both the hydrochloric acid and the sodium carbonate extracts and determined in the usual way. After removing boric acid the rest of the analysis was accomplished by well-known methods, boric acid being determined in a separate portion by distillation with methyl alcohol and titration with standard sodium hydroxide in the presence of mannitol.

Larsen and Hicks—Searlesite, a new mineral. 439

The results of the quantitative analysis are as follows (W. B. Hicks, analyst):

	Per cent
Residue insoluble in HCl	11.88
CO <sub>2</sub>	12.84
SiO,	
$B_{\alpha}O_{\alpha}$	
Na <sub>2</sub> Ö	7.70
K <sub>2</sub> Ó	0.60
CaO	
MgO	4.20
FeO*	. 1.14
H <sub>o</sub> O below 105° C	0.78
H <sub>0</sub> O above 105° C	5.72
Aĺ <sub>2</sub> O <sub>3</sub>	0.22
Cl	none
SO,	none
	100.98

\* The state of oxidation of the iron was not determined.

Since it has been shown by microscopic examination that the material as analyzed contained large amounts of calcite and considerable quartz, feldspar, and chlorite, we are justified in removing these constituents from the analysis before attempting to calculate the formula for searlesite. Since the index of refraction of the carbonate was found to be that of nearly pure calcite ( $\omega = 1.658$ ), all of the calcium has been calculated as carbonate and the excess of carbon dioxide allotted to magnesium. Determined in this way, the extraneous matter in the sample is as follows:

Composition of extraneous matter.

	Per cent
Residue insoluble in HCl	11.88
CaCO,	21.63
MgCO,	6.41
H <sub>2</sub> O below 105° C.	0.78
	40.70

By removing this foreign matter from the analysis, and calculating the remaining constituents to 100 per cent, the following data are obtained :

	Original analysis	Calculated to 100 per cent	Ratios			Calculated for Na <sub>2</sub> O.B <sub>2</sub> O <sub>3</sub> . 4SiO <sub>2</sub> .2H <sub>2</sub> O
SiO <sub>2</sub>	34.00	56.41	·940	$3.72^{-1}$	$4 \times 0.93$	58.82
$B_2O_3$	9.80	16.26	.232	0.91	$1 \times 0.91$	17.15
Na <sub>2</sub> O	7.70	12.78	•206 ]			15.20
K <sub>2</sub> Ô	0.60	1.00	.011	1.14	1.1.1.1.1	
MgO	1.10	1.82	.045	1.14	1×1.14	
FeO	1.14	1.89	·026 j			
$Al_2O_3$	0.22	0.32	·004			
H <sub>a</sub> O	5.72	9.47	.525	2.08	$2 \times 1.04$	8.83
-						
	60.28	100.00				100.00

Analysis and ratios.

The ratios correspond approximately to the following formula: Na<sub>2</sub>O.B<sub>2</sub>O<sub>3</sub>.4SiO<sub>4</sub>.2H<sub>4</sub>O, or NaB(SiO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O, in which a portion of the sodium is replaced by magnesium, iron, and potassium. It seems probable, however, that the iron, magnesium, and alumina in the analysis have been derived from the associated gangue as a result of the solvent action of hydrochloric acid on the chlorite and other silicates known to have been present in the sample, rather than as having been constituents of searlesite itself. The presence of the large amount of foreign minerals makes an analysis of purer material highly desirable, but the optical study has enabled us to correct for calcite and the material insoluble in hydrochloric acid with some confidence. Searlesite differs from most other borosilicates in that it is a derivative of metasilicic acid. Its formula shows a striking analogy to that of analcite :

Searlesite	NaB(SiO,),.H,O
Analcite	

# ART. XXXVI.—The Occurrence of Unusually Large Bowlders in Gravel Deposits; by John L. Rich.\*

VARIOUS observers, particularly in western United States, have described the occurrence of very large bowlders embedded in the finer material of piedmont gravel deposits, some of them in such situations that their transportation

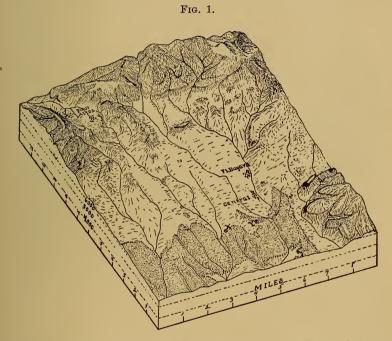


FIG. 1. Block diagram illustrating general relations of various features described. Dotted area is gravel. On the right is the eastern escarpment, the nearest possible source for the large bowlders at X and Y.

thither is difficult to explain.<sup>+</sup> In some cases the great size of the bowlders and their situation with respect to their nearest possible source is such as to render almost incredible the idea of their having been transported by running water, in spite of the well-known fact that the transporting power of torrential streams is very great. In such cases the temptation is sometimes strong to invoke the aid of glacial ice as the only agent capable of having performed the task.

\* Published by permission of the Director of the U. S. Geological Survey. + See references following; also Trowbridge, A. C., Jour. Geol., xix, 706-47, 1911. Capps and Leffingwell, Jour. Geol., xii, 702, 1904.

## 442 J. L. Rich-Large Bowlders in Gravel Deposits.

An occurrence of such bowlders in a desert gravel deposit 6 miles east of Silver City, New Mexico, happens to be so related to surrounding topographic features that a clue as to a possible mode of accumulation independent of water or ice presents itself. The belief that the explanation suggested for this particular occurrence is one of general application where topographic conditions are favorable, and should be considered and eliminated before resort to glacial ice, even in the neigh-





FIG. 2. Nests of large bowlders in piedmont gravels (at Y, fig. 1). The size of the bowlders in the group in the foreground may be judged by comparison with the cattle. A second "nest" lies in the background to the left.

borhood of glaciated mountains, leads me to present a description of the bowlders, in relation to their surroundings, together with an outline of the proposed explanation of their origin.

The location of the masses of bowlders in question with respect to the gravel deposit in which they lie, and of this to surrounding higher lands, is indicated on the accompanying block diagram (fig. 1) constructed from the Silver City, N. M. Sheet, U. S. G. S. (see also Silver City Folio, U. S. G. S., soon to be published). The gravels constitute the partially dissected northern and mountainward edge of an extensive piedmont alluvial plain, continuous toward the south with a series of

#### J. L. Rich-Large Bowlders in Gravel Deposits. 443

great waste-filled basins which make up a considerable part of southern New Mexico, but separated on the north from its parent high lands by a gravel-free lowland, 3 to 5 miles in width, developed to old age on shales and intrusives of moderate resistance. From the highlands on the east it is separated by a relatively narrow valley. The gravel plain faces the lowland to the north as a low, irregular escarpment 50 to 100 feet in height.

On the northwestern border of the lowland, near Pinos Altos, stands a group of conical peaks of intrusive rocks.



FIG. 3.

FIG. 3. One of the large bowlders in the group at X (fig. 1). Note size in comparison with the horse. In middle ground is the gravel-free inner lowland between the gravel plain and the mountains which appear in the background.

Bounding it on the north and northeast, and running in a direction a little south of east, is a great, sub-maturely dissected escarpment of flat-lying lavas—rhyolites at the base and basalts above—rising 1500 to 2500 feet above the general level of the lowland. On the east of both lowland and piedmont gravel plain stands a similar escarpment of lesser height, capped mainly by rhyolite, overlying thick and relatively weak gravels and tuffs. A temporary stream at the base of this escarpment keeps it sharp in outline, and continually retreating.

#### 444 J. L. Rich—Large Bowlders in Gravel Deposits.

The large bowlders under discussion lie at or near the northern edge of the gravel plain (at X and Y, fig. 1) and in the upper part of the gravels, 100 feet and more above the level of the streams which dissect them.

The bowlders, which so far as observed are rhyolites like those forming the escarpments to the east and the base of that to the north, occur in groups or nests of many individuals, lying close together. Three such groups, two of which appear in fig. 2, were noted. Doubtless others might be found.

One of the bowlders in place in the gravels measured 15 feet in length and 4 feet in thickness for the exposed part. How much thicker or how wide the bowlder was could not be determined. Twenty feet away, but not exactly in place lay another (fig. 3), which measured roughly 15 feet in diameter and from 6 to 9 feet in thickness. Others of smaller size lay nearby.

The cattle shown in fig. 2 indicate by comparison the size of the bowlders there exposed.

The matrix in which they lie is a desert conglomerate of medium to fine texture, the components ranging for the most part from 1-8 inch to one foot in diameter—the finer material predominating. The nearest highland from which the bowlders could have come is the escarpment to the east, 2 or 3 miles away and separated from the gravel plain by the halfmile wide valley of Whitewater Creek. Another possible source is the escarpment to the north 6 to 7 miles away, across the intervening lowland.

It might be argued, and possibly correctly, that the bowlders were carried to their present position by torrential streams before the development of the lowland, and when the escarpment stood nearer; or it might be argued that the gravels must be of glacial origin. The latter, however, clearly is not the correct explanation of this case, for there are no evidences of former glaciation in the region.

The possible explanation of the phenomenon which the writer would propose, and which seems to him the most satisfactory, is that the bowlders may have rolled down to their present position as landslides, or rockslides, from one or another of the escarpments (probably that to the east) when it stood near where the bowlders now lie. The retreat of escarpments by sapping and landsliding is too well known to require explanation. These escarpments are *now* retreating, and they must have retreated in the past. So far as it is known the geological evidence is in accord with the hypothesis that the scarp-forming lavas once covered the area now occupied by the lowland and by the part of the gravel plain where the bowl-ders lie.

#### J. L. Rich-Large Bowlders in Gravel Deposits. 445

The clue to the explanation outlined above presented itself when it was observed that huge bowlders, similar in size to those in the gravels, lie either singly or in groups at the base of the present eastern escarpment where they have rolled or slid down from the cliffs above. It is conceivable that under an aggradational regimen of Whitewater Creek these bowlders might become buried in gravels as the others seem to have been, and further retreat of the escarpment might leave them buried far out on a gravel plain.

Bowlders rolled or slid into position in this way might in some cases exhibit striation, and thus lead still further astray the geologist inclined to look upon them as of glacial origin.

If one may judge from the published descriptions, without having been on the ground, some of the so-called older drift of the San Juan region described by Cross and Howe and others\* may be susceptible of an alternative interpretation similar to that outlined above.

Several of the deposits in question occur in or at the margins of desert gravel plains; they are marked by enormous bowlders, in many cases without undoubted glacial striations; they are so situated with respect to high scarps of flat-lying lavas as to be within the area probably once covered by those lavas and therefore within the areas of possible landsliding from the scarps; and finally, at the base of the present scarps are extensive masses of landslide debris, in many respects resembling the so-called old drift, which may on further retreat of the scarps come to occupy a similar position.

In view of these considerations, it seems hazardous to assign to a bowlder-bearing deposit a glacial origin until the alternative outlined above has been specifically considered and positively eliminated.

University of Illinois, Urbana, Ill.

\*U. S. Geol. Survey, Folio 153, Rico, Colo. Cross and Howe, Bull. Geol. Soc. Am., xvii, 251-74, 1906. Hole, A. D., Jour. Geol., xx, 710-37, 1912. Atwood, W. W., Jour. Geol., xx, 385-409, 1912.

#### ART. XXXVII.—Original Color Markings of two species of Carboniferous Gastropods;\* by P. V. ROUNDY. With Plate III.

Notices of Paleozoic shells retaining original coloration have been published from time to time but no bibliographic list of such notices appears to have been collected. The appended list, though probably not complete, comprises all the references which I have been able to find.

Coloration can be recognized as original or inherent much more readily when it takes the form of a design or pattern, than when it appears as a uniform tint overspreading the shell. Of the former type are most of the instances found in the literature as well as the two noticed here. On the other hand, Waagen thought that in a solid dark violet or reddish brown tint which distinguished certain specimens of Productus abichi found in the Salt Range of India, he had found an original color-character of these shells. Another brachiopod, Cleiothyridina incrassata of our American Carboniferous faunas, frequently has the shell of a dark purplish or blackish color, in marked contrast to that of other associated species. Again, specimens of a Spirifer from a certain locality in southwestern Missouri are conspicuously tinged with lilac, but this may be due to mineralization. So too, many specimens of Naticopsis of the Altonensis group, which are not uncommon in our Pennsylvanian faunas, are conspicuous by being of a light brown color. This tint, which is more or less superficial, may be due to original coloration, but it may also be the vestige of an epidermal coating.

In so far as it has been remarked and recorded, coloration has been most frequently retained in the Brachiopods and Gastropods, while it is extremely rare in the Pelecypods and Cephalopods, though a few of the Orthocerata have been reported with such markings.

Although original color markings are undoubtedly retained in some of these Paleozoic shells it is much less certain that we have in them the original color. There can scarcely be a doubt that the processes that have obliterated the color in most of the specimens have sadly dulled it on those on which it is now found.

With the exception of *Dielasma hastatum*, of which Davidson says that he had many examples, instances of coloration in Paleozoic shells appear to be rare and occasional. It is remarkable then to find two species in a single collection which have

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furnished numerous examples clearly showing coloration. One of these is the well-known *Holopea proutana*, of which 33 specimens show this character. The other is a new species which seems to belong to DeKoninck's genus Glyptobasis and of this no less than 71 specimens retain color markings. The collection which furnished this interesting material is from the Spergen limestone at Stinesville, Indiana.

Acknowledgments are due Dr. George H. Girty for his assistance in the study of this material, and Dr. E. O. Hovey of the American Museum of Natural History of New York for the loan of Hall's type specimens of *Holopea proutana*.

#### Glyptobasis marshalli n. sp.

Shell small, averaging about 7<sup>mm</sup> in height and 3.5<sup>mm</sup> in greatest diameter and consisting of 6 to 7 whorls. Shape nearly conical; whorls usually with a slight angle just below the periphery causing the base to be somewhat flattened; sutures distinct and slightly depressed. The side of the volution is smooth but the base is covered with strong, regular revolving striæ, which become obsolete toward the periphery so that each whorl conceals the striæ on the base of the preceding one. Height of last whorl slightly greater than height of spire. In a very few shells, 12 in 325 specimens, persistent striæ

In a very few shells, 12 in 325 specimens, persistent striæ are shown which are visible on the sides of the whorls. In these specimens, however, the striæ on the sides are very obscure and might pass unnoticed even with a strong hand lens, while those on the base are very much stronger.

The aperture is roughly rhomboidal without a callous. The part forming the extension of the axial portion appears to be slightly folded backward. There appears to be no umbilicus when the shell is examined from the outside. A longitudinal section, however, shows a narrow umbilicus extending to the apex.

In the Stinesville collection there are 265 specimens, of which 71 retain distinct remains and 10 more show traces of coloration. The body color of these shells is a brownish gray while the ornamentation consists of darker yellowish-brown to mahogany colored transverse stripes. Were growth lines present the color bands would roughly correspond with them in direction. In the umbilical region, however, they merge, making the central part of the base dark-colored.

Unlike the bands on *Holopea proutana* these do not have sharp boundaries although they are very distinct. Furthermore, on this species the stripes vary considerably in arrangement. Their width is rather constant, about  $\cdot 13^{\text{mm}}$ , but in some specimens they are close together; in others they are

widely spaced. Some are persistent, extending from the suture to the dark area on the base, while others are interrupted. Often the arrangement consists of alternate persistent stripes with discontinuous stripes, as shown in fig. 5.

This is probably the first American species to be placed in DeKoninck's genus Glyptobasis.\* It has been confused with *Holopea proutana* in the past, as is shown by a few specimens in Hall's collection being included with that species. However, it is easily distinguished from *H. proutana* by its striated base and by its somewhat flattened sides.

This species is named in honor of Elliott Marshall, who made the collection from Stinesville which furnished practically all the specimens showing coloration, one specimen, however, being noted in the collection from Spergen Hill.

Locality and horizon.—Spergen limestone, Stinesville, Spergen Hill, and Harrodsburg, Indiana.

#### Holopea proutana Hall.

The specific characters of this well-known species require no comment. It is represented in the Stinesville collection by 120 specimens, of which 33 show distinct and regular color markings. These markings consist of revolving bands, six in number, of alternating light and dark tints, the first, third, and fifth being light and the second, fourth, and sixth dark. The dark bands may be described as of a grayish brown color and the others as light gray. They are very distinct on the last whorl with regular and well-defined boundaries, but are usually faint or wanting on the spire. Narrow, thread-like lines of color are also sometimes present but their occurrence is sporadic and they may best be considered as modifications of the bands.

The bands are of nearly equal width; in some specimens the third and fifth are wider, in others the second and fourth, while in still others the fourth is wider than any of the rest.

The third band, which as stated is light-colored, usually occupies the peripheral zone of the whorls. The fourth band (dark-colored) is probably the most conspicuous one of the body whorl but in the spire it is mostly covered by the overlap of the succeeding volution.

On the whorls of the spire it is the second band which is most conspicuously seen when it can be seen at all. The fifth and sixth bands are of course completely concealed on the whorls of the spire.

In 16 specimens there is but little variation from this \* DeKoninck, L. G., Annales du Mus. Royal d'Histoire Nat. d. Belgique, vol. vi, pt. 3, p. 92, 1881.

arrangement. In 3 some of the bands are much wider than the others. In 7 specimens some of the bands are divided by the above-mentioned thread-like lines; usually but one of these is seen dividing either the second, third, or fourth band. In one specimen, however, there are three of these thread-like lines (in this case dark-colored) dividing the third band. Seven specimens show only portions of some of the revolving color markings.

In addition to the specimens from Stinesville, there is one shell in the United States Geological Survey collection from Spergen Hill, Indiana, and two in Hall's original collection from same locality which also clearly show the characteristic color markings.

LIST OF CITATIONS DESCRIBING COLOR-MARKINGS IN PALEOZOIC Fossils.

Phillips, John, Illustrations of Geol. of Yorkshire, vol. 1836. ii, p. 226, pl. 15, fig. 2.

Pleurotomaria flammingera, Mountain limestone. Shows a series of zigzag color marks on one figure.

M. d'Archiac and de Verneuil, Trans. Geol. Soc. London (2), vol. vi, p. 346, pl. 27, fig. 6.

One specimen Orthocerus anguliferum with definite color marks. Devonian at Paffrath on Rhine.

Davidson, Thomas, Mon. British Fossil Brachiopoda, 1858-63. vol. ii, pt. 5, p. 12, pl. 1, figs. 6, 8, 9, and 16; pl. 49,

fig. 12. Terebratula hastata, Carboniferous with radiating color marks. Many examples.

Marsh, O. C., Proc. Am. Asso. Adv. Sci., 17th meeting, p. 325.

Mentions an Orthoceras and several gastropods with color marking, collected from same locality as the one described in 1842 by d'Archiac and de Verneuil. He states that he has Cephalopods from the Trenton limestone with indications of original color and Endoceras proteiforme Hall with distinct traces of the original color arranged in cancellated pattern.

Waagen, Palæontologia Indica, ser. 13, Salt Range Fossils, vol. i, pp. 699, 701, pl. 74, figs. 1, 4, and 8.

He considers the solid color of a few specimens of Productus to be probably the original color, stating, "While all the other specimens in the same beds are of a gravish-yellow, these are of a dark violet or reddish-brown."

1890.

Keys, Chas. R., The Nautilus, vol. iv, p. 30. He speaks of *Trachydomia wheeleri*, Swallow, from the "Coal Measures" of Illinois, where in a number of specimens " coloration of the callous portions and of the interior surface is still visible. In some indi-

1842.

1869.

1887.

viduals the color is an intense shining black, in some a purplish-black, in others a dull, faded purple."

White, Theodore G., New York Acad. Sci., Trans., vol. xv, p. 85, foot note.

Holopea symmetrica from Trenton limestone of New "Two of the specimens of this species ..... York. preserve the original shell material and one the irridescent lustre of the pearl."

Raymond, Percy E., The Nautilus, vol. xix, p. 101, two text figures.

Two specimens of Straparollina harpa from the Lower Ordovician of New York, which show lines of original color markings and possibly the original color. Raymond, Percy E., Carnegie Mus. Annals, vol. iv, p. 212, pl. 53, fig. 13; pl. 55, figs. 16 and 17. (Chazy formation.)

Holopea harpa here described are the same two specimens mentioned in The Nautilus in 1906 by the same author under the name of Straparollina harpa.

Greger, Darling K., this Journal (4), vol. xxv, p. 313, 7 text figs.

Cranaena morsii, Devonian, brachiopod which retains original color markings. Professor Greger mentions in his paper that Professor Kayser records the retention of color markings in a Devonian rhynchonelloid, but I have not been able to locate this article.

1912.

Girty, George H., this Journal (4), vol. xxxiv, p. 339, pl. 1, figs. 9–11.

Naticopsis picta here described is a Mississippian shell retaining zigzag color markings.

#### DESCRIPTION OF PLATE III.

Giyptobasis marshalli n. sp.

- FIG. 1. Apertural view showing smooth side and revolving striæ on base. FIG. 2. Base of same specimen.
- FIG. 3. Outline view of same specimen, natural size.
- FIG. 4. Specimen showing the most regular color bands.
- FIG. 5. Specimen showing alternation of persistent bands with small dots of color.
- FIG. 6. Outline view of 5, natural size.
- FIG. 7. Specimen showing the color bands varied and interrupted.

Holopea proutana Hall.

- FIG. 8. Specimen showing the six color bands on last whorl.
- FIG. 9. Base of same specimen.
- FIG. 10. Apertural view of same specimen. The second band is hardly visible on this side of specimen.
- FIG. 11. Specimen in which only the fourth band shows.
- FIG. 12. Specimen showing color bands on last two whorls. A dark thread-
- like color band is seen in upper part of third band. FIG. 13. Another specimen in which a light-colored thread-like line is shown in the upper part of fourth band on both of the last two whorls.

All specimens figured are from the Spergen limestone, near Stinesville, Indiana, and all figures save 3 and 6 are enlarged four diameters.

1906.

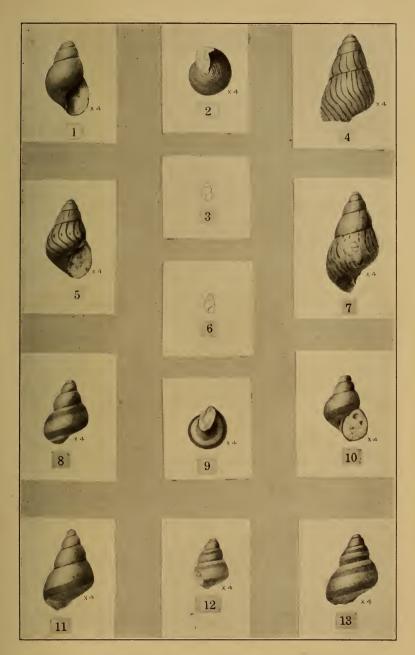
1896.

1908.

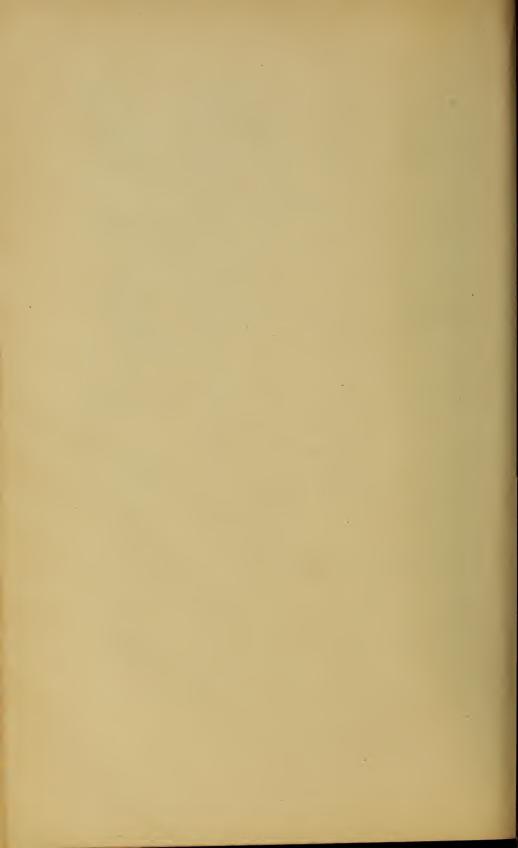
1908.

Am. Jour. Sci., Vol. XXXVIII, November, 1914.

Plate III



Carboniferous Gastropods retaining color markings.



## G. R. Wieland-Origin of Dicotyls.

## ART. XXXVIII.— Was the Pterophyllum Foliage Transformed into the Leafy Blades of Dicotyls? by G. R. WIELAND.

THE Angiospermous mode of sporophyll emplacement in the form of a compacted bisporangiate fruit-producing branch of limited growth, or "flower" with its perianth, was, so far as the paleontologic record has as yet disclosed, first evolved in Permo-Triassic time. Omitting any discussion of the catkins of Cordaites, the oldest example yet recovered characterizes Wielandiella from the uppermost Trias or Rhät. But the fruit of this slender stemmed, rather freely branching plant is of even smaller size than in existing Magnolias, and shows rather more staminate reduction than any of its mid-Mesozoic Williamsonian relatives; while the foliage may even be of very old type, the leaf taken by itself being difficult to separate from the fern Taniopteris. However it is only a few years since this ancient flower was first discovered and on recalling the similar rare occurrence of typical Angiospermous fossil flowers inferentially abundant throughout most of Cretaceous time, it becomes evident enough that the apparent absence of Cycadophytan flowers in the collections from the early Triassic has little significance.

Following this scantily recorded advent and the worldwide dispersion of the Cycadaceous bisporangiate strobilus or bisexual flower as it may equally well be called, the next great event in Mesozoic plant-history was the displacement of dominant macrophyllous cycadaceous leaf types by the microphyllous bladed net-veined leaf of the post-Wealden forest facies. How absolute and complete this change was any one may vividly realize for himself by recalling merely the outlines of the paleontologic record as he walks through any presentday forest, tropic or temperate. And any one who is willing to either leave in abeyance the Monocotyls or to very reasonably suspect them to be a secondary or early lateral offshoot from the main dicotyl stem, may thus simply vizualize the net result of plant development in the Mesozoic, since the signi-ficance of conifer culmination in the Lower Cretaceous appears to be mainly ecologic. But how was the great transition from a dominant forest of dichotomously-veined cycadophytan leaf types over into net-veined blades actually accomplished ?

Seward has recently stated that stem structures offer no difficulty in hypothesizing the descent of dicotyls from gymnospermous types. In fact the magnoliaceous genus *Drimys* has as simple stem structure as conifers, which in part are of course near to cycad stems, especially some of the older ones. While

Am. Jour. Sci.—Fourth Series, Vol. XXXVIII, No. 227.—November, 1914. 31 on the other hand Berry says that flowers are more plastic than stem structures, which are "conservative." He sees no great difficulty in the way of derivation of dicotyls from members of the Williamsonian tribe or allied forms if the stems were not in the way! And as is well known, Arber and Parkin, Dr. Scott, Professor Bessey, Hallier, and many others see no insuperable difficulty to dicotyl derivation from somewhere within the Mesozoic cycad alliance either on the score of stem, leaves, or flowers.

Evidently the view of these latter eminent students comes not only near to the true facts, but in the main represents the consensus of botanical opinion as to the origin of the Angiosperms, so far as such opinion has taken definite form.

But in any case, the question which seems hardest to answer and which leaves the paleobotanists in a more "puzzle-headed" position than any other is not the origin of either leaf or floral or stem structures so much as how it is that the dicotyls appeared so suddenly. The plant histologist may doubtless find a means whether by way of *Drimys* or *Gnetum* of leaping the hiatus of stem structure. He may too, depending somewhat on temperament and knowing how strikingly few fossil flowers have so far been found, conceive floral transformations and reductions as relatively easy.

Not so may we bridge the foliage hiatus just because instead of scattered and isolated forms on which to base a general and fairly accurate philosophic conception of the course of change in stem and in floral structure leading up to Angiosperms, there is a vast mass of representative leaf material from plantbearing terranes throughout the Mesozoic. And it all points to a post-Wealden advance of comparatively modern types of Angiosperms, seemingly from the north, and more sudden and widespread than perhaps any other supplantation faunal or floral throughout geologic history,— Une revolution, as Saporta has said, ainsi rapide dans sa marche qu'universelle dans ses effets.

Indeed we are brought face to face with the problem in even severer aspect when a notoriously conservative botanist like Seward emphasizes the general view that "the study of the plant life of past ages tends to the conviction that too much stress may be laid on the imperfection of the geological record as a factor in the interpretation of paleontological data."

Accepting however, in the hope of reaching some result that other students may be willing to accept, the hardest conditions of solution in which the knotty problem of dicotyl origin may be put, it is evident that some of the fairly obvious factors have been left needlessly obscure. And several of these facts it is now the aim to bring together in the simplest possible manner.

The early dicotyl leaves of the Potomac, like *Celastrophyllum* and *Cissites*, quite the oldest that are well known, yield no clues of direct relationship to either cycads or gnetaleans. They only show that the primitive dicotyledonous forms, whatever their flowers, soon became modern in type. Whence we are forced to note more general facts.

Ferns are frequently net-veined, and the magnificent meter broad palmate and lyre-shaped net-veined fronds of the Dictuophyllum and Camptopteris type flourished notably in the climatic conditions of the Mesozoic; although there is, with the sole exception of the net-veined cycad *Dictyozamites*, a singular absence of gymnospermous types with net-veined leaves. But that many such could have existed is sufficiently attested by *Dictyozamites*, which occurs in India, England and Antarctica; while a most important chain of possibilities is suggested by the pinnately net-veined leaf of *Gnetum gnemon* differing in no essential from leathery dicotyl leaves (Coulter and Chamberlain), and by the huge Welwitschia blades with a venation type similar in most respects to monocotyls, but also intermediate between that of the mono- and dicotyls (De Bary). Moreover, it must be a fundamentally significant fact that the plants of the great Williamsonian alliance had early in the Mesozoic developed a free branching habitus with elongated leaf-bearing nodes, and numerous and rapidly dehiscent Cycadolepis scales or just plain bud scales.

Though, so far as I know, no one has called direct attention to the further simple quantitative fact of a virtual microphylly in the Jurassic and in some Triassic cycadophytans. Even in the early Mesozoic great numbers of the cycadophytans were no longer megaphyllous and had as distinctly reduced frond contours as any dicotyledonous types. Many Otozamites and Pterophyllum leaves had, too, all through the Jura, elliptical, ovate and obovate forms which, could the pinnules have grown together and net venation arisen, would at once have produced leaves in size and form like those of oaks, chestnuts, magnolias, and much smaller-leafed plants. Indeed a leaf like the Indian Pterophyllum fissum of Feistmantel (fig. 1), a small pedunculate obovate form which may have fallen within the same family as Dictyozamites but also resembles Anomozamites, must always have its venation well conserved to prevent being mistaken for some lesser angiospermous form, like a small Dryophyllum. Furthermore in the small Wielandiella leaf the petiole expands basally, so that a second conceivable method of derivation from *Pterophyllum* blades would be by

the gradual growing forward of the basal wings along the midrib with adoption of the netted venation and suppression of the apical pinnules. The varied transformations in leaves as seen for instance in Orchids do not permit such a method of derivation to remain an unnoted possibility, but there being no evidence that the basal wing advanced beyond the condition seen in *Wielandiella*, it is necessary to further consider the method of origin by fusion of pinnules.

The venation, and especially the size and form of *Dryophyl*lum and *Liriodendropsis*, to cite definite generic examples of

FIG. 1.

A Contraction of the second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second se

FIG. 1. Pterophyllum fissum Fstm.  $\times 1/1$ . Abundant in shaly beds near Burio, Rajmahal Hills. After Feistmantel.

FIG. 2.

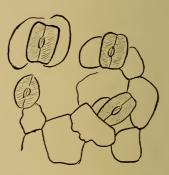


FIG. 2. Cycadeoidea ingens (type). Freehand drawing of young stomata showing their somewhat fernlike and generalized character. The form appears somewhat nearer to that of Dicotyls than does that seen in existing cycads.

Cretaceous dicotyls, do lend some plausibility to the idea of direct derivation from cycad fronds, more especially *Pterophyllum.* And according to the view of Arber and Parkin\* a cycadean type of foliage was probably long retained in a simple stemmed angiosperm ancestry, while concomitantly with development of the branch habit these early megaphyllous forms finally acquired netted veined microphyllous foliage, the so-called "sudden appearance" of the angiosperms in Neocomian times, thus being the simple resultant of rapid transition in an already highly evolved and "diversified" group.

\* The Origin of Angiosperms. Linn. Soc's. Journal-Botany, Vol. xxxviii, p. 69, July, 1907.

## G. R. Wieland-Origin of Dicotyls.

But it is not unfair to note that this theory of dicotyledonous foliage is neither more nor less than a corollary to my earlier theory of the origin of angiospermous flowers expressed in general terms, the only ones possible, evidence being limited to Cycadeoidean fructification. For Arber and Parkin do not refer to any other fossil forms directly, and draw no additional conclusions from the structure of existing forms. They simply iterate the well-known fact that while the angiosperms arise abruptly as highly evolved forms belonging to existing orders, and at once become dominant, fossil botany affords no direct evidence of types of foliage understood to be transitional from the groups peculiar to the early Mesozoic.

Because of this very hiatus, however, no one has been able to say much on the question of foliage; though the reduced condition of the flowers of Wielandiella later led me to look upon that form as the nearest known approximation to the hypothetic primitive Angiosperm line, despite the netted venation in *Dictyozamites*.\* For I regarded those flowers as offering incontestable evidence of the manner of Angiosperm And furthermore this general conception of a evolution. direct cycad-angiosperm relationship has also been reached independently by Hallier, whose wide acquaintance with existent plants entitles his views to great respect. More recently too Hallier has shown that the Berberidaceæ may be considered even more primitive than the Magnoliaceæ; while he also gives interpretory figures of the essentially primitive leaf types seen in Godoya, Touroulia and the Californian Lyonothamnus foribundus.

Now perforce the "small blade-like leaves" of Wielandiella, a distinctly *Pterophyllum*-like form, are the nearest known approach amongst Cycadophytans to the leaves of dicotyls. But after all it must be admitted that it would be a more or less gratuitous guess to go on and say that *Pterophyllum* leaves just as we know them in the Trias were extensively transformed into magnoliaceous and other dicotyledonous types. The point is that however plausible such a theory, direct evidence is lacking. For a change of this character going on in many genera simultaneously, in others less regularly, but all over the globe, must surely have left its impress so indelibly stamped on the known Mesozoic record that transition forms would long since have been found.

Were it not, then, for the vast and dominating amount of cycadophytan foliage in mid-Mesozoic deposits, and were

\* Wieland, G. R. Historic fossil Cycads, this Journal, p. 101, Feb. 1908. † Hallier, H. L'Origine et le Systeme Phylétique des Angiospermes, Exposes à l'Aide de leur Arbre Généalogique.—Extrait d. Arch. Néerlandaises d. Sc. Ex. et Nat. Série III B, Tome I, p. 146 (1912).

relatively few forms known, no doubt the student of gross morphology might very well content himself with the theory that the *Wielandiella* and other *Pterophyllum*-like leaf types

FIG. 3. Otozamites hespera Wieland.  $\times 2/3$ .

were largely metamorphosed into net-veined forms. And the more especially might this be true because there is every gradation from Nilssonias with strong tendency to pinnule fusion and blade-like form into typical Pterophyllums, and thence into

FIG. 3.

## G. R. Wieland-Origin of Dicotyls.

forms with one basal ear (*Ptilophyllum*), two basal ears (*Otoza-mites*) and finally modern and specialized cycad pinnule types. It is indeed a striking fact that the more generalized types are the older, and equally interesting to find that, as I have proven, it is exactly in the lowermost Liassic that transition types of pinnules are very abundant (fig. 3).\* While too it must never be forgotten what rarities fossil flowers really are, and what a botanic incognito with endless possibilities of primitive relationships to the Angiosperms is involved in the mere mention of the forms just now cited.

Nevertheless, this first hand point of view of transition from Cycadophytes already known must be left in abeyance, not because it is unthinkable, and not because it is in itself regarded as inherently impossible or unlikely, but just because there is such an astonishing lack of evidence for it, such an extraordinary absence of adumbrant forms, while in the existent flora there is a group of plants which would undoubtedly be classed as a possible Angiosperm precursor were it definitely recognized in Liassic or later deposits. I refer to the Gnetales, Welwitschia, etc. These, however, lack a fossil record almost entirely while in strong contrast the characteristic old cycadophytan types are the Pterophyllums; and though the latter are cosmopolitan all through Mesozoic time, nowhere do they show traces of net venation, the last members of the group being as devoid of such traces as the first. Indeed the Wealden cycads still include Pterophyllums which are on the whole even more strictly and fixedly cycadophytan in their general appearance and structure than the Triassic forms. The cycadophytan race in short appears as time goes on to rigidly fix its leaf characters, to even become senile, rather than to exhibit hypothetic transition types toward net venation. The isolation of Stangeria with slight marginal venation doubly proves this tendency to fixity.

Nor can we on last analysis consider *Dictyozamites* in itself an adumbrant form. It is not only specialized and exceptional, but distinctly cycadaceous in form to a degree emphasizing even more sharply the absence all over the globe from Triassic to Wealden time of transition forms pointing towards dicotyledonous leaf types. But what the Indian *Dictyozamites* and the accentuated form of pinnule border-netting seen in *Stangeria* do suggest, I contend, is the fundamentally

\* The leaf shown in figure 3 is from horizon 19 of the Rio Consuelo section. See my paper on the Liassic Flora of the Mixteca Alta, etc. in this Journal for Sept. 1913. This is an abundant and interesting type, and could quite as well be placed in the the genus *Pterophyllum* as *Otozamites*. The further interesting feature commented on in the text is that the obovate form is common to many species and varieties of Liassic cycads of virtually microphyllous habit. important fact, that the Williamsonian tribe must have included still other net-veined types which led directly into the Angiosperms. Although by reason of their entire nature and structure the Mesozoic examples of these true dicotyl ancestors would indubitably find place in the same section of the Cycadophytans as the known and typical Williamsonians. What further relationship such hypothetical forms had to the ancestral Gnetaleans can of course only be answered as discovery goes on.

But considering only the broader fact that these intermediate ancestral types have so long remained inscrutable, where was their home? In the Arctic and Antarctic areas of course. This is the inevitable conclusion to which the negative evidence must lead. For we are bound to assume the Angiosperm ancestry was wide in occurrence and widely related to other groups. It is indeed very difficult to believe that any of the dominant plant types have had sudden or confined origins.

Theoretically it is, as already noted, fairly easy to assume transitions from cycad to dicotyledonous leaves. But that transition, as already noted, does not appear to have passed from known forms. I repeat, in India, in Turkestan, in North America, all over Europe, the absence of precursor and adumbrant net-veined forms suggestive enough in character or impressive of number, is so universal that it is safe to say from the facts of known distribution alone that such mainly originated in the peculiar climatic conditions of the Polar areas, and there developed that invasive power which so suddenly transformed the forest facies of the globe in post-Wealden time.

The idea of extensive northern origins of dicotyls is however far from new. It has been canvassed by many botanists from the time of Forbes and Darwin. It was given speculative form by Saporta; while Nathorst and Gray showed an extensive Tertiary movement of plants from the Arctic.

Earlier than any of the above the learned Rütimeyer, in his famous essay of 1867 "Ueber die Herkunft unsere Thierwelt," recognized clearly enough that an Arctic and Antarctic continent had played a great rôle in present and past distribution; while Haacke's subsequent paper on the *north pole* as the great "Schöpfungscentrum" of the Mammalia is, in view of the intervening work of Wallace, simply a recessional view rather than a step forward. Later Wortman considered the extensive parallelism of the fossil mammalian fauna of Europe and America pointing to Arctic origin; and in the same year (this Journal, December 1903) the present writer examined the general subject, probably for the first time extending on a sufficiently broad geophysical basis the original bipolar view which is justly that of Rütimeyer and Scribner into an adequately stated general polar theory of life.

There is therefore not only negative evidence for the Polar areas as the early home of the dicotyls, but every philosophic consideration tends to emphasize this as the best hypothesis. It would be mere temerity to assert that a great majority of species originated in the polar areas, or that races have been mainly first established there. But prepotency of Arctic climatic factors in evolution is a philosophic conception which simply cannot be ignored. In fact, there can be no question that in nearly all past discussion and study of distribution the actual details in the distribution of ancient life have often been obscured and the adequate development of the boreal theory much retarded by a form of statement amounting to an assertion that "Arctic land bridges" were areas in which new forms did not originate as freely as elsewhere; notwithstanding it slowly becomes clearer that zonal distribution has existed far back in time. The distribution of the Glossopteris flora first suggests it, and one of the most striking facts of similar import brought to light in recent years has been my own discovery of the persistence of well marked Cordaites in the Oaxacan Lias.

The dicotyls present such a varied structural facies that it must be quite gratuitous to conceive them as being of monophyletic, or in any sense restricted origin. It is much better to hypothesize them as originating simultaneously in various related groups already well established in the polar areas, when climatic and geographic conditions were sharply varied, and possibly just about the period when the very first differential changes leading toward the frigid polar climates of Tertiary time set in.

The subsequent radiations of these early dicotyls over the globe we might even without fossil evidence conceive to have taken place with the greatest rapidity, long stretches of the xerophyllous evergreen cycadophytan vegetation being replaced by dicotyls with every succeeding season. All the causes for such a quick movement cannot be discerned, but the mode may. It is easy to see that as compared with the dicotyls the unchanged cycadophytans probably were over-tenacious forms holding their evergreen foliage and place in the plant community too stubbornly, while maturing their flowers too slowly. Whereas the dicotyls, with their great possibilities of seed production and continuous summer growth of succulent leaves, include a vast number of forms which are quick to spread and grow in every situation, and quick to die. Thus does it seem that the dicotyls early proved the more potential. Able to live not alone in the swamp but to form and hold on the dry hillside with every fall of leaves a rich warm humus favoring

a continual growth of new plants, they better withstood cold and quickly grew over and out beyond all their essentially conservative competitors. Thus was alike displaced first the cycadophytan underbrush and then the great coniferous forests of the early Cretaceous. And thus do we also find inescapable ecologic reasons why the paleontologic record reflects true conditions in so universally suggesting a most rapid spread of angiosperms over the globe following extensive polar development of the more characteristic initial types in the late Jurassic.

Peabody Museum, Yale University, New Haven, Conn.

# ART. XXXIX.—Unios in the Triassic of Massachusetts; by Edward L. TROXELL.

Among the Triassic specimens of Amherst College Museum there is a unique slab of sandstone containing several casts of fresh-water pelecypods, apparently of the genus *Unio*. This slab came from the Upper Triassic at Wilbraham, Massachusetts, and was the gift of Mr. Charles S. Merrick.

Professor Emerson has figured and described the best cast on this slab as *Anoplophora wilbrahamensis*,\* and the writer has developed the other casts and found that two species are present on the slab. At the time of Professor Emerson's publication, he appears to have regarded these bivalves as of possible marine origin and accordingly referred them to the genus *Anoplophora*, whose species occur in the brackish-water deposits of the Triassic of Germany. It is true that these German forms, at least in name, are usually associated by authors with fresh-water bivalves, but as they are found in association with a brackish-water fauna it is very probable that *Anoplophora* cannot be extended to embrace the American shells. While the latter cannot be definitely referred to *Unio*, it can be said that the Triassic of eastern North America has not yielded a single marine animal, while all the physical evidence points to its continental character.

Zittel says that *Anoplophora* is thin-shelled, is not bellied, and is without teeth, characters which are in strong contrast to those of the Massachusetts specimens.

U. emersoni, n. sp. (fig. 1).—The most striking features of this species are its elongation and narrowness, though these

\* This Journal, (4), x, p. 58, 1900.

Fig. 1.



Cast of Unio emersoni, n. sp. FIG. 1. Holotype.

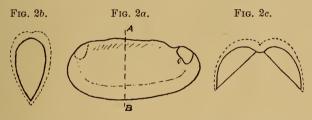


FIG. 2a. Diagram of same, showing outline, muscle scars, and pallial line;
b. Cross section of same on line AB.
FIG. 2c. Section through umbones of paratype.

F1G. 3.

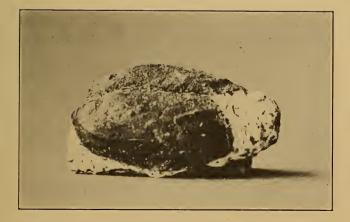


FIG. 3. Unio emersoni, n. sp. Paratype. Showing the valves opened.

#### 462 Troxell—Unios in the Triassic of Massachusetts.

characters would be less marked if the shell could be viewed from the outside. The largest specimen, a cast of the inside of the left valve, has an internal length of  $47^{\text{mm}}$ , is  $22^{\text{mm}}$  high, with a body cavity, including both valves,  $10^{\text{mm}}$  wide. The muscle scars and large hinge teeth, so far as they can be determined, are shown in the illustration, figure 2a.

A second specimen of U. *emersoni*, shown in figure 3, is an interior cast of the valves, connected and considerably opened. The section of this specimen (fig. 2c) is taken through the umbones.

In none of the specimens on the slab is there a trace of the original shell; the fossils are merely the molds of the body cavity.

The new species is named after Professor B. K. Emerson, who has spent so many active years in deciphering the difficult geology of western Massachusetts.

The presence of this second species of Unio was first noted by Professor Charles Schuchert, while Professor R. S. Lull in his memoir on the Connecticut valley\* first designated the specimen as U. emersoni. As this is a nomen nudum, the writer was asked to describe the species, and he takes this opportunity to thank the gentlemen mentioned for this privilege.

\*Bull. 24, Conn. Geol. Nat. Hist. Surv. (in press).

#### B. Smith—New Locality for Castoroides.

#### ART. XL.-A New Locality for Castoroides; by BURNETT SMITH.

THE extinct, beaver-like Castoroides obioensis Foster was first made known to the scientific world in the year 1837.\* Since then more or less fragmentary remains of this gigantic rodent have been obtained at irregular intervals and from scattered localities. For nearly seventy years, however, the Clyde find<sup>+</sup> has been the only one recorded from the State of New York. The discovery of an incisor tooth at a new locality in this state is, therefore, regarded as a matter of some interest, especially so because the collector<sup>‡</sup> took the somewhat unusual precaution of determining its horizon with considerable accuracy.

The locality of the find is in lot 10, Town of Lenox, Madison County, New York. The specimen was obtained from a bluish clay which is exposed in that portion of Cowaselon Creek§ which is commonly known as the "State Ditch." The spot is about 225 paces from the southeast line of lot 10, the distance being measured from this line in a northwesterly direction along the creek.

The exact horizon is about 8 feet below the present land surface and probably about 4 feet below the top of the blue clay, which for convenience will be designated the Cowaselon Clay. The horizon of the specimen is unfortunately below the water level of the creek. It has furnished pieces of wood, seeds, and a few molluscan shells, but, so far, no additional vertebrate remains have been found.

At the locality of the find the banks of the creek are sloping and densely overgrown. About 190 paces northwest, however, a slide has exposed a clean section, and the conditions at this point have been determined as follows:

5. About 2 feet of material probably representing a mixture of sandy soil and artificial fill.

4. About 6 inches or more of peaty matter locally known as muck.

3. From 2 to 6 inches of marl.

2. From 1 to 1.5 feet of clay with peaty bands.

1. Bluish Clay (Cowaselon Clay); about 2 feet exposed above the level of the creek and passing downward under water to an unknown depth.

\* This Journal, xxxi, p. 80. † J. Bost. Soc. Nat. Hist., v., pp. 385-391 (Hall), and pp. 391-401 (Wyman). ‡ Mr. A. A. Grant of Chittenango Station, to whose intelligent enterprise we are indebted for a knowledge of the specimen. § See U. S. G. S. Topographic Sheet of the Chittenango Quadrangle, about 3 miles northwest of Canastota. The spelling of the word Cowaselon is taken from this and other maps. The local pronunciation and understand-ing of the word appears to be Sanaws Alane. ing of the word appears to be Squaws Alone.

The blue clay (number 1 of the section) is without doubt a part of the same stratigraphic unit (Cowaselon Clay) which furnished the *Castoroides* tooth, and from the standpoint of Quaternary paleontology it is the important member of the section. Though no detailed survey of Cowaselon Creek has, as yet, been attempted, a certain number of sections have been examined. It is therefore believed that sufficient is known to warrant the presentation of a few preliminary conclusions con-

Fig. 1.



FIG. 1. Castoroides obioensis Foster. Town of Lenox, Madison County, New York. Left lower incisor tooth. A, outer view; B, inner view,  $\times \frac{1}{2}$ . Straight line between the extremities of the specimen =  $210^{\text{mm}}$ .

cerning the distribution and stratigraphic relations of the Cowaselon Clay.

On descending the creek this formation is first noticed near the road which is the northward extension of Main Street, Canastota. It appears to be perfectly continuous, and also to be the lowest exposed formation for a distance of three miles or more along the creek in a northwesterly direction. Through-

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out this stretch it is overlaid by the peat or muck. Locally thin bands of marl intervene between the basal Cowaselon Clay and the muck. In places the muck itself is covered by a sandy soil which may possibly represent stream wash from the originally meandering Cowaselon Creek.

In the vicinity of Oniontown,\* about five miles northwest of Canastota, the basal stratum in the creek bank is no longer clay but a light colored shell marl. Possibly the Cowaselon clay passes into this marl by lateral transition, but it is believed that the clay dips under the marl. The marl is overlaid by the dark peaty muck. These two formations are apparently continuous for a distance of two or three miles in a northwesterly direction.

About two miles below Oniontown the creek bends sharply toward the north. Just beyond this turn the section shows in descending order muck, marl, and a grayish or bluish clay. The marl is now quite thin. The basal clay is here the interesting member for it is highly probable that it represents the Cowaselon clay returning to the surface.

On following the northern portion of the creek to its mouth at Lakeport on Oneida Lake, it is found that all of the above described formations disappear. The banks, which are now cut through higher and more irregular ground, show only bowlder clay at base capped by a reddish laminated clay. Except for a few feet of Paleozoic bed rock at Lakeport, these latter formations are the only ones encountered in the lower stretches of the creek.

Though the investigations so far undertaken are of an admittedly preliminary character the evidence points to the conclusion that the Cowaselon Clay (yielding Castoroides) and the shell marl were both deposited in a shallow water body slightly higher than the present Oneida Lake and probably cut off from it by the barrier of glacial deposits which have just been mentioned as occurring south of Lakeport. Bluish clay is the basal formation at the northwest end of the section through this hypothetical lake. A considerable stretch at the southeast end of the section is likewise underlaid by bluish clay (the Cowaselon Clay). It is, therefore, believed that the Cowaselon Clay passes under the marl and that the two deposits represent consecutive stages in the shallowing and contraction of the lake. The almost universal capping of peat or muck illustrates the final or swamp stage which caused the extinction of the water body, and which was only terminated by the drainage ditches of civilized man.

\*See U. S. G. S. Topographic Sheet of the Chittenango Quadrangle.

#### B. Smith—New Locality for Castoroides.

The time range of *Castoroides obioensis* must be extended back as far as the Aftonian interglacial epoch.\* On the other hand, there is some evidence in favor of its contemporaneity with the North American Indian of the Delaware Valley.+ In any case it is generally recognized that the species survived the final glaciation. Of the specimen which has formed the subject of this note it can be said that it came from a formation (the Cowaselon Clay) which was deposited in a water body whose level was apparently well below that of the last icecontrolled lake, and that its position in the Quatenary time scale is probably much nearer to the present than to the period of ice-margin retreat.

No attempt will here be made to definitely correlate the Clyde and Cowaselon finds. In this connection, however, it is well to call attention to the fact that both of the New York examples of *Castoroides* were obtained from the low level swamp and lake system which extends in an east and west belt through the central portion of the state and whose deposits seldom rise far above the 400-foot contour line.

#### Department of Geology, Syracuse University.

\* "Pleistocene of Sioux Falls, South Dakota and Vicinity," B. Shimek, Bull. Geol. Soc. Am., vol. xxiii, pp. 143 and 148. + "Re-exploration of Hartman's Cave near Stroudsburg, Pa., in 1893,"

H. C. Mercer. Proc. Acad. Nat. Sci. Phila., pp. 96-104, 1894.

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## ART. XLI.—Notes on Arctic Paleozoic Fossils; by CHARLES SCHUCHERT.

#### [Contributions from the Paleontological Laboratory, Peabody Museum, Yale University, New Haven, Conn., U. S. A.]

It is becoming more and more apparent in the study of the paleogeography of North America that the lack of knowledge concerning the stratigraphy of Arctic lands is a great hindrance to a fuller realization of the geologic succession in the United States. In a broad way it is known that the Arctic faunas during the Ordovician, Silurian and Devonian spread far to the south, but as to the particular ones that attained the United States little is as vet established. In the hope of adding somewhat to this knowledge, the writer has recently examined the collections gathered by A. P. Low, C. F. Hall and J. G. Mc-Millan, with a view to fixing more accurately the geologic horizons indicated by the various fossils. Deputy-Minister Brock was so kind as to loan for this purpose the fossils in the Victoria Memorial Museum at Ottawa, and Professor B. K. Emerson sent those he described many years ago, which were collected by Hall and are now at Amherst College. For these favors the author is very thankful.

It is the general belief that the Silurian formations are the most widely distributed of Paleozoic strata in Arctic America, and this is probably true. This distribution, however, is seemingly not so general as is held, for it is now known that Ordovician and Lower Devonian strata have been mapped as Silurian. In the end it may turn out that the Ordovician formations have the greatest distribution. Of these latter, two series appear to have equally wide range: (1) those of Black River-Trenton time, and (2) those of Middle Richmond time.

That the Devonian is well represented in Arctic America first became plain through the collections made by Per Schei of the Sverdrup Expedition in the "Fram," 1898–1902. Probably all of Devonian time is represented in Ellesmereland, from the earliest Lower Devonian (Keyser) to the middle of the Upper Devonian. The Lower and Middle Devonian are well recorded here. The former appears to be very much like the Helderbergian of the United States, but the Oriskanian so far is wanting in the collections. On the other hand, the Middle Devonian is of the Euro-Asiatic realm and not of the American province, a fact not fully realized in the work of Meyer (1913).

The following faunal lists record only the more conspicuous fossils. The localities are arranged from the south northward.

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#### Northernmost Labrador, Cape Chidley.

Doctor A. P. Low spent the greater part of the years 1903– 1904 in the Hudson Bay country and the Arctic islands. While at the trading post of Port Burwell, which is just around from Cape Chidley in Ungava Bay, Low made an interesting collection of fossils from drift pieces of limestone that he thought had been brought there by the ice from Akpatok Island, many miles to the west. Among these fossils are unmistakable Helderbergian species, and as such are unknown on Akpatok it is a question whether this island is the source of these loose limestones. They may be rather from the north and from not far away, on Baffin Island.

The fossils of Cape Chidley represent three distinct horizons, as follows:

#### 1. ORDOVICIAN. From dark gray limestones.

- Labyrinthites chidlensis Lambe. A coral suggesting Halysites, and referred by Lambe to the Halysitidæ. The writer did not see the material. (Described by Lambe in Low 1906: 327.)
- Orthoceras, sp. undet. In form like Ormoceras tenuifilum but with a small siphuncle about 0.25 inch in diameter at the septa.
- Endoceras cf. annulatum Hall. A more slender form than E. annulatum, and with a smaller apical angle.
- *Endoceras*, sp. undet. In shape like the last one, but without annulations.
- Spyroceras cf. vertebrale (Hall). The annulations are about as numerous as in Hall's figures (Pal. N. Y., I) but less abruptly arched. The siphuncle does not show.
- Plectoceras cf. jason (Billings). Ami labels this P. obscurum Hyatt?. It differs from Ruedemann's description of P. jason (Bull. 90, N. Y. State Mus. : 484) in that the siphuncle is smaller, but chiefly in that the living chamber occupies three-fourths of the last volution, instead of "less than one-half volution." Diameter of shell 8.5 inches. A large and fine fossil.
- *Eurystomites*, n. sp. Ami labeled this *E. undatus* Emmons, to which group of *Eurystomites* it undoubtedly belongs. It attains, however, a larger growth, has a very wide dorsum and a shallow hyponomic sinus. It is a fine specimen with a diameter of 6.5 inches.

These cephalopods, as they all appear to occur together, indicate the lower part of the Black River formation as developed at Watertown, New York. It is probable that this horizon is also exposed on Akpatok Island in Ungava Bay. C. Schuchert-Notes on Arctic Paleozoic Fossils. 469

2. ORDOVICIAN. A black, fine-grained, thin-bedded limestone.

Basilicus canadensis (Chapman). A large tail of this very characteristic trilobite is present.

This horizon is clearly in the lower part of the Collingwood as developed at Collingwood, Ontario, a formation of wide occurrence in that province. It is of wide distribution in southern Baffin Island and will probably be found generally throughout the Arctic region where Ordovician strata are exposed. It may also occur on Akpatok Island.

3. LOWER DEVONIAN. A light-colored, thin-bedded limestone replete with fossils. The following are the species:

Zaphrentis roemeri Edwards and Haime. Rare.

Stropheodonta varistriata (Conrad). The specimens are very small here.

Strophonella like euglypha (Dalman) of the Silurian.

- Leptœnisca concava (Hall). This very characteristic thinshelled brachiopod is present in many fragments. It attains a larger growth here than in New York. The species is now known to occur almost everywhere where the Helderbergian is exposed.
- Gypidula (Sieberella) pseudogaleata (Hall)?. Ami has given this the name of Clorinda lowi (nom. nud.).
- Gypidula (Sieberella) coeymansensis chidleyensis Ami. Specimens of this form make up a slab of limestone, and differ from the New York species in being more decidedly plicated.
- *Pleurotomaria labrosa* Hall?. The revolving and growth lines are finer in this specimen than in New York examples.

This geologic horizon is clearly Helderbergian and agrees remarkably well with the uppermost Coeymans division as developed in the United States. *G. pseudogaleata* in New York is, however, restricted to the uppermost Helderbergian (Becraft), but at Dalhousie, New Brunswick, it occurs at a lower level and is there associated with *Leptœnisca concava* and other New Scotland fossils.

#### Frobisher Bay Collections of Hall.

A part of the collections made by Mr. C. F. Hall of New London, Connecticut, on his first expedition to the Arctic regions in 1860–1862 is now in the museum of Amherst College. This material was originally described by Professor Emerson and is that which was loaned the writer for the present study.

#### 470 C. Schuchert-Notes on Arctic Paleozoic Fossils.

In southern Baffin Island the strata appear to lie horizontally. The Ordovician rocks and fossils are from widely scattered localities, extending from the eastern Hall's Islet into southwestern Fox Land. The locality, however, that has furnished subsequent collectors the largest results and the most definite stratigraphic information is at the head of Frobisher Bay at Silliman's Fossil Mount (see Schuchert 1900).

The Hall collections at Amherst also have Silurian fossils from the southwestern corner of Baffin Island. These are from Rescue Harbor in Cyrus Field Bay to the north of Blunt Peninsula.

Three general horizons can be made out in southern Baffin Island, as follows :

1. ORDOVICIAN. Dense gray to cream colored or whitish limestones, in some places approaching lithographic stone. In other places or other horizons the material is a fine-grained, light pinkish, magnesian limestone, but in general the color of all these limestones is the opposite of dark. As a rule fossils are absent in them. In the purer and less dense limestones very small fossils occur, chiefly Ostracoda. The latter were first identified by Professor Emerson, and have been recently restudied by Doctor R. S. Bassler, with the following results :

Leperditia canadensis Jones } These two species seem to Bassler to be other forms than

Primitia muta Jones ) those indicated by Emerson. Primitia frobisheri Emerson = Eurychilina frobisheri.

Beyrichia symmetrica Emerson = Drepanella symmetrica (related to the Richmondian B. richardsoni).

Krausella cf. anticostiensis Jones | Identified by Bassler.

Macrocypris cf. subcylindrica Jones ) ler. Other associated fossils are a small Scenidium, sp. undet.

- (=*Rhynchonella* Emerson, p. 578), a small *Plectambonites*, sp. undet. (=*Chonetes* cf. *striatella*, p. 578), and fragments of undeterminable trilobites (=Emerson's *Phacops* and *Asaphus*).
- The fine-grained, light pink, magnesian limestone from Hall's Island has minute crystalline cavities that Emerson thought might be casts of *Tentaculites*. These the writer could not make out to be due to organisms. Other undeterminable fossils are *Buthotrephis* (p. 575, fig. 1), and *Stictopora ramosa*? (p. 577, may be burrows).

On the basis of the Ostracoda, the only reliable fossils present, the horizon appears to be of Richmondian time, a formation of very wide distribution in North America. Bassler thinks the horizon and faunal realm represented are those of the English Head formation so well developed on the Island of Anticosti, Gulf of St. Lawrence.

- 2. ORDOVICIAN. Black, impure, thin-bedded, fine-grained limestones and black limy shales that weather vellowish white, with scattered small fossils as follows :
  - Climacograptus bicornis (Hall). Common at French Head in Cyrus Field Bay and in Fox Land on western Baffin Island. (Also called *Diplograptus dentatus* by Emerson, p. 576.)

Leptobolus lepis Hall ( $=Lingula \ curta$ , p. 578).

- $Cyclora \ parvulu \ (Hall) \ (= Cyclonema \ bilix, p. 578).$ "Endoceras proteiforme Hall" (p. 579). Not seen by the writer.
- " Orthoceras laqueatum ?", p. 579. Too poor and fragmentary to make out even the genus.

Conularia trentonensis Hall, p. 578. A small fragment of a Conularia is present.

- Triarthrus beckii Green. Common in fragments. It is probable that the Collingwood T. magnificus Twenhofel is also present (the tails are labeled Calymene senaria by Emerson, p. 582).
- Cyphaspis (?) frobisheri Emerson, p. 583, fig. 11. Based on a free cheek ; the genus is not determinable.

Ampyx? (Emerson's trilobite sp., p. 583, fig. 10).

Leperditia alta (Conrad). This is not Conrad's Silurian species but appears to be a new form of Leperditia.

This horizon, on the basis of the above fossils and the further fact that Basilicus canadensis (=Asaphus canadensis Chapman) occurs not far to the south at Cape Chidley, Labrador, seems to correlate with the Collingwood formation of Ontario. The same black shale is also present at Countess Warwick Sound, Blunt Peninsula, and probably as well at the head of Frobisher Bay.

3. SILURIAN. Gray, fine-grained dolomites of Rescue Harbor, Cyrus Field Bay, have Orthis cf. davidsoni, Halysites catenularia, and a pentamerid, probably the same as the next species. Further west in Frobisher Bay in the identical dolomite occurs Conchidium nysius tenuicostatum (Hall), a form first described from the Falls of the Ohio. The Cyathophyllum pickthorni identified by Emerson (p. 577) are too poor to determine.

This horizon is well up in the Silurian, probably in the lower Lockport, and about the horizon of the Louisville as developed at Louisville, Kentucky.

#### Silliman's Fossil Mount, Frobisher Bay.

Schuchert in 1900 described the fauna of seventy-two species occurring at this interesting locality. None of it had, however, been collected stratigraphically, and as most of the widely distributed species agreed with identical or similar forms occurring in the Galena formation of Minnesota and Iowa (57 per cent) he concluded that all the fossils came from strata of about Galena-Trenton time. On the other hand, the many corals found at Silliman's Fossil Mount he interpreted as "an early introduction of Upper Silurian genera." Since then he has collected the same corals at a much higher horizon, in the Richmond formation on Anticosti Island, and has seen them as well at other places in this country and in Norway and Esthonia, always above the Galena-Trenton equivalents. It therefore follows that the Richmond must also be present at the head of Frobisher Bay.

The above mentioned fauna is kept in the U. S. National Museum and has been restudied by Bassler (1911: 32-36). The latter writes: "There is just as much if not more reason for believing that the Black River, Trenton and Richmond rocks are actually present in the section as for assuming that only Trenton strata occur. . . The Richmond age of the corals was further evidenced by the fact that two very characteristic brachiopods, a variety of *Platystrophia acutilirata* and of *Plectambonites sericeus* came to light when I carefully searched a fragment of limestone adhering to one of the corals. This particular variety of *Plectambonites* is highly characteristic of the Richmond in America and Europe. It is distinguished by the occurrence of small teeth along the edge of the cardinal area of the dorsal valve."

In conclusion, the writer agrees with Bassler that there are at least two Ordovician horizons represented at Silliman's Fossil Mount, namely, (1) a lower one containing the bulk of the fauna and equivalent to the Lower Trenton of Minnesota, and (2) an upper fauna here essentially made up of corals and the equivalent of that of Middle Richmond time. It is probable that the Black River equivalent is also present at the Mount, though less well exposed and on or below the débriscovered lower slope of the Mount.

#### Southampton Island, Hudson Bay.

Doctor A. P. Low on his first expedition in 1903–1904 collected fossils on Southampton Island along "the southern half of the west coast of the island" (1906: 211). Two horizons are clearly indicated, as follows: C. Schuchert-Notes on Arctic Paleozoic Fossils. 473

1. ORDOVICIAN. Gray to white, dense, magnesian limestone with a scarcity of organisms.

Rafinesquina alternata (Emmons). Small specimens up to one inch across.

Rafinesquina alternata loxorhytis (Meek)?. Much smaller than the typical specimens.

Leptæna nitens (Billings). Common.

Zygospira, n. sp. Reminds of Z. cincinnatiensis, but is more coarsely plicated.

Rhynchotrema, sp. undet. Recalls small R. perlamellosum but no lamellæ show.

Leperditia sp. A large form  $9^{mm}$  in width.

Encrinurus sp.

This formation is clearly the Richmond, and of about the same zone as the ostracod limestone of southeastern Baffin Island.

2. SILURIAN. In a crystalline, slightly granular limestone.

- "Streptelasma robustum Whiteaves." Grows to a diameter of 2.5 and a length of upward of 7 inches. A transverse section is not round but oval, with the septa much twisted in the center into a false columella. No fossula is to be seen. In some ways these specimens look like Streptelasma and in others like Zaphrentis. If they are associated with the undoubted Silurian corals listed below, they are not Whiteaves' species, but as the Richmond formation is also present on Southampton Island it is possible that they are from the Ordovician and then related to S. robustum. Lambe has labelled them S. robustum, a form common in the Richmond formation of Lake Winnipeg, Manitoba.
- "Pycnostylus elegans." As the specimens are molds of the exterior this identification is not yet established.

Syringopora verticillata Goldfuss. The corallites are here larger than is usual for this species.

Plasmopora follis Edwards and Haime.

Halysites catenularia (Linné). As usual there is also here considerable variation in the size of the corallites.

- Favosites gothlandicus Lamarck. Very common in the typical form with small corallites.
- Favosites gothlandicus variety. Also very common. Here the corallites are nearly twice as large as in the typical forms of this species. As there are no transition specimens between this and the typical forms of the species, it may be a distinct species.
- Favosites favosits (Goldfuss). Rare. Here the corallites do not attain the larger sizes of this species seen elsewhere.
- Clathrodictyon vesiculosum (Nicholson and Murie). This characteristic hydroid is present in three specimens.
- "Pentamerus oblongus Sowerby ?." A fragment of a dorsal valve too poor to identify.

Clorinda, n. sp. A very large form with relationship nearest to C. barrandei, but larger and less plicate. Strophonella euglypha (Dalman)?.

Actinoceras, said to be A. keewatinense Whiteaves. Very large annulate siphuncles, completely filled with deposits of lime, up to 1.5 inches in diameter. Very much like but larger than the siphuncles of A. infelix of the Silurian of Anticosti Island.

These fossils are clearly from the Silurian and the majority of species are indicative of a horizon of about Clinton time, as developed on Anticosti Island.

#### Winter Harbor, south side of Melville Island.

Ordovician.—McMillan, with Captain Bernier on the latter's expedition to the Arctic islands and Hudson Strait in 1908– 1909, found in a drift piece of limestone a very large *Tripter*oceras that originally had a length of one foot. Forms similar to this occur in the Trenton of Iowa, Minnesota and Manitoba. The horizon and faunal realm appear to be in harmony with those of the Galena-Trenton of Iowa and Minnesota. It is unfortunate that this interesting fossil has no direct stratigraphic value because of its drifted source on an island whose native rocks are of Carboniferous age. For other details see Lambe in Bernier 1910: 485.

#### Beechey Island, southwestern corner of North Devon Island.

Lower Devonian .- At Cuming Creek in the center of the southern shore of North Devon Island, Low states that the Archean gneisses are unconformably overlain by horizontal formations consisting of "red and purple arenaceous shales and thin-bedded sandstones having an aggregate thickness of fifty to one hundred feet. These in turn were succeeded by beds of impure limestone of light gray or creamy color. The beds are usually under two feet in thickness, and separated by thinner beds containing a considerable amount of clay. These light-colored limestones have a thickness of over 1000 feet in the cliffs on both sides of the creek. . . . Fossils are only found in the beds immediately overlying the dark shales and sandstones of the base." The limestone cliffs rise above the sea up to 1200 feet. Farther inland they rise in steps to nearly 2000 feet.

"Similar conditions prevail in the cliffs at Beechey Island [at the southwestern corner of North Devon Island], where a large collection of fossils was obtained from the lower limestone beds, while others, picked up loose, but evidently fallen from the cliffs above, showed that the upper beds passed close to if not into the Devonian.

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"Similar Silurian limestones constitute the island of Cornwallis, to the westward of North Devon" (220-221).

The following fossils were gathered by Low on Beechey Island in 1904 and again by McMillan on the expedition of 1908–1909. It was on Beechey Island, it will be remembered, that Franklin and the crews of the "Erebus" and "Terror" came to their sad end. From dark-colored, thin-bedded limestones replete with fossils but in no great variety were found the fossils listed below. This is the widely distributed *Lissa-trypa phoca* fauna and may be, as noted by Holtedahl, some-what younger than the Ellesmereland fauna noted beyond. (For other details see Ami in Low 1906:329, and Lambe in Bernier 1910: 479.)

- "Strephodes pickthornii" (Salter). This common cup coral looks to the writer more like Zaphrentis roemeri Edwards and Haime.
- Favosites cf. helderbergiæ præcedens Schuchert. Small hemispheric masses. Has been erroneously labeled F. gothlandicus.
- Boreaster lowi Lambe. A Favosites-like coral with septa as in Calapæcia. Described in Low 1906: 323.
- Acervularia austini (Salter). Very common and in colonies of up to 10 inches across. They are found in the lowest 50 feet of the limestones following the basal shale series. A very similar species occurs rarely in the basal Devonian limestones of New York and Maryland.
- Atrypa phoca (Salter). Common. A smooth atrypoid to be placed in Lissatrypa, a new genus to be defined by Twenhofel, and based on a much older species found on Anticosti Island. L. phoca and Acervularia austini are the guide fossils to the basal Devonian strata of North Devon.
- Meristella, sp. undet. A small species that is exceedingly common and erroneously labeled by Ami as Atrypa phoca. Hormotoma and Holopea. Small forms that remind much of those found in the Manlius of New York.
- Leperditia, sp. undet. A large form up to 0.5 inch in width. It may be identical with *L. elongata* Weller, found in the Rondout of New Jersey and Keyser of Maryland.

This horizon is in the Lower Devonian and of about the time of the Keyser of the Maryland section (see Lower Devonian volume of the Maryland Survey, 1913). The writer could not have made out this correlation if he had not had the advantage of studying another collection made further north by Per Schei of the Sverdrup expedition of 1901–1902. This material has just been described by Doctor Olaf Holtedahl of the University of Kristiania, Norway, where the Per Schei collections are kept, in a work noted beyond. Ami in Low's report has listed a fauna of thirty-five species.

#### Ellesmere Island.

An excellent stratigraphic work by Holtedahl of the University of Kristiania has just appeared, dealing with the fossils collected by Per Schei in his "series B" on Goose Fiord, which is at the southwestern corner of Ellesmere Island. Overlying the brown limestones of the Silurian, here of great thickness, are dark, more or less thin-bedded limestones about 1000 feet thick, which, so far as can be judged from the fossils at hand, are determined by Holtedahl to be of Lower Devonian age, that is, equivalent to the Keyser of Maryland, and apparently entirely beneath the New Scotland of the New York Helderbergian. It is, however, possible that the Coeymans may be represented in the upper strata of series B. Even though but a few of the Keyser species can be determined in the Arctic region, it is remarkable that any are found there, since the two areas are more than 35 degrees of latitude or about 2400 miles apart.

Holtedahl describes a fauna of forty-three species, of which twenty-one are named, and of these nine are new. The more important of these fossils are as follows (those marked\* also occur in Maryland, and those marked + have closely related representation):-

\* Favosites cf. helderbergiæ Hall.

\* Cladopora rectilineata Simpson.

Thecia swinderenana (Goldfuss).

- Monograptus allied to Pristiograptus colonus Barrande. There is also a form of *Monograptus* in the New Scotland of New York.
- Stropheodonta patersoni antiqua Holtedahl. This species occurs in New York in the Onondaga.

\* Gypidula coeymanensis prognostica Schuchert.

- + Stenochisma deckerense arcticum Holtedahl. This species occurs in Maryland.
- † Camarotæchia litchfieldensis angustata Holtedahl. Also found in Maryland.

Lissatrypa scheii Holtedahl. Closely related to L. phoca.

† Spirifer modestus striatissimus Holtedahl. This species is common in Maryland.

\* Spirifer vanuxemi prognosticus Schuchert.

\* Loxonema fitchi Hall.

† Leperditia symmetrica Holtedahl. Large forms of this genus are characteristic of the American Lower Devonian.

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  Per Schei: Report of the Second Norwegian Arctic Expedition in the "Fram," 1898–1902. Out of the collections made on this expedition have come the following papers: O. E. Meyer, Die Entwicklung der arktischen Meere in paläozoischer Zeit; Neuer Linder and Schutzer (1992). 1912. Jahrb. f. Min., etc., Beilage-Bd., xxxi, 1912, pp. 184-219.—Die Devonischen Brachiopoden von Ellesmereland; Videns.-Selsk. Kristiania, 1913, pp. 1-40. Olaf Holtedahl, On the fossil Faunas from Per Schei's Series B in southwestern Ellesmereland, ibid., 1914, pp. 1-48.

#### SCIENTIFIC INTELLIGENCE.

#### T. CHEMISTRY AND PHYSICS.

1. The Radium-Uranium Ratio in Carnotites.-S. C. LIND and C. F. WHITTEMORE have made determinations of uranium and radium in 21 samples of American carnotite ore, which has become an important commercial source of radium. The samples varied greatly in their contents of uranium oxide, ranging from 1.52 to 33.22 per cent of U.O.. The object of the investigation was to study the uranium-radium ratio which was first shown by Boltwood to be constant in many samples of uranium minerals, and has since been studied by a number of investigators. Some cases of lack of constancy have been found which have been explained, either by supposing that the minerals are too young to have reached equilibrium, or that radium has been leached out in the case of porous minerals. In the investigation of carnotite under consideration it was found that the radium-uranium ratio was constant and like that of pitchblende in all large quantities of well sampled ore, which comprised about one-half of the samples examined. Several small samples gave practically the same ratio, but there were four small samples that gave a low proportion of radium, ranging from 72.4 to 94.9 per cent, while four others gave an excess of radium ranging from 107.8 to 137.8 per cent of the normal amount, which is taken to be  $Ra/U = 3.33 \times$ 10<sup>-7</sup>. The explanation given by the authors for the variation of the small samples is that there has been transposition of radium

in the ore beds producing local differences which are equalized in mixing large quantities.—Jour. Amer. Chem. Soc., xxxvi, 2066. II. L. W.

2. A New Method for the Precise Standardization of Hydrochloric Acid Solutions .- LAUNCELOT W. ANDREWS has devised an ingenious and simple method for the accurate standardization of volumetric hydrochloric acid solutions. It depends upon adding a measured quantity of the acid solution to an excess of pure, dry silver nitrate in a dish, evaporating to dryness, drying at 240° C., and determining the loss in weight due to the conversion of a part of the silver nitrate to chloride. As the process involves no transferring or washing of a precipitate, it is very accurate as well as easy to carry out. The author recommends the use of a companion dish containing no silver nitrate, in which the same quantity of acid solution is evaporated in order to make a correction for any non-volatile impurities that the liquid may have derived from glass vessels. The precaution should be taken that the silver nitrate is entirely free from the ammonium salt, and it should be dried at 240° C. before the weight is taken. A short stirring rod should be weighed with the silver nitrate, in order that it may be used after the addition of the hydrochloric acid, and the rod should remain in the dish throughout the operation. The dishes should be covered with light watch-glasses while being weighed. The author states that he has employed the method for several years, and gives the results of four determinations where, for the sake of the greatest accuracy, the acid solution was weighed. These results show surprisingly small variations, the results being 0.53063, 0.53062, 0.53095 and 0.53054 in terms of normality.-Jour. Amer. Chem. Soc., xxxvi, 2089. H. L. W.

3. Introductory Notes on Quantitative Chemical Analysis; by CHARLES WILLIAM FOULK. 8vo, pp. 250. New York 1914 (The McGraw-Hill Book Company. Price, \$2.00 net).—This is the third edition of a useful book for students of quantitative analysis. Its plan is unusual, as the larger part of the book is devoted to a general discussion of operations, many of which are taken up in great detail. For instance, 16 pages are devoted to the balance and weighing. In connection with this part it may be observed that it seems very unfortunate that a long swing of the balance pointer is recommended for ordinary weighing instead of a very short swing, since the use of the latter is much less laborious, and certainly just as accurate if a good balance is employed. However, the advice given in this book appears to be excellent in almost every particular.

The practice work laid out in the book includes both gravimetric and volumetric operations. The course is not a very extensive one, but as far as it goes the directions are full in regard to every detail, with frequent references to the general part of the book, and many explanatory notes. H. L. W.

4. Elementary Household Chemistry, by JOHN FERGUSON SNELL. 12mo, pp. 307. New York, 1914 (The Macmillan Company. Price, \$1.25).—This text-book is designed for the use of students who have had no previous instruction in chemistry, so that it gives a considerable amount of instruction in fundamental facts and theories. It may be expected, however, that, with suitable omissions, it will be useful for students who have had a training in general chemistry. The book appears to be an excellent one in many ways. The numerous experiments are well chosen and usually so arranged that the student draws his own conclusions. The treatment of the subject is modern as well as clear and interesting. Some of the practical subjects discussed are fuels, illuminants, hard water, fats, soaps, textile fibers, bleaching, and dyeing, while much attention is given to foods. A striking feature is the introduction of a number of full-page portraits, comprising those of Mrs. Ellen S. Richards, Robert Boyle, Berzelius, Dalton, Mayow, Priestley, Lavoisier, Rumford, Black, Arrhenius, Emil Fischer and W. O. Atwater. Each of the portraits is accompanied by a biographical note. H. L. W.

5. A Popular Treatise on the Colloids in the Industrial Arts. by KURT ARNDT. Translated from the Second, Enlarged, Ger-man Edition, by NAHUM E. KATZ. 8vo, pp. 73. Easton, Pa., 1914 (The Chemical Publishing Co.).-This little book gives an interesting account of the subject indicated by the title. Definitions of the technical terms are given, and the general principles relating to colloids are briefly discussed. Then the important bearings of these substances in a great variety of industries are described. The book contains much that will be of interest to chemists, especially to those whose line of work or study is in the industrial side of the science. The English of the translator, while usually clear, is not entirely free from the complications of German construction and idiom, and there is occasionally a mis-translation, as, for example, when in two instances it appears that the German word Leim, meaning glue, is rendered as "lime," which has the same sound, but a very different meaning, except in an obsolete sense. H. L. W.

6. The Fixation of Atmospheric Nitrogen, by JOSEPH KNOX. 12mo, pp. 110. New York, 1914 (D. Van Nostrand Company. Price, 75c.).—This "Chemical Monograph" gives an account of this very interesting and important recent development of chemical industry. It deals especially with the theoretical aspects of the processes, and it is divided into three principal sections : Fixation of atmospheric nitrogen as nitric and nitrous acids, or as their salts ; synthesis of ammonia and ammonium compounds from atmospheric nitrogren ; conversion of atmospheric nitrogen into compounds which readily yield ammonia. The work is a very satisfactory one, and the references to the literature of the subject are particularly extensive and useful. H. L. W.

7. Lehrbuch der physikalischen Chemie; by KARL JELLINEK. Vol. I. Pp. xxxvi, 732, with 81 tables, 253 text-figures, 4 portraits. Stuttgart, 1914 (Ferdinand Enke).—Since the only comprehensive text-book on general physical chemistry, by W.

Ostwald, has not kept pace with the rapid strides which have been made in physics in the last decade, and since the excellent text-books of W. Nernst and J. H. van't Hoff are primarily restricted to the chemical aspect of the subject, Jellinek has undertaken the enormous task of writing a text-book (not a "Handbuch") on physical chemistry which is intended to cover the entire field and to lay due emphasis on the physical side of the appertaining phenomena. In pursuance of this high ideal the author proposes to present the subject in four volumes, namely "1. Buch (Bd. I and II). Die Lehre von den Aggregatzuständen (reine Stoffe und verdünnte Lösungen der Nicht-elektrolyte)"; "2. Buch (Bd. III). Die Lehre vom Aufbau der Materie (Weltäther, Elektronen, Ionen, Atome und Moleküle)"; "3. Buch (Bd. IV). Die Lehre von den Umwandlungen der Materie (chemische Statik und Kinetik)"; "4. Buch (Bd. IV). Die Lehre von den Umwandlungen der Energie (Mechanochemie, Thermochemie, Magnetochemie, Elektrochemie, Photochemie)".

Therefore the volume before us is the first Part of the first Book. It is stated in the preface that the manuscript of the second Part of Book 1 is finished and that the work may be expected from the press in the fall of this year. A general idea of the scope of the present volume may be obtained from the following facts. Pages 13 to 159 treat of the fundamental principles of physical chemistry. The gaseous state comprises pages 160 to 431, and the passage from the gaseous to the liquid state has pages 432 to 468 devoted to it. The rest of the text proper, as far as page 711, relates to the liquid state. Fortunately the author does not avoid mathematics, such as the more elementary parts of the differential and integral calculus and of the theory of probability. From the physical point of view the work is fully up to date and involves Planck's "quanta", etc. Also, great pains have been taken by the author, by his brother, and by his wife to make the technical side of the book as perfect and complete as possible. For example, twenty pages are devoted to the bibliography and literature of the subject, and to abbreviations and symbols. The volume ends with a list of typographical errors and supplementary comments, and with author and subject indices. The text merits the attention of physicists as well as of physical chemists and, if the author succeeds in maintaining the very high standard maintained throughout the first volume, the work will doubtless become the standard text-book on the subject. H. S. U.

8. Complex Ions in Aqueous Solutions; by ARTHUR JAQUES. Pp. vi, 151. London, 1914 (Longmans, Green & Co.).—"The chief aim of the book is to give some account of the more important experimental work in this subject, and no apology is offered for the absence of theories of valency." The introductory chapter is followed by five chapters which deal respectively with the chemical, ionic migration, distribution, solubility, and electrical potential methods for the identification and investiga-

#### Chemistry and Physics.

tion of complex compounds. The seventh chapter is devoted to concrete examples of the methods discussed in the earlier pages. The remaining chapters deal with ammoniacal salt solutions, with certain cobalt and copper solutions, and with some special cases of equilibrium. The "hydrate theory" is touched upon in an appendix. The chemical and mathematical equations and formulæ are clearly and accurately printed, and errors in the original articles have been carefully corrected. The general usefulness of the compilation is increased by the inclusion of numerous bibliographical references and of author and subject indices.

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9. Lichtmessungen mit Selen ; by WILLY JAENICHEN. Pp viii, 76, with 22 figures and 5 plates. Berlin-Nikolassee, 1914 (Administration der "Zeitschrift für Feinmechanik").-In the first part of this little book (pages 8-30) an account is given of fifteen different types of apparatus and methods which have been proposed for making determinations of the intensity of light by the aid of selenium. The second part deals with the apparatus designed by the author and with the experimental tests made by him. The text concludes with final deductions concerning the usefulness of selenium as regards (a) accuracy of measurements and (b) color-sensitivity. Since the material has been presented with care and since the folding plates show a relatively large number of useful and instructive curves, the monograph should be gladly received by all who are interested in the practical applications of selenium. н. s. u.

10. The Crystalline Structure of Copper.-The chief difficulty encountered in the investigation of copper by means of the X-ray spectrograph arises from the fact that native crystals have faces which are too much warped and distorted to produce the necessary "reflections" of the Röntgen rays. The experimental problem has been recently solved by W. LAWRENCE BRAGG. He first attempted to produce artificial faces by grinding, but this process was found to be of no avail because it destroyed the crystalline character of the surface and thus prevented the reflection of the short electromagnetic waves. "It was observed, however, that when the crystal was placed in nitric acid until the surface was eaten away to an extent of perhaps 1/4 millimetre, the faces were etched deeply into numerous parallel facets, which all reflected the light simultaneously in the usual way." "This suggested that, internally the crystal structure was perfect, and showed further that in some cases the whole specimen was composed of a single crystal." "Moreover, in this case the surface layers are not pulled about, and so are capable of reflecting the X-rays falling on them."

Since copper crystallizes in the holohedral class of the cubic system it was natural to assume, as a working hypothesis, that the copper atoms are arranged at the corners of cubes, thus forming a simple cube lattice. The predicted glancing angles for the palladium rays can then be calculated as follows. First, the dis-

tance,  $d_{(100)}$ , between the lattice planes is derived from the obvious relation :—(mass of 1 copper atom) = (volume)(density) =  $(d_{(100)})^3$ . 8.96 = (atomic weight of copper)(mass of 1 hydrogen atom) = 63.57. 1.64.  $10^{-24}$  gram, therefore  $d_{(100)} = 2.26 \times 10^{-8}$  cm. For an anticathode of palladium, such as was used in the experiments,  $\lambda = 0.576$ .  $10^{-8}$  cm. Hence, substitution of the values for  $d_{(100)}$  and  $\lambda$  in the well-established equation  $\lambda = 2d_{(100)} \sin \theta$ gives  $\theta_{(100)} = 7^{\circ} 20'$ . In like manner,  $\theta_{(110)} = 10^{\circ} 22'$  and  $\theta_{(111)} =$ 12° 50'. These angles were not found experimentally when the crystals were studied by means of an ionization X-ray spectrometer. On the assumption that the copper crystals have one atom at the center of each cube face in addition to the atoms at the vertices of the cubes the above method of calculation leads to the following glancing angles, namely  $:-\theta_{(100)}=9^{\circ}13', \theta_{(110)}=13^{\circ}2'$ , and  $\theta_{(111)}=8^{\circ}0'$ . The angles actually obtained by reflection were 9° 24', 13° 18', and 8° 0' respectively. The experimental check used to avoid ambiguity of solution need not be discussed in this place. Bragg says "... there can be little doubt that the atoms of a copper crystal are arranged on a face-centred cubic lattice". "The crystal structure is the most simple of any as yet analysed."-Phil. Mag., xxviii, p. 355, Sept., 1914. H. S. U.

#### II. GEOLOGY AND MINERALOGY.

1. The Deseado Formation of Patagonia; by FREDERIC B. LOOMIS. Pp. i-xi, 1-232, with frontispiece and 160 text figures. Amherst, published under the auspices of the Trustees of Amherst College, 1914.—This volume is the technical conclusion of a previous work, "Hunting Extinct Animals in the Patagonian Pampas," published by Dodd, Mead and Company in 1913, and together the two sum up the exploration and anatomical work done by the Eighth Amherst Expedition, which, under the leadership of Professor Loomis, explored a little known portion of Patagonia in 1911.

The material described in the volume under consideration forms a unified body of data which adds much to our knowledge of the animals of the Patagonian Tertiary. The field, however, has only been touched and a vast amount of further work can be profitably done on the horizons immediately preceding and following the one described in this volume, after which an interesting study can be made on the evolution of a fauna which developed in a considerable degree of isolation.

Material was found in various beds, from the Cretaceous up to the Lower Miocene; but the major part of the fossils and most of the facts new to science came from the Deseado formation, otherwise known as the Pyrotherium beds and attributed by geologists to the Upper Oligocene period. Chapters I and II discuss the localities and age of the formation in Patagonia,

#### Geology and Mineralogy.

while from chapter III on the fauna is treated in detail. An interesting table is prepared showing the percentage of speci-mens obtained of each of the species represented in the collection. This sums up not only the range of species but their relative abundance in the fauna and suggestions as to the sort of food they ate and the character of the country wherein they lived. Of the general types perhaps the most interesting in view of their almost exclusively South American character are the Edentates, which, however, comprise only 8 per cent of the fauna as compared to 50 per cent in the later Santa Cruz beds. They seem to have been indigenous to South America, where they later flourished in the greatest variety and profusion of numbers.

Hoofed animals are abundant and peculiar, and to appreciate their significance it should be borne in mind that South America was geographically isolated from early Eocene until late Miocene or early Pliocene time, during which a remarkable evolution occurred uninfluenced by immigration from other lands. Of these ungulates the most interesting were the Litopterna, paralleling in their development the horses; the Typotheria, with chisel-like front teeth and permanently growing grinders from which Loomis infers a harsh diet of grass and bark, while the feet seem to indicate adaptation to hard ground; and the Toxodontia, represented by the Nesodontidæ and Leontinidæ, which are heavier forms, the latter being browsers living among bushes. All these types, which are included under the order Notoungulata, form a group with apparently a common ancestry and their relationships appear to the author to be with the Hyracoidea, which are generally credited with originating in Africa.

The Pyrotheria were very large browsing animals, the skull of which is so very proboscidean in appearance that they are said to be "related to the early elephants which also arose in Africa, but it seems to me [Loomis] that this form came to Patagonia at least at a later period, making its first appearance in the upper part of the Astraponotus period. Ultimately the elephants and Hyracoidea had a common origin in Africa." Scott in his "Land Mammals in the Western Hemisphere" says of the grinding teeth of Pyrotherium: "These teeth are decidedly reminiscent of the dentition of the aberrant proboscidean Dinotherium, from the Miocene and Pliocene of Europe, and this resemblance, together with the form of the tusks, has led to the reference of this group to the Proboscidea, but the assignment is undoubtedly erroneous, as is shown by the character of the skull and skeleton." Professor Scott is high authority, and in addition to his testimony may be offered the very great difficulty of finding evidence for a possible land bridge from Africa after the close of the Mesozoic, and Cretaceous time seems to the reviewer too early for an immigration of either proboscidean or hyracoidean stock. It would appear, therefore, that the remarkable likenesses which Loomis clearly demonstrates between the Pyrotherium and Palceomastodon skulls are, as in the case of the true horses and Litopterns, only the result of convergent evolution.

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The flesh-eaters of Deseado time are all marsupials, and their origin gives rise to further perplexing problems. Some are of the opossum series, which could well have been developed from some remnant of the Mesozoic marsupial fauna that had a worldwide distribution; but the presence of diprotodonts, which are characteristic of Australia, and of the Borhyænidæ, which are closely related to the Thylacinidæ of Australia, suggests a migration from that continent as late as Tertiary times. However, to the author's mind this involves a connection which is almost too difficult to postulate.

The birds, Loomis thinks, probably came from Africa with the invasion of the ancestors of the Notoungulata.

The remaining chapters contain careful technical descriptions of the material, well illustrated by the author's own drawings. A table of contents is present, but an index would have added to the working value of the book, especially as it deals with such unfamiliar forms.

Professor Loomis has performed a notable service to science, not only in the production of this work, but in the way in which the expedition was conceived, organized, and carried through to its successful termination. Such accomplishment is worthy of generous support. R. S. L.

2. Publications of the United States Geological Survey, GEORGE OTIS SMITH, Director.—Recent publications of the U.S. Geological Survey are noted in the following list (continued from vol. xxxvii, pp. 280-282):

TOPOGRAPHIC ATLAS.—Forty-three sheets.

PROFESSIONAL PAPERS.—No. 83. The Middle Triassic Marine Invertebrate Faunas of North America; by JAMES P. SMITH. Pp. 254, 99 pls.

Pp. 254, 99 pls.
No. 86. The Transportation of Débris by Running Water;
by GROVE K. GILBERT, based on experiments made with the assistance of EDWARD C. MURPHY. Pp. 263; 3 pls., 89 figs.

No. 90. Shorter Contributions to General Geology. B. Erosion and Sedimentation in Chesapeake Bay around the Mouth of Choptank River; by J. FRED. HUNTER. Pp. 7–15; 1 pl., 1 fig. C. Dike Rocks of the Apishapa Quadrangle, Colorado; by WHITMAN CROSS. Pp. 17–31; 4 pls. D. The Composition of Crinoid Skeletons; by F. W. CLARKE and W. C. WHEELER. Pp. 33–37. E. Contributions to the Stratigraphy of Southwestern Colorado; by WHITMAN CROSS and E. S. LARSEN. Pp. 39–50; 1 plate, 2 figs.

MINERAL RESOURCES of the United States. Calendar year 1912. Part I. Metals. Pp. 1079; 3 pls. 13 figs. Part II. Non-metals. Pp. 1218; 8 pls., 11 figs.—The important information permanently preserved in these massive volumes has already been given to the public in the form of advance chapters. Similarly the data for 1913 are now being rapidly arranged and published.

BULLETINS-No. 548. Electric Activity in Ore Deposits; by ROGER C. WELLS. Pp. 78; 7 figs.

No. 549. The Shinumo Quadrangle ; Grand Canyon District, Arizona; by L. F. Noble. Pp. 100; 18 pls. (map in pocket), 1 fig.

No. 550. The Ore Deposits of Northeastern Washington; by HOWLAND BANCROFT; including a section on the Republic Mining District; by WALDEMAR LINDGREN and HOWLAND BANCROFT. Pp. viii, 215; 19 pls., 26 figs. No. 552. Results of Triangulation and Primary Traverse in

Ohio, 1898 to 1911, inclusive. R. B. MARSHALL, Chief Geographer. Work from 1900 to 1911, inclusive, done in coöperation with the State. Pp. 232; 2 pls.

No. 556. Results of Spirit Leveling in Oregon, 1896 to 1913, inclusive. R. B. MARSHALL, Chief Geographer. Work done in coöperation with the State from 1905 to 1913, inclusive; JOHN H. LEWIS, State Engineer. Pp. 175; 1 pl. No. 557. Results of Spirit Leveling in the State of Washing-

ton 1896 to 1913, inclusive. R. B. MARSHALL, Chief Geographer. Work from 1909 to 1913, inclusive, done in coöperation with the State. HENRY LANDES, State Geologist. Pp. 178; 1 pl. No. 571. Results of Spirit Leveling in Kansas, 1896 to 1913,

inclusive. R. B. MARSHALL, Chief Geographer. Pp. 47; 1 pl.

No. 574. Mining Districts of the Dillon Quadrangle, Montana, and adjacent Areas; by ALEXANDER N. WINCHELL. Pp. 191; 8 pls., 16 figs.

No. 577. Geology of the Phosphate Deposits Northeast of Georgetown, Idaho; by R. W. RICHARDS and G. R. MANSFIELD. Pp. 77; 14 pls., 3 figs.

No. 578. The Iditarod-Ruby Region, Alaska; by HENRY M. EAKIN. Pp. 45; 6 pls. (3 maps in pocket), 1 fig. No. 579. Reconnaissance of Oil and Gas Fields in Wayne

and McCreary Counties, Kentucky; by M. J. MUNN. Pp. 105; 6 pls., 6 figs.

No. 580. Contributions to Economic Geology, 1913. Part I. D. The Grand Gulch Mining Region, Mohave County, Arizona; by JAMES M. HILL. Pp. 39-58; 5 figs. E. A New Gypsum Deposit in Iowa; by GEORGE F. KAY. Pp. 59-64; 1 fig. F. Deposits of Mica in the United States; by Douglas B. STERRETT. Pp. 65-125; 33 figs. G. Gold Placers on Wind and Bighorn Rivers, Wyoming; by FRANK C. SCHRADER. Pp. 127-145; 1 pl., 1 fig. H. Carnotite near Mauch Chunk, Pennsylvania; by EDGAR T. WHERRY. Pp. 147-151. I. Lode Deposits of the Alleghany District, California; by HENRY G. FERGUSON. Pp. 153-182; 7 figs. J. The Phosphate Deposits of South Carolina; by G. SHERBURNE ROGERS. Pp. 183-220; 1 pl., 2 figs. K. Ore Deposits in the Sawtooth Quadrangle, Blaine and Custer Cos., Idaho; by J. B. UMPLEBY. Pp. 221-249; 2 pls., 1 fig.

No. 581. Contributions to Économic Geology. Part II. A. Oil Shale of Northwestern Colorado and Northeastern Utah; by E. G. WOODRUFF and DAVID T. DAY. Pp. 21; 1 pl. B. Oil and Gas in the Western Part of the Olympic Peninsula, Washington; by CHARLES T. LUPTON. Pp. iv, 23-81; 1 pl., 1 fig. C. The Moorcroft Oil Field and The Big Muddy Dome, Wyoming. Papers by V. H. BARNETT. Pp. 83-117; 2 pls., 1 fig.

No. 583. Colorado Ferberite and the Wolframite Series; by FRANK L. HESS and WALDEMAR T. SCHALLER. Pp. 75; 14 pls., 35 figs.

Bibliography of North American Geology for 1913 No. 584.

with Subject Index; by John M. NICKLES. Pp. 183. No. 585. Useful Minerals of the United States; compiled by SAMUEL SANFORD and RALPH W. STONE. Pp. 250.

No. 586. Slate in the United States; by T. NELSON DALE Pp. 220; 26 pls., 18 figs. and others.

The Constitution of the Natural Silicates; by FRANK No. 588. WIGGLESWORTH CLARKE. Pp. 128.

No. 592. Mineral Resources of Alaska. Report on Progress of Investigations in 1913; by ALFRED H. BROOKS and others. Pp. 413, xi; 17 pls., 13 figs.

No. 599. Our Mineral Reserves: How to Make America Industrially Independent; by GEORGE OTIS SMITH. Pp. 48.

WATER-SUPPLY PAPERS.-Nos. 321, 323, 325, 327, 328, 332. Surface Water Supply of the United States, 1912. Part I. North Atlantic Coast Basins; by C. C. BABB, C. C. COVERT, and J. G. MATHERS. Pp. 240; 3 pls. Part III. Ohio River Basin; by A. H. HORTON, W. E. HALL, and H. J. JACKSON. Pp. 118; 2 pls. Part V. Upper Mississippi River and Hudson Bay Basins; by A. H. HORTON, W. G. HOYT, and H. J. JACKSON. Pp. 193; 2 pls. Part VII. Lower Mississippi River Basin; by ROBERT FOLLANSBEE. Pp. 84; 2 pls. Part VIII. Western Gulf of Mexico Basins; by W. W. FOLLETT, ROBERT FOLLANSBEE, and G. A. GRAY. Pp. 121; 2 pls. Part XII. North Pacific Coast Drainage Basins. C. Lower Columbia River and Rogue, Umpqua, and Siletz Rivers; by F. F. HENSHAW and E. S. FULLER. Pp. 226.

No. 336. Water Resources of Hawaii, 1912; by C. H. PIERCE and G. K. LARRISON. Pp. 392.

No. 339. Quality of the Surface Waters of Washington; by WALTON VAN WINKLE. Pp. 105; 2 pls., 1 fig.

No. 340-B, C. Stream-Gaging Stations and Publications relating to Water Resources 1885-1913. Part II. South Atlantic Coast and Eastern Gulf of Mexico Drainage Basins ; compiled by B. D. WOOD. Pp. xix. Part III. Ohio River Basin; compiled by B. D. Wood. Pp. xxii, 31-42.

No. 345-E. A Method of Determining the Daily Discharge of Rivers of Variable Slope; by M. R. HALL, W. E. HALL and C. H. PIERCE. Pp. 53-65; 2 figs.

No. 345-F. The Discharge of Yukon River at Eagle, Alaska ; by E. A. PORTER and R. W. DAVENPORT. Pp. 67-77; 2 pls., 2 figs.

No. 346. Profile Surveys in the Basin of Clark Fork of Columbia River, Montana-Idaho-Washington; prepared under the direction of R. B. MARSHALL, Chief Geographer.

No. 363. Quality of the Surface Waters of Oregon; by WALTON VAN WINKLE. Prepared in coöperation with the State of Oregon, JOHN W. LEWIS, State Engineer. Pp. 137; 2 pls., 1 fig.

No. 364. Water Analyses from the Laboratory of the United States Geological Survey; tabulated by F. W. CLARKE, Chief Chemist. Pp. 40.

The Publications of the United States Geological Survey (not including Topographic Maps). July, 1914. Pp. 136.

3. Minerals of California; by ARTHUR S. EAKLE. Califor-nia State Mining Bureau, Bulletin No. 67, F. McN. Hamilton, State Mineralogist. Pp. 226. San Francisco, 1914 .- The great extent of the State of California, and the varied character of its mineral products, makes a summary as to the various mineral species which it contains a matter of particular interest. The first list of California minerals was published nearly fifty years ago by Professor W. P. Blake, and included seventy-five species. Twenty years later this work was repeated by the State Mineralogist, Mr. Henry G. Hanks. Recent years have served to develop and make known the mineral riches of the State, and the present list by Dr. Eakle enumerates 325 well-recognized species. The localities in the southern counties where gem tourmalines and other important minerals have been exploited, deserve special mention, while the borate deposits have also yielded much that is interesting and new. Besides these, there is the great mineral wealth of the central part of the State, and the various species occurring in their ore deposits. This volume contains in addition to the list of species, with the localities at which they occur and many special points of interest about them, a chapter giving the mineral distribution by counties, and also a very complete bibliography of California minerals.

4. Gems and Precious Stones in 1913.—The chapter on this subject, by DOUGLAS B. STERRETT, forming pp. 649-708 of Part II of the Mineral Resources of the United States for 1913, has recently been issued. The general results of the year's work are summarized as follows:

"The precious and semiprecious stone mining industry of the United States in 1913 was marked by a fairly large output of sapphire, a real advance in the work of testing the Arkansas diamond field, a greater activity in the Nevada opal field, and by a decrease in the output of the majority of the other gem minerals mined. The sapphire came chiefly from Montana and consisted of both blue and varicolored gems and culls for mechanical purposes. In Arkansas one diamond-washing plant was in operation about three months and recovered several hundred diamonds, and the construction of another plant was practically completed. Many new claims were located in the Nevada opal field, development of which, along with those previously opened, resulted in a fairly large output of beautiful gems. Prospecting work at the emerald mine near Shelby, N. C., was continued during the first part of 1913, but the last find of emeralds was made in August, 1912. Prospect work was renewed at the Ruby mine in Cowee Valley, Macon County, N. C., and is being continued into 1914. The output of the gem minerals tourmaline, spodumene, etc., in southern California was small, but some good gem material was obtained. The exploitation of the less valuable native semiprecious stones has continued with fair success, but the increasing use of cheap, artificial products is making big inroads on this industry."

In regard to the diamond field in Arkansas it is stated that "more active development was carried on in 1913 than in any previous year. The nature of the work was not such as to definitely prove or disprove the value of the deposits, but it served to show in what ways improvements could be made in the mills and machinery so far used to treat the peridotite. The companies making the tests have not seen fit to announce the results of their work, but they kindly allowed examination of their mines and mills at the time of the writer's visit in July, 1913. Two washing plants were built, one by the Ozark Diamond Mining Corporation on their holdings at the northeast side of the original peridotite area, and the other by the Kimberlite Diamond Mining & Washing Co., on the west side of Prairie Creek.

"The Ozark Co. operated its washing plant about three months during 1913. Mr. Warren, the superintendent, estimated that about 5,000 loads of 16 cubic feet of decomposed peridotite from the original area and about 1,000 loads of gumbo and wash gravel from the west foot of Twin Knobs were washed. The last of this gumbo and gravel were being washed at the time of the writer's visit, but no diamonds had been found in it. Several hundred diamonds were recovered in washing the peridotite from the original area. This peridotite was obtained from an open cut 300 feet long, 15 to 35 feet across, and 8 to 20 feet deep, with tracks leading to the mill. A quantity of surface material was washed in sluice boxes with riffles and yielded a larger per cent of diamonds than the underlying peridotite. Most of the peridotite, even from the bottom of the open cut, was found to be so decomposed as to be ready for washing as mined.

"The Kimberlite Diamond Mining & Washing Co.'s plant is nearly a mile from its lease holdings on the original peridotite area. . . . The earth to be treated will be fed through a revolving screen and into a 10-foot diamond concentrating pan of South African pattern. It is estimated that this pan will treat from 100 to 150 loads of 16 cubic feet per day, reducing 100 tons of earth down to about 1 ton of concentrates. The concentrates will be further screened and then treated on jigs, and the final concentrates examined on metal-covered tables in a well-lighted room."

The peridotites of Syracuse, N. Y., have also received attention, although no diamonds have been found thus far. It is remarked that "The peridotites of Syracuse bear a marked resemblance to those of South Africa, Arkansas, and Kentucky in composition, texture, inclusions, and weathering. No careful search for diamonds has been made in the peridotite of Syracuse, though the nature of the material would seem to justify such attempts as much as the peridotite of Kentucky, on which considerable work has been expended."

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The Ring Burner of Dr. Wolcott Gibbs; by WALLACE GOOLD LEVISON (communicated.)—In a biographical notice of Dr. Wolcott Gibbs by Dr. C. L. Jackson in this Journal for March, 1909 (pp. 253-259), there is a reference (p. 256) to his invention of the Ring Burner where the writer states that it dates from 1873. I think it should date from 1869.

While a student under Dr. Gibbs in the laboratory of the Lawrence Scientific School, where I graduated in 1870, what he called a Ring Burner was frequently used by me and others in the laboratory during some part of the years 1869 and the early part of 1870. It consisted of a circular iron tube perforated with small holes at intervals around the inside of the ring through which the gas issued and provided small blue flames directed toward the center. It was supported on a ring stand and could be adjusted to surround a crucible or other container and gradually lowered as occasion required, thus permitting the fusion of the contents of the crucible to be conducted from the top to the bottom, and extreme effervescence of the assay avoided until a complete frit or fusion was effected. It somewhat resembled the ring burners now in general use in gas stoves, except that the flames issued from the inside toward the center instead of from the top upward. Perhaps it is to some later form of the instrument that Dr. Jackson referred, or, perhaps we had then the privilege of using it before an account of it was officially published.

Attention may also be called to a typographical error on p. 240, vol. l, Sept. 1870, where the writer's name is given as W. G. Leison. This is in the title of an article on "Contributions from the Laboratory of the Lawrence Scientific School: 1. On the precipitation and determination of the metals of the Magnesium Group as Oxalates." This paper has been repeatedly quoted, but with the error noted in the author's name.

2. Publications of the Carnegie Institution of Washington. – Recent publications of the Carnegie Institution are noted in the following list (continued from p. 111):

No. 27, Vol. III. Bacteria in Relation to Plant Diseases; by ERWIN F. SMITH. Pp. viii, 309; 47 pls., 155 figs. No. 90-A. Vol. II. Guide to the Materials for American

No. 90-A. Vol. II. Guide to the Materials for American History, to 1783, in the Public Record Office of Great Britain ; by CHARLES M. ANDREWS. Pp. viii, 427. No. 149. Part III. The Production of Elliptic Interferences in Relation to Interferometry; by CARL BARUS. Pp. vi, 169-173; 54 figs.

No. 165. List of Prime Numbers from 1 to 10,006,721; by DERRICK NORMAN LEHMER. Pp. 133, folio.

No. 183. Vol. VI. Papers from the Tortugas Laboratory of the Carnegie Institution of Washington. Pp. 323. Contains twelve papers by the Director, A. G. Mayer, and others, with numerous plates and text figures.

No. 185. Part I. Index to United States Documents relating to Foreign Affairs 1828–1861. In three Parts. Part I, A to H; by ADELAIDE R. HASSE. Pp. 793.

No. 193. The Salton Sea: A Study of the Geography, the Geology, the Floristics, and the Ecology of a Desert Basin; by D. T. MACDOUGAL and Collaborators. Pp. xi, 182; 32 pls., 4 figs., 4to.

No. 197. North American Anura. Life-Histories of the Anura of Ithaca, New York; by Albert H. WRIGHT. Pp. vii, 98; 31 pls.

No. 198. The Osmotic Pressure of Aqueous Solutions. Report on Investigations made in the Chemical Laboratory of the Johns Hopkins University during the years 1889-1913; by H. N. MORSE. Pp. v, 222; 5 pls., 49 figs.

No. 199. A Montane Rain-Forest : A Contribution to the Physiological Plant Geography of Jamaica ; by FORREST SHREVE. Pp. 110 ; 29 pls., 18 figs.

No. 201. The Gaseous Metabolism of Infants, with special reference to its relation to Pulse-rate and Muscular Activity; by FRANCIS G. BENEDICT and FRITZ B. TALBOT. Pp. 168; 65 figs.

#### OBITUARY.

DR. W. H. GASKELL, University professor of physiology at Cambridge, England, died on September 7 at the age of sixtyseven years.

DR. H. J JOHNSTON-LAVIS, professor of vulcanology in the University of Naples, was killed in a motor accident at Bourges early in September.

DR. R. J. ANDERSON, professor of natural history in the University College, Galway, Ireland, died during the past summer.

DR. WILLIAM LOFLAND DUDLEY, professor of chemistry in Vanderbilt University, Nashville, Tenn., died on September 8, at the age of fifty-five years.

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# THE

# AMERICAN

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No. 228—DECEMBER, 1914.

WITH PLATE IV.

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1914.

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# AMERICAN JOURNAL OF SCIENCE

# [FOURTH SERIES.]

# ART. XLII.—A Reconnaissance of a Portion of the Little Colorado Valley, Arizona; by HERBERT E. GREGORY.\*

THE following geologic notes are the incidental results of a study of the water resources of that portion of the Little Colorado Valley between Coconino Point and Tanner's Crossing.

## Geography.

The area under discussion (see fig. 1) is a portion of the Colorado Plateau Province, and presents in its topography many features common to the arid sections of northern Arizona and southern Utah. In the vicinity of Tanner's Crossing the valley floor of the Little Colorado is fourteen miles wide. Its eastern boundary is sharply defined by the red sandstone cliffs of Ward Terracet and its western border is equally well marked by the bold front of Coconino Point. The Little Colorado occupies a narrow rock trench 40 feet deep at the Government Bridge ; below that point the depth of the canyon increases until a gorge 3000 feet deep unites with the Colorado canyon. Cedar Wash joins the Little Colorado after a long course from San Francisco Mountains, but the other western tributary valleys are flat-floored, narrow canyons with drainage areas of a few square miles. An intricately dissected surface, above which rise buttes and mesas of small dimensions carved from red sandstones and shales, may be taken as typical for this portion of the Little Colorado Valley.

The annual precipitation in the lower Little Colorado Valley is probably less than 3 inches, and varies over 100 per cent from season to season. The rain comes as infrequent sudden showers; and is hurried away to innumerable channels or

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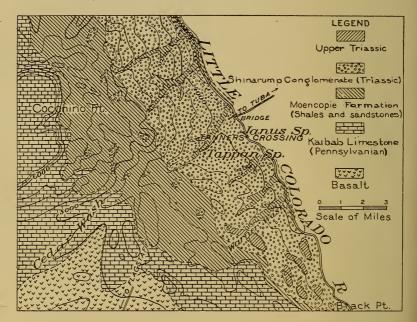
#### THE

AM. JOUR. Sci.—Fourth Series, Vol. XXXVIII, No. 228.—Dec., 1914.

## 492 H. E. Gregory-Reconnaissance of a Portion of the

dissipated into air by evaporation, which in this region exceeds four feet per year. The streams are in consequence all ephemeral : even the Little Colorado itself displays a dry floor for several months in the year. Following showers, the Moencopie from the east and Cedar Wash from the west, aided by numerous companions, pour quantities of thick muddy water into the Little Colorado, filling its canyon to a height which makes crossing dangerous. Depressions in canyon beds and





rock basins on divides, which are filled with water by occasional showers, are likewise short-lived. Two days after a rain may find a large part of the region without sufficient water for horse and rider. Permanent water of excellent quality is found however in three springs: Tappan, issuing from the contact of lava and sandstones; A1 Ranch, bubbling up from joints in shale: and Janus, oozing from the bedding planes between strata of sandstone. Coconino Point, 3000 feet above the bed of the Little Colorado, is also supplied with springs and with fairly long-lived, natural "tanks".

The region is hot during the summer season, when temperatures exceeding 100° may be expected for several days in succession.

#### Little Colorado Valley, Arizona.

Vegetation on the lowlands bordering the Little Colorado consists of scattered clumps of grass set in the midst of yucca and cactus and interspersed with lone piñons and struggling cedars of small size. Along the river a few cottonwoods and willows furnish welcome shade. On the Coconino Plateau the wide, open valleys and the broad, flat divides are mantled with grass and support a forest of yellow pines, piñon and cedars.

The soil of the lowlands is, in many places, absent; where present it forms a thin coating for bed rock and its fine ingredients are continuously removed by sudden downpours and by the wind.

The few Navajos who inhabit this region maintain a precarious existence as nomads and range widely with their flocks in search of forage and water. The area is distinctly unfavorable for agriculture even in its most primitive form, and the absence of ancient ruins indicates that it has long remained unsuited to the needs of sedentary cliff-dwellers and their descendants, the Hopis.

#### Physiography.

The primary features of this area are structural. The surface of the Coconino Plateau is developed in harmony with limestone strata which vary little from horizontality. The steep east face of the plateau is the stream-gashed limb of a monocline: the slopes leading to the river are the dip slopes of sedimentary beds. The master stream of the region, the Little Colorado, throughout its course in the area under discussion, has developed along the strike of the tilted beds and has cut its way downward in the effort to maintain an accordant junction with the Colorado. In the shales and weak sandstones of the Upper Triassic, the river has opened a wide valley; in the Shinarump conglomerate and especially in the resistant Kaibab limestone, narrow canyons are normal features. The tributaries of the Little Colorado are consequents whose direction is slightly modified by jointing. The prevailingly flat interstream spaces are dissected by tiny canyons and carry on their surface many small mesas and buttes of rock of younger age, which are frequently eroded by water and wind into fantastic forms.

In physiographic development the Tanner's Crossing area has experienced the episodes which mark the history of the Plateau Province as a whole. Following a period of monoclinal folding, whose record may be read in Coconino Point, Black Point, and in the gentle fold located midway between the east face of the Coconino Plateau and the Little Colorado, the region was reduced to a plain of low relief. Remnants of

#### 494 H. E. Gregory-Reconnaissance of a Portion of the

this late Tertiary erosion surface are preserved at Black Point\* beneath a lava flow, and also at points east of the Little Colorado. Uplift and tilting reëstablished the Little Colorado, whose subsequent history is to be read chiefly in terms of structural control exerted by eastward-dipping sedimentaries of Triassic and Carboniferous (Permian? and Pennsylvanian) age. The ungraded state of the Little Colorado reflects the relative erodibility of shales, sandstones, conglomerates and limestone. Both master-stream and tributaries present valleys of youthful features, --flat-floored, precipitous-walled canyons of steep gradients determined by structural slopes.

The normal course of physiographic development has been interrupted by volcanic activity. Patches of basalt overlying dissected strata of both Moencopie formation and Shinarump conglomerate were noted along Cedar Wash. At Tappan Springs and at the mouth of Cedar Wash these remnant flows attain a thickness of 30 feet; and near the mouth of the Moencopie the canyon of the Little Colorado is rimmed on both sides by palisaded basalt cliffs 30 to 40 feet high. About five miles below Tanner's Crossing the west bank of the river consists of a narrow lava terrace of undetermined length. thickness of these flows and their lack of connection with any of the lavas of San Francisco Mountain or with Pogue Buttes, † a volcanic cone five miles north of this area, suggests a local origin.

No large faults were noted in this area, but several faults of a few inches to a few feet displacement were mapped, and at a point about three miles below Tanner's Crossing a fault trending N. 70° E. with a throw of 70-80 feet was noted by Mr. Heald.

A view of a typical portion of this area is reproduced in fig. 2.

#### Stratigraphy.

The formations represented in the vicinity of Tanner's Crossing are Kaibab (Pennsylvanian) limestone, Moencopie formation (Permian?) shales and sandstone, Shinarump conglomerate (Triassic), and to a limited extent the Upper Triassic shales including the Leroux of Ward. The Kaibab limestone forms the east face of the Coconino Plateau, the floor of the upper parts of several streams leading northeastward from Coconino Point, and the base of the canyon walls of the Little Colorado beginning about three miles north of

\* For a detailed description of this occurrence see Robinson, H. H.: The Tertiary Peneplain of the Plateau District and Adjacent Country in Arizona and New Mexico. This Journal, xxiv, pp. 109-129, 1907. † Named for Dr. J. E. Pogue.

#### Little Colorado Valley, Arizona.

the Government suspension bridge. The Moencopie forms the surface over thirty or forty square miles at the base of Coconino Point and lines the Little Colorado and its western tributaries throughout the greater portion of their courses in this area. The Shinarump conglomerate is exposed as a continuous stratum or as detached mesas on the west side of the Little Colorado, and forms the higher cliffs and the tops of canyon walls along that stream. Patches of upper Triassic

FIG. 2.



FIG. 2. View looking southwest across the Little Colorado canyon from a point about five miles below Tanner's Crossing. The bottom of the west canyon wall is formed of Kaibab limestone, the top is a basalt flow. In the immediate foreground and in the middle distance are buttes composed of shales of the Moencopie formation capped by Shinarump conglomerate.. Coconino Point is seen in the background.

shales, outliers of widespread exposures east of the river, overlie the Shinarump conglomerate between Black Point and Warner Wash.

The stratigraphy of the Little Colorado Valley was discussed by Lester F. Ward in connection with a report on the Older Mesozoic Flora of Arizona.<sup>\*</sup> In this report is included a section of the east wall of the Little Colorado canyon five or six

\* U. S. Geol. Survey, Monograph XLVIII, 1905.

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miles below the mouth of the Moencopie, in which the following formations are represented :

Shinarump formation	
- Leroux member	600 feet
Lithodendron member	500
Moencopie formation	600
Carboniferous limestone	100

The Moencopie formation, consisting of shales and sandstone, was believed by Ward to pass by normal gradation into

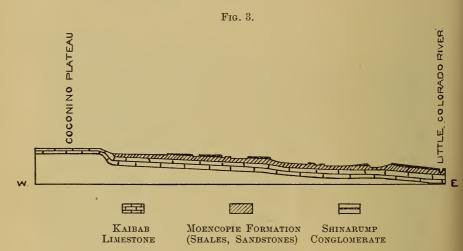


FIG. 3. Diagrammatic section from Coconino Point to the Little Colorado River.

the "Lithodendron member," consisting of conglomerate, sandstone and marls; and this member in turn was found not to be sharply differentiated from the overlying marls, sandstones and limestones of the "Leroux member." "All these beds really constitute one great series."\* No detailed sections were published by Ward, but the descriptions given indicate that the Moencopie includes beds classed as Permian by Walcott and the writer, that the "Lithodendron member" is in part the Shinarump conglomerate of the Navajo Reservation, and that the shale members of the "Lithodendron" and all or part of the "Leroux" are substantially the equivalent of the Dolores formation of Cross.

In other parts of the Colorado Plateau Province the Moencopie formation is separated from the Shinarump conglomerate

\* Idem, p. 22.

#### Little Colorado Valley, Arizona.

by an erosional unconformity, and the probability of finding this erosion surface in the lower Little Colorado led to an examination of the position of the Moencopie with reference to adjacent formations. About three miles below the recently constructed suspension bridge the entire Moencopie section was found displayed, rising above the Kaibab limestone and capped by the Shinarump conglomerate.

A section measured by Mr. K. C. Heald, combined with one measured by the writer, shows the following arrangement:

# Section in wall of the Little Colorado Canyon, $5\pm$ miles below Tanner's Crossing.

Strike N. 15° W.

Dip N.E. / 2°

- Shinarump conglomerate; grey or yellow-grey with patches of black, red and yellow; bottom few inches black sands; consists of partially rounded pebbles 0-2 inches in diameter of white (90 per cent), yellow, red, and black quartz, reddish quartzite, chunks of calcareous shale one inch and less in long diameter, and petrified wood. Cement in part calcareous. About equal amounts of coarse sandstone and of conglomerate. Stratum cross-bedded and lenticular.
- 2. Unconformity ; marked by sudden transition shale to conglomerate, and by wavy, irregular contact including pockets in shale filled with sandstone and conglomerate.

#### Moencopie formation :

Shale, red; bleached white at top; compact, hard, of microscopic fineness: weathers into rounded	
	3 feet
	25
	16
Sandstone	3
	2
Sandstone	2
Shale, arenaceous ; tiny veins of gypsum	11
Sandstone	3
Shale	8
Sandstone, thin-bedded at top. Forms bench	6
Shales, arenaceous, argillaceous and calcareous;	
banded red and grey-green	26
Sandstone, thin-bedded, ripple-marked	1
Shale	20
marked by ripples, mud cracks, worm casts, and	
plant impressions. Muscovite on bedding planes.	2
	of microscopic fineness; weathers into rounded disks Shale, red-brown, argillaceous Shale, red-brown, and thin sandstones; abundant plant impressions like grass or stems of reeds arranged in masses Sandstone Shale Sandstone Shale Sandstone Shale Sandstone Shale Sandstone, thin-bedded at top. Forms bench Shales, arenaceous, argillaceous and calcareous; banded red and grey-green Sandstone, thin-bedded, ripple-marked Shale Sandstone, red-brown, thin-bedded, cross-bedded,

# 498 H. E. Gregory-Reconnaissance of a Portion of the

	Shale	10 feet
	Sandstone, like No. 16	2
19.	Shale	12
	Sandstone in $3 \pm$ inch beds, wavy, irregular, lenti- cular laminæ; cross-bedded, ripple-marked	4
	Shale, red-brown, arenaceous, calcareous, banded and lenticular	7
22.	Sandstone, thin-bedded, lenticular, with bands of shale	2
23.	Shale, calcareous, argillaceous, arenaceous ; banded	
-0.	dark red, light red and purple	18
24	Sandstone, like No. 22	2
	Shale. like No. 23	$\tilde{6}$
	Sandstone, like No. 22	$\overset{\circ}{2}$
27	Shale, like No. 23	$\frac{2}{2}$
28.	Sandstone, chocolate, calcareous, with scattering limestone pebbles	3
90	Shales, chocolate to red, with grey lenses ; arenace-	U
29.	ous, imbricated, ripple-marked; 15 feet from the	
	bottom is a 6-inch bed of sandstone; top 10 feet is	
	dark red, argillaceous shale in regular beds tra-	
	versed by veins of gypsum	40
30	Sandstone, chocolate-red; fine-grained quartz with	40
00.	calcareous cement; cross-bedding both angular and	
	tangential; fine to medium-grained; size of grain	
	varies with each lamina. Near middle of bed are	
	lenses of conglomerate 2 inches to 12 feet wide, 6	
	inches to 100 feet long, highly irregular in shape	
	and composed of chunks and slabs of argillaceous	
	shale, sandy shale and sandstone; muscovite abun-	
	dant; forms vertical cliff	52
31	Shales, chocolate with white bands ; arenaceous and	02
01.	micaceous strata, thin as cardboard, or 2-3 inches	
	thick ; show ripple-marked, mud-cracked, sun-baked	
	surfaces, curled disks, tiny folds and faults	100
32	Unconformity (?)	100
	Kaibab limestone, beds 2-6 feet; buff; fossilifer-	
00.	ous; cavities filled with calcite.	
	Total	390

A portion of the measured section is shown in fig. 4.

## The Moencopie-Shinarump Unconformity.

In another connection\* the writer has discussed the unconformity between the Moencopie and the Shinarump conglomerate as it is expressed at various localities on the Navajo \* This Journal, xxxy, 424-43, 1913.

### Little Colorado Valley, Arizona.

Reservation. This erosion surface is also shown along the Lower Little Colorado at a number of points.

At A1 Ranch in Warner Wash, the lower parts of the canyon wall are formed of chocolate and brown shales essentially identical with the Moencopie exposures at Holbrook and elsewhere along the Little Colorado River. The top of the wall consists of 30 feet of coarse conglomerate; between these

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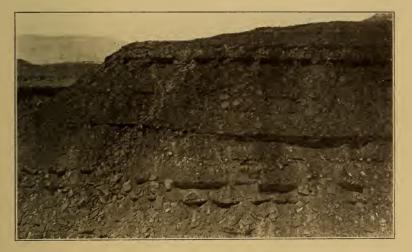


FIG. 4. The upper half of the Moencopie formation, five miles below Tanner's Crossing.

diverse lithologic units is a marked unconformity. Immediately at the contact the section is as follows:

- Shinarump conglomerate. Coarse to very coarse sandstone and conglomerate with pebbles 1-4 inches in diameter arranged as lenses and stringers or embedded as individuals. Many pebbles are rounded, some have lost only their salient angles. About 75 per cent consist of white, grey, and red quartzite, the remainder being quartz, chert, and limestone. The stratum is cross-bedded and banded grey and red on cross-bedding laminæ. Fragments of petrified wood, including logs, are common, and teeth and bones occur in the upper part.
- 2. Unconformity. Wavy surface with troughs 3 inches to 3 feet below crest. Large pebbles and petrified logs in base of Shinarump conglomerate lie directly upon No. 3. The plane of unconformity was mapped at two points (figs. 5 and 6).

30 feet

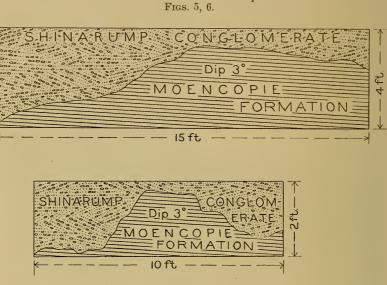


FIG. 5. Diagram of the Moencopie unconformity along Warner Wash.FIG. 6. Detail of the Moencopie unconformity at A1 Ranch.

FIG. 7.



FIG. 7. View of the contact between Moencopie formation and Shinarump conglomerate in wall of Little Colorado River,  $1\pm$  mile below the Government suspension bridge.

### Moencopie formation :

3.	Shale, arenaceous, muscovitic. Excessively fine-	
	grained; grey and purple in tone, blotched with	
	white	1.5 feet
4.	Sandstone in 3-5 irregular beds, separated by films -	
	of shale. Contains thin lenses of red clay pellets	6
5.	Shales, arenaceous and argillaceous in thin beds,	
	banded dark brown and chocolate. The parting	
	planes exhibit sun-baked surfaces, mud cracks,	
	muscovite flakes, and minute imbrications. Many	
	impressions of twigs and branches were noted	20
	Total	57.5

About one mile below the suspension bridge, the angular unconformity between the Moencopie and the Shinarump conglomerate is again exposed as indicated in the photograph (tig. 7). At this point Mr. K. C. Heald found the red-brown shales and sandstones of the Moencopie overlain by 97 feet of Shinarump.conglomerate, "about 40 per cent heavy conglomerate, the rest coarse sandstone with occasional pebbles."

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### ART. XLIII.—Mineral Notes; by W. E. FORD.

#### I. Occurrence of Chalcophanite at Leadville, Colorado.

THE Brush Mineral Collection recently acquired through the gift of Dr. F. B. Laney several additional specimens of the zinc-manganese oxide, hetærolite, from the Wolftone mine, Leadville, Colorado. This occurrence was recently described in an article from this laboratory.\* The hetærolite on the specimens showed no new features worthy of note, but associated with it was a crystallized mineral which on examination proved to be the rare species, chalcophanite, (Mn, Zn)O.2MnO<sub>2</sub>. 2H<sub>2</sub>O. This mineral has been previously observed only at Sterling Hill, Ogdensburg, N. J. It occurred on the Leadville specimens as crusts of minute hexagonal plates covering the botryoidal surfaces of the hetærolite or lining the cavities in the specimen. No crystal faces were observed other than the basal plane. The color of the mineral was a blue-black to an iron-black. Its streak was chocolate-brown. Very thin plates under the microscope showed a dark brown color. These were sufficiently transparent in one or two cases to give a distinct uniaxial interference cross. The mineral proved to be optically negative. While the chalcophanite from the original locality is stated to be opaque to light, an examination of it under the microscope showed that on very thin edges it also had a dark brown color. The Leadville material when heated in the closed tube yields water and its crystals exfoliate somewhat and change to a bronze color. It gives reactions for manganese and zinc. These tests leave no doubt as to the identity of the mineral.

#### II. The Index of Refraction of Manganosite.

Recently it became desirable in the course of another investigation to know the index of refraction of manganosite, the manganese oxide, MnO, this having apparently never been determined. Some specimens of the mineral from Franklin, N. J., were in the Brush Mineral Collection, having been presented by Prof. Charles Palache. A small fragment of the pure mineral was secured from which a prism could be ground. The mineral is colored a deep green and is only transparent on quite thin edges, but after several attempts a small angle prism was obtained through which light could be transmitted. When this prism was illuminated on the refractometer with white light it unexpectedly gave two distinct images of the refracted ray, one colored red and the other green, instead of

\* This Journal, xxxv, 600, 1913.

### W. E. Ford-Mineral Notes.

the usual broad signal showing the colors of the continuous spectrum. The signals were faint but distinct and well separated from each other. This peculiar phenomenon was more clearly explained when a thin section of the mineral was placed between a source of white light and the slit of a spectroscope. The resulting spectrum seen through the instrument showed strong absorption, there being two distinct bands of light, one rather narrow in the red and the other somewhat broader in the yellow-green with only faint light showing in the other parts of the spectrum. The green band was found to occupy approximately that portion of the spectrum between  $520\mu\mu$ and  $575\mu\mu$  and the red band that portion between  $650\mu\mu$  and  $700\mu\mu$ . The indices of refraction of these two bands of light as determined by means of the prism were for green, n = 2.19and for red, n = 2.16. The results are given only to the second place of decimals because of probable errors involved in using such a small angle prism  $(15^{\circ})$  and the difficulty of the measurements due to the faint signals obtained. The index of refraction for sodium light, which could not be measured on account of the absorption of that light, was calculated to be approximately 2.18.

#### III. New Occurrences of Spangolite.

Spangolite, Cu<sub>s</sub>AlClSO<sub>10</sub>.9H<sub>2</sub>O, was first described in 1890 by S. L. Penfield.\* The original specimen, now preserved in the Brush Mineral Collection, showed a group of fine hexagonal crystals proved to be rhombohedral by etching figures. associated with cuprite and azurite. The exact locality of the occurrence of this specimen is not known, but is supposed to be in the neighborhood of Tombstone, Arizona. Later, Mierst discovered the same mineral on specimens from Cornwall, and proved that it was hemimorphic in symmetry. More recently Pelloux<sup>‡</sup> has described its occurrence from Arenas, Sardinia.

Within the last year the Brush Collection has acquired through Mr. Lazard Cahn specimens of spangolite from two American localities. The first specimen came from the Copper Queen Mine at Bisbee, Arizona. The specimen consists of a granular mass of cuprite with small crystals of the mineral upon one surface. With these crystals is one small but well defined crystal of spangolite. The crystal shows a tapering hexagonal pyramid with prominent horizontal striations. It is terminated on the free end by a prominent basal plane so that the crystal presents a strikingly hemimorphic character. Of

\* This Journal, xxxix, 370, 1890. † Nature, xlviii, 426, 1893; Min. Mag., x, 273, 1894. ‡ Ann. Mus. Civico Storia Nat. Genova, iv, 194, 1909; Ref. Zs. Kr. 1, 493, 1912.

course it is possible that the base is a cleavage face rather than a natural plane, although the appearance of the face is rather against this possibility. The identity of the mineral was proven by qualitative tests on some very small fragments of the material obtained from another specimen of the same occurrence and kindly given by Mr. Cahn for that purpose.

The second locality that has recently furnished spangolite is the Grand Central Mine, Eureka, Tintic District, Utah. These specimens show very small hexagonal crystals with horizontal striations in the prism-pyramid zone and are of the characteristic color. The base is again prominent; in some cases apparently as the natural face and in others as the cleavage plane. The hemimorphic symmetry is not obvious. The crystals occur upon massive limonite and cuprite with traces of an earthy copper mineral, probably chrysocolla. It was impossible to get material from the specimens upon which to make chemical tests, but the appearance and association of the crystals is so characteristic as to leave no doubt as to their identity. It is interesting to note that Miers\* pointed out the similarity between the minerals found on the Cornwall specimens and those occurring in the Tintic District, and suggested, therefore, that the original specimen might have come from that locality. The original specimen, however, is quite distinct in character from either of the occurrences described above.

Mineralogical Laboratory, Sheffield Scientific School, Yale University, New Haven, Conn.

\* Loc. cit.

### E. H. Barbour-Medusina Walcotti.

## ART. XLIV.—Medusina Walcotti, a Carboniferous Jellyfish; by Erwin H. Barbour.

THE purpose of this paper is to announce briefly the occurrence of jelly fishes in the Carboniferous limestone of Nebraska, and to propose a new species, *Medusina walcotti*.

In exploring the quarries and exposures of the State, certain quadripartite objects suggesting the form of jelly fishes have long attracted the writer's attention. They are large and coarse, and at first were assumed to be imitative concretions. However, the total number observed seems to strengthen the probability that they are of organic origin. In the fall of 1913, while conducting a field class through the Burlington quarries, located about two miles southwest of South Bend, they were noted again in a new locality, and three specimens were obtained. Two of these were unusual examples, and showed sufficient structure to identify them with the Medusæ.

Dr. Charles D. Walcott, to whom a specimen was submitted, concurs in the belief that these are jelly fishes. Since this group is composed so largely of water, in some species as much as 99 per cent, or more strictly speaking excessively watery gelatine, the wonder is that even traces of such delicate and perishable organisms are to be found. That they are found at all is due to the toughness of their filmy skins. Some of the larger and coarser varieties are even cartilaginous. Under especially favorable conditions, the impressions of jelly fishes are left in fine sands and mud. In this connection, it may be of interest to note that the United States Geological Survey has a collection of 9,000 specimens of jelly fishes. They are reported from the Cambrian, Jurassic, Permian, and Cretaceous. Their period of greatest abundance seems to have been the Cretaceous. We recall no reports of fossil Medusæ from the Carboniferous, outside of Nebraska. Those found in Nebraska are in upper Pennsylvanian strata. According to Mr. W. W. Stoner, mechanical engineer in charge of the Burlington quarries, these casts occur in considerable numbers. However, in a hurried visit but three were secured. The best of these is shown in fig. 1. They are of a good size, about 7 to 8 inches across  $(178 \text{ to } 203^{\text{mm}})$ . The convexity is 3 inches  $(76^{\text{mm}})$ . The oral lobes must have been large. They are They are plainly indicated by the radiating angles of the mouth, aptly called the mouth-cross. The mouth-cross is distinctly shown in each of the three specimens from the Burlington quarry. Traces of the more delicate structures are wanting. Yet it is not impossible that some of them may be determined when a larger number of specimens is at hand. The difference in the geological horizon and the distance from regions productive of fossil Medusæ seem to justify the belief that these jelly fishes are new. Arrangements have been made for the care-

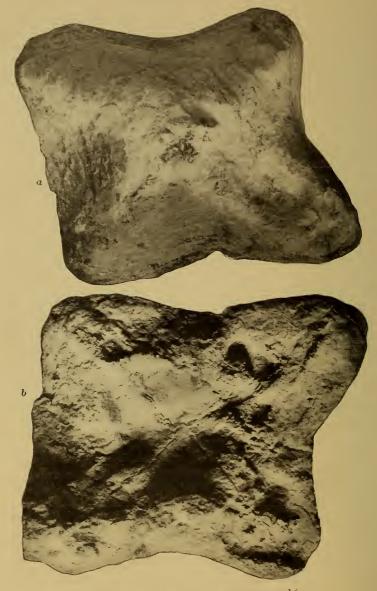


FIG. 1. Medusina walcotti sp. nov.  $\times \frac{1}{2}$ . a, apical view. b, oral view showing mouth-cross.

ful preservation of all specimens exposed in quarry operations at this place, and it is hoped that additional material and data may be secured.

Lincoln, July 20, 1914.

### ART. XLV.—Carboniferous Eurypterids of Nebraska; by ERWIN H. BARBOUR.

DURING the field season of 1912 the Nebraska Geological Survey found a bed of eurypterids about one mile south of Peru. This adds one more to the list of known eurypterid localities, and adds one form believed to be new. Nowhere apparently are eurypterids found in such variety and in such excellent preservation as in New York State, yet the Nebraska beds bid fair to make an unusual showing numerically.

The eurypterid shales of Nebraska, as far as known, outcrop one mile south of Peru, in the Coal Measure bluffs facing the Missouri River. The alternating limestone and shale in the bluffs at the edge of the town change rapidly to shale, which becomes increasingly arenaceous and merges finally into massive sand some forty to fifty feet thick about a mile south of Peru. Here the eurypterid bed is found. The walls and bluffs are vertical, because only recently they were deflection banks of the Missouri River. The tracks of the Burlington Railroad run close to the base of the bluffs. About ten feet above the tracks, and about thirty feet above the river level, may be noticed in the massive sand a distinct shaly band scarcely a foot thick, and two to three hundred feet long. This local band is composed of thin, irregular, shaly layers, seldom a half inch thick, alternating with micaceous sand. The shale seams in the topmost two inches yield the eurypterids. These thin shale seams cleave readily, exposing the eurypterids and numerous associated plants. Because of shrinkage joints, the shales tend to break into rather small blocks, and unfortunately many good specimens are damaged or destroyed.

Since removing a dangerous overhanging ledge the work of collecting has been rendered quite safe and easy, and about forty specimens were found on as many square feet of shale, or approximately one to each square foot. Their chitinous shells are reduced to mere carbonaceous films sometimes scarcely distinguishable from the shaly matrix. Accordingly, some specimens are faint. Others are distinct, however, and well differentiated from the slate-colored background. Some specimens are so well preserved that the details of the gross anatomy may be made out, and even some of the ornamentation and minute sculpturing.

Associated with the eurypterids at Peru are innumerable leaves, stems, and fragments of certain land plants, conspicuously Neuropteris pinnules, stems of Calamites, and leafwhorls of Asterophyllites. The last mentioned add to the beauty of some of the specimens in our collection, because the AM. JOUR. SCI. - FOURTH SERIES, VOL. XXXVIII, NO. 228. - DECEMBER, 1914.

whorls closely imitate pale yellow flowers pressed in the shale. The association of land plants with eurypterids has been observed before. They suggest the probability that this group, the sea scorpions, which originally were distinctly marine, had undergone adaptive modifications suiting them to a brackish, or even fresh-water habit.

Intimately associated with the eurypterids were considerable amounts of actual plant tissue, preserved as such since Carboniferous times. It still retains its pliability, can be stripped from the shale, floated on glass slips, and made into permanent mounts. There are now about one hundred of these mounts in our collection. The preservation of actual plant tissue in such amounts and in large pieces is quite unique. The tissue is of a bright, transparent orange color. It is capable of close study, and photomicrographic reproductions of the cell structure are readily obtainable. This matter will be made the subject of a special leaflet.

As compared with well-known eurypterids, those of Nebraska are small, the average being a trifle over two inches in length, while the largest, as far as known, do not equal three inches. Whether these represent adult or immature forms, is not apparent. They may be immature forms. However, since no evidences of larger individuals have presented themselves, it may be that this is a group of diminutive eurypterids. Average eurypterids are five to ten times as large. The presumption is that many of the specimens at hand are exuviæ.

The prominent feature of any eurypterid is its scorpioid outline. It has a broad flat head, two broad paddles, and a long segmented abdomen or body tapering towards the tail, which usually ends in a sharp spiniform telson. The head-shield is commonly semi-circular, or, in some instances, somewhat quadrate. It bears two prominent compound eyes, and certain simple eyes, or ocelli, which are generally obscure. The headshield probably enabled Eurypterus to shovel and burrow as does the horseshoe crab when in pursuit of marine worms. The jawless mouth of Eurypterus is centrally located on the ventral side of the cephalothorax, and is surrounded by six pairs of appendages, some of the bases of which are so serrated, spined, and dentated, as to serve functionally as jaws, or maxillipedes.

The appendages aside from the paddles are rather inconspicuous. The paddles are greatly enlarged for swimming, and perhaps for roiling water to conceal and protect the creature. The paddles are evidence, rather than proof, of active swimming habits. In fact, Eurypterus may have been rather sluggish, content perhaps with grovelling. Its life habits may be inferred from the closely related form, Limulus.

Eurypterus probably swam well, but it is not unlikely that it chose to frequent sandy and muddy bottoms.

Undoubtedly the Nebraska eurypterids are closely related to Anthraconectes of the Illinois Coal Measures, described some years ago by Meek and Worthen.

#### Eurypterus (Anthraconectes) nebraskensis, sp. nov.

The main features of *Eurypterus nebraskensis* are the vermiform appearance, the long spatulate paddles, and the spinous ridges upon the last five tergites of the postabdomen.

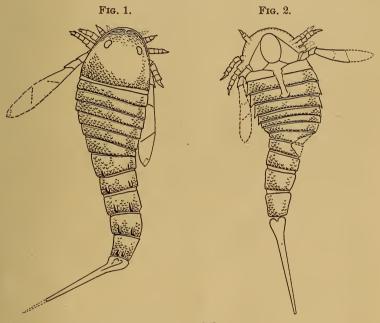


FIG. 1. Eurypterus nebraskensis.  $\times 3/2$ . FIG. 2. Eurypterus, sp., ventral view, showing a very large metastoma and opercular process.  $\times 3/2$ .

In *Eurypterus nebraskensis* the preabdomen is but slightly inflated, and grades insensibly into the postabdomen, giving a vermiform appearance. The telson is long and slender. The scale markings are distinct, and very regular in pattern over the tergites. They are semilunar, and the effect is that of imbricated scales of fishes. The scale-markings continue upon the base of the cephalothorax, but in decreasing numbers anteriorly. At the genal angles, the scale-markings are smaller and closely crowded together. The preabdomen is widest at

the second and third somites, and tapers gradually to the telson. In none of the somites are the pleura produced into sharp angles or spines as far as can be observed. The eyes are roundish-reniform, and are set far apart, close to the cephalic rim. Ocelli are not discoverable. The front of the cephalon is ornamented by fine, closely crowded, vermicular lines, which curve forward and outward from the median line until they meet the cephalic rim.

Measurements: The cephalothorax is  $9 \cdot 5^{mm}$  long by  $11^{mm}$  wide at its base. The preabdomen is  $9^{mm}$  long by  $12^{mm}$  wide at segment 3, its widest point. Segment No. 7 is  $\cdot 5^{mm}$  long by  $11^{mm}$  wide. No. 8 is  $1 \cdot 5^{mm}$  long by  $12^{mm}$  wide.

Each of the others approximate  $1.75^{\text{mm}}$ . In the postabdomen segment No. 13 measures  $2.5^{\text{mm}}$  long by  $8^{\text{mm}}$  wide. No. 18 is  $5^{\text{mm}}$  long by  $3^{\text{mm}}$  wide. See fig. 1;  $\frac{3}{2}$  nat. size.

#### Eurypterus, sp.

This form, possibly a different species, has a noticeably inflated body; long narrow paddles; and pleura seemingly produced into spines. See fig. 2.

Segments 11, 12, 13 are short, possibly because telescoped. This may account also for the expanded body. At any rate this specimen was the only one of the kind found. It is pressed as flat as tissue paper, and it seems to be the ventral surface which is exposed.

The elliptical portion of the head, which is unmistakably defined, is taken to be the metastoma, and yet it is altogether too large. It extends well across the head-shield. The median opercular process, assuming it to be such, is broad and well defined proximally, and is fairly distinct along one border. Segment 1, coxa, of the paddles seems plain, while 2 and 3 are reasonably so.

The specimen is small and colored like its background. Accordingly blemishes and irregularities are not always distinguishable from articulations. The greatest width of the preabdomen is between segments 10 and 11. The head-shield is  $7^{mm}$  long by  $8^{mm}$  wide. Figures 1 and 2 ( $\frac{3}{2}$  nat. size) were obtained by tracing around enlarged photographs, and are thought to be reasonably accurate.

Lincoln, Nebraska, July 15, 1914.

MacCurdy—Passing of a Connecticut Rock Shelter. 511

### ART. XLVI.—The Passing of a Connecticut Rock Shelter; by GEORGE GRANT MACCURDY. With Plate IV.

OF the several dozen rock shelters in the State of Connecticut, that at Pine Rock in Highwood, a suburb of New Haven, was in many respects the most important. In addition to its occupancy by the Indians, it has an interesting geological history.

To the tens of thousands who annually attend the games at Yale Field, West Rock is a familiar feature. Because of its proximity to the main artery of travel between New York and Boston, East Rock is known to even greater numbers. These are only two of New Haven's four rocks. They form two of the principal parks. The other two, though smaller and in private hands, add to the grandeur of New Haven's natural setting. They rise from the plain between and are so related to the two greater rocks as to form with these a series of four convenient stepping stones for the Sleeping Giant\* of Mount Carmel were he to wake from his long sleep. The names of the four rocks in succession are East Rock, Mill Rock, Pine Rock, and West Rock.

The rock shelter formerly known as the "Cave" was on the southern face of Pine Rock. J. W. Barbert gives, perhaps, the first published account of it:

"At the base of this rock there was formerly a cave well known to the inhabitants of New Haven as 'Fry's Cave,' so called from being first occupied by a family of that name, who retained possession of it for several years. In front of this cave there was a small patch of ground which they converted into a neat garden. They obtained a subsistence principally by money received from those who visited their habitation, and by begging. The family of Frys left the cave in 1826, and its next occupants were a colored man and his wife, named Mc-Daniel. These two persons lived in this cave about a year, supporting themselves by making baskets, but in consequence of the death of Mac (as he was commonly called) the cave was deserted. The falling of rocks from above has ruined the habitation and garden, which now has the appearance of a heap of rubbish."

Mrs. Rhoda Wolcutt of 729 Dixwell Avenue, still living at the age of 92, is able to supplement Barber's account. She remembers when "Mac" and "Clo" lived in the Cave. When

\* Now being beheaded by the Connectient Trap Rock Co. † History and antiquities of New Haven, Conn. New Haven, 1831. The location of "Fry's Cave" is indicated on Barber's map.

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her father, Chester Alling, killed game he used to send some of it by his little daughter, Rhoda, as a gift to the old colored pair. Mrs. Wolcutt says she was very fond of going to the Cave, and often staid with Mac, who was an invalid,

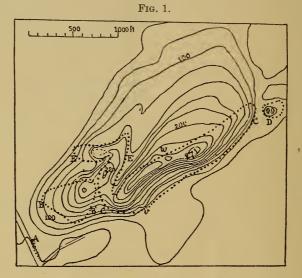
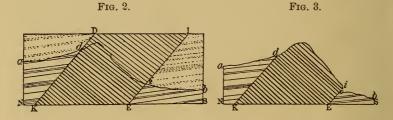
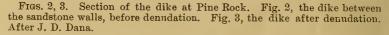


FIG. 1. Contour map of Pine Rock; the Cave is at v. After J. D. Dana.

while Clo went of errands or was away to do a day's washing. They, or some one before them, had built up an artificial front to the cave. Within there were a board floor, cupboard, two





or three chairs, and a table; but there was no stove, only a rude fireplace with stones for andirons, and no chimney. The place was perfectly dry; and according to Mrs. Wolcutt, the inmates "really lived like folks." Finally, Mac died; and Clo, feeling that she could not live there alone, departed, but not until after she had pulled down the artificial front. Another colored man and his wife came and took possession of the cave for a time, although they never made any attempt to rebuild the front, finding evidently that the cave met their needs well enough just as it was.

Mr. W. H. Farnham (brother of the last owner of the Cave), who has lived at the Farnham homestead on Crescent street for sixty-four years, says that the last occupant of the Cave, Indian George, continued to live there until about 1856. Indian George, who had "distinctly Indian features," lived there alone for years as hunter and trapper with only the additional protection that a brush front to the Cave afforded.

The first geological description of Pine Rock is from the pen of James Gates Percival\*:

"Crossing an isthmus of the New Haven and Hamden plain at the passage of the Farmington Canal, we meet a similar dikelike range, that of Pine Rock, directed W.S.W. towards the S.E. point of West Rock. This forms a nearly straight ridge, occupied in its eastern part by a higher, more uniform line of trap, abrupt to the South, where it apparently sinks below the level of the adjoining plain, and bordered on the North by a highly inclined mass of indurated (porphyroid) sandstone."

Percival makes no mention of the Cave, or the sandstone formation on the south, which had been removed by nature to form it. The next notable contribution to the geology of Pine Rock was by Professor James D. Dana. Pine Rock, like all the rocks previously mentioned, is composed chiefly of trap. According to Dana the width of the principal mass of trap (figs. 1-3) at Pine Rock is 300 feet, making it "one of the widest dikes." The dip of the dike is 50° to 55° northwestward, giving to the protecting wall of the Cave an incline of 35° to 40° from vertical. A section of the dike and the sandstone abutting on each side before denudation took place is seen in fig. 2; while a section through the Cave is repro-duced in fig. 4. Both Dana and Barrell believe that seashore waves and breakers were the chief agent in the removal of the sandstone on the south side, thus resulting in the formation of the Cave. The surface of the overhanging wall of trap was of fine texture and fissured, showing that it cooled in contact with the sandstone.

The maximum overhang of the wall of trap was fifteen to twenty feet and the habitable portion of the Cave extended for at least one hundred feet along the rock. It was a dry and sunny shelter, facing the southeast. Since being vacated by

\* Report on the geology of the State of Conn. New Haven, 1842. + On the four rocks of the New Haven region. New Haven, 1891. Indian George, Pine Rock and its Cave had been visited by many classes in geology, but no one suspected that it had been an Indian habitation.

Prior to 1910, Mr. and Mrs. Henry Woodcock of Highwood, local collectors of Indian relics, had noted the presence of quartz and other chips on the surface. The eity having failed to take advantage of an opportunity to buy Pine Rock at a reasonable price for park purposes, it was recently partitioned among three or four local concerns that exploit trap rock. That part containing the Cave fell to the lot of A. N.

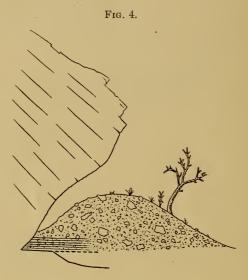


FIG. 4. Section of the Cave as it appeared before the removal of the talus. The relic-bearing deposits are indicated by horizontal lines, beneath which is the level of the sand plain.

Farnham. When he began in 1910 to remove the talus from the Cave preparatory to blasting away the overhanging mass of rock, Mr. and Mrs. Woodcock not only established beyond a doubt the presence of a relic-bearing deposit, but were also able to gather nearly a hundred specimens, chiefly stone implements. They found a considerable quantity of pottery fragments, but saved only a few pieces. Meanwhile other local collectors and even Mr. Farnham's workmen were reaping an archeological harvest; a number of important specimens were also secured by the owner.

The gradual spoliation of the Cave continued over a period of perhaps two years, until on October 18, 1912,

Mr. E. C. Woodcock, of New Jersey, representing the Maltzyme Company, called at the Museum to notify me. He had met the Woodcocks of Highwood and by them had been told of the Cave and the finds made there. That same afternoon I visited the Cave to find it practically emptied. Near the east end were still to be seen a good many sea shells and fragments of bones. With Mr. Farnham's permission, Messrs. Bostwick and Darby of the Museum staff were detailed by Prof. Schuchert to assist me in gathering faunal and other specimens from the kitchen refuse still remaining. In the search, continuing over a period of some three days, several stone implements were found. Cart loads of shells, broken bones, ashes, and black earth had already been removed, most of it going to Mr. Farnham's market gardens.

The condition of the Cave on the occasion of my first visit is shown in Plate IV. A few stone relics were picked up by the Museum staff in the unremoved talus at the right. Evidence of progress in the blasting away of the overhanging trap rock is seen in the upper left-hand corner. The man stands on the sand bench, which served as a floor for the Indian habitation and which is on the same level as the adjoining cultivated fields. A search of the field immediately in front of the shelter failed to reveal Indian relics. Mr. W. H. Farnham, however, has a collection of more than a hundred specimens, including some fine tomahawks and a gouge, gathered by him in former years from fields adjacent to the Cave; and the Woodcocks had previously found many artifacts in the field to the northeast of Pine Rock near the head of Beaver Brook.

According to Professors Dana and Barrell, during an interglacial epoch the sea wore away the sandstone, thus undercutting the trap cliff and leaving the overhanging shelter. The last glaciation swept away all the talus, and upon its retreat the overflowing waters deposited the sand and gravel plains on which New Haven is largely built; the one at Pine Rock is some 75 feet above the present level of the sea. After the retreat of the ice (no one knows how long after, the record having been destroyed), the Red Men came and made the shelter a home evidently for a considerable length of time. The principal deposit they left was exposed to view only after a talus covering of considerable thickness had been removed for road-making purposes.

Copper coins bearing the following dates were found on the surface at the Cave by Carlo Davio : 1784 (or 1754), Georgius II Rex; 1787; 1802, one cent, U. S.; and 1812 one cent.

Another surface find, now in the possession of Mr. A. N. Farnham, is a large stone slab bearing the following incised inscriptions:\*

\* The commas do not appear on the original.

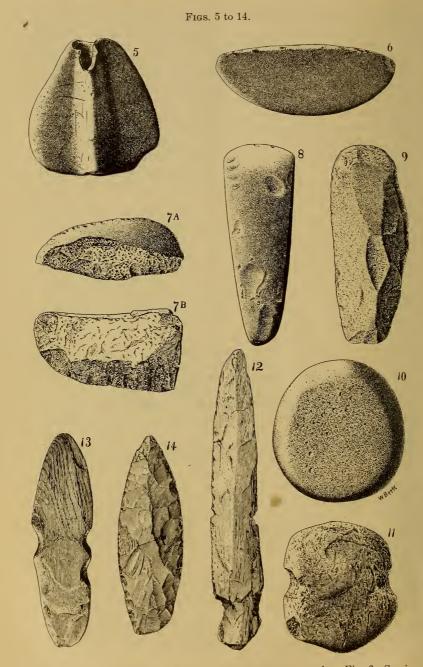


FIG. 5. Banner stone with tally marks along one margin. Fig. 6. Semilunar knife. Fig. 7. Quartz knives. Fig. 8. Polished tomahawk of greenstone. Fig. 9. Rude pick of trap rock. Fig. 10. Grinding stone. Fig. 11. Grooved hammer of granite. Fig. 12. Dagger of schist. Fig. 13. Sinker of schist. Fig. 14. Poniard of hornstone. Fig. 12 is one-third natural size; all the others are approximately one-half. I X B 1753, I Forward 1753, Thomas Williams 1753, John Pell, Jeffrey Smith 1754, W. Williams, Ezra L'hommedieu.

Both Mr. and Mrs. Woodcock insist that there was a thick solid layer of black earth and ashes resting on the sand beach. This layer contained many artifacts and a number of waterworn pebbles of various shapes and sizes carried there by the Indians and for the most part bearing marks of utilization; but very few angular pieces (talus) of trap were encountered. Above was a deposit of talus mixed with more or less black earth and ashes, in which artifacts were likewise found.

If their observation was correct, one of two conclusions may be drawn: (1) The Indians came there so soon after the glacial retreat that a talus formation had not yet encroached upon the floor of the Cave; or (2) finding talus there, they removed it. Had they taken up their abode on the talus covering, some black earth and ashes would have sifted through to the sand bench, but hardly enough to produce the effect of a deposit comparatively free from talus; the presence of artifacts near the sand bench would be even more difficult to explain.

In front of the most protected part of the shelter and near the top of the black layer were two or three wagon loads of shells. Farther to the east were heaps of bones of favorite game animals, chiefly the Virginia deer. Mr. and Mrs. Woodcock estimated the thickness of the black layer at about three feet, which estimate would seem to be confirmed by the author's finding of a fish vertebra still sticking in a crevice of the rock at least three feet above the sand beach.

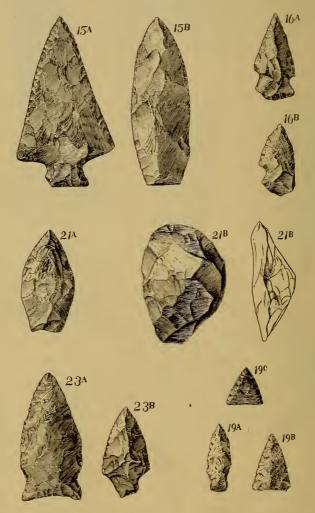
The faunal remains,\* exclusive of shell, include: Bear (Ursus americanus), Raccoon (Procyon lotor), Dog, Lynx, Gray Fox (Urocyon cinereoargenteus), Wapiti (Cervus canadensis), Beaver (Castor canadensis), Porcupine (Erethizon dorsatus), Gray Rabbit (Lepus sylvaticus), Muskrat (Fiber zibiticus), Gray Squirrel (Sciurus carolinensis), Field Mouse (Arvicola riparia), Whitefooted Mouse (Hesperomys leucopus), Turkey (Meleagris gallopavo), Snapping Turtle (Chelydra serpentura), Blackfish (Labrus tautoga). Of human skeletal remains Messrs Bostwick and Darby found only two fragments: the upper portion of a bone of the forearm (radius) and a part of the left temporal and sphenoid. These came from the talus near the east end of the cave.

The shells + comprise: Ostrea virginiana, Venus mercenaria, Pecten irradians, Mya arenaria, Modiola plicatula, Ilyanassa obsoleta, Tritia trivitatta, Balanus eburneus, Crepidula convexa, Crepidula fornicata, Littorina irrorata Say, and common species of land shells. The presence of Littorina

> \* Identified by Mr. George F. Eaton. † Identified by Prof. A. E. Verrill.

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*irrorata*, no longer found north of the Florida coast, instead of *Littorina littoria*, living to-day on the Connecticut coast, suggests a considerable antiquity for the cave deposits. The same



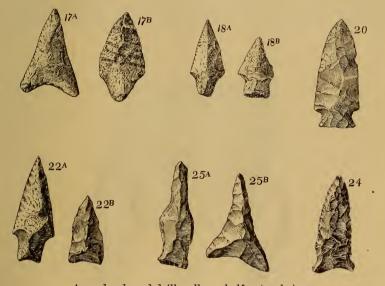
Spearheads and arrowheads, all one-half natural size. FIGS. 15A, 16, 19c, and 21 are of hornstone. Fig. 15B, trap. Figs. 19A, 19B, quartz. Fig. 23, chert.

is true concerning the presence of Wapiti, which at present is not found in the United States east of the Rockies.

I continued to visit the Cave at intervals for a month. One

### MacCurdy—Passing of a Connecticut Rock Shelter. 519

day after an extra charge of dynamite had been set off loosening an enormous mass of trap, the foreman warned me not to approach the Cave. That same evening at about 10 o'clock, with a " roar that shook houses in the vicinity and awoke the inmates of Springside Home," a mass of rock estimated at thousands of tons, in fact all that remained of the overhang, and reaching up and back to the top of Pine Rock, became dislodged and fell like an avalanche, burying several nearby

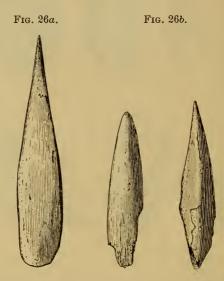


Arrowheads and drills, all one-half natural size. FIGS. 17, 18, are of quartz. Figs. 20, 22B, and 25A, hornstone. Fig. 22A, quartzite. Fig. 24, felsite porphyry. Fig. 25B, trap.

pigpens owned by Mr. Farnham. The number of killed and injured swine is said to have been over two score. The workmen would have met a similar fate had the accident occurred during working hours. The noble shelter has completely disappeared, but thanks to the generosity of several local collectors, the Museum possesses the major part of the relics found there. The two-fold regret is that the removal of the deposits could not have been scientifically controlled, and that the shelter itself could not have been spared as a sort of outdoor annex to the University Museum. Of the specimens figured all we know is that they came from the Cave. There is absolutely no record as to the relative positions of the various objects in the relic-bearing deposits.

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Compensating in part for the lack of scientific control in the removal of the deposits and the destruction of the shelter itself was the ready and generous coöperation of nearly all the local collectors into whose hands specimens from the shelter had found their way. Mr. and Mrs. Henry Woodcock gave their series of nearly 100 specimens. Next in point of size was the combined gift of Frank, James, and Tony del Greco. Oscar and Harry Olson presented their collection of 24 specimens: and Wilbert Bennett, who had found but one artifact, gave that. Two small collections were purchased and the collection of Mr. Farnham, the owner, has been loaned to the Museum.



FIGS. 26a, 26b, Bone points ; fig. 26a is one-half, fig. 26b, two-thirds natural size.

The industrial remains from the Pine Rock Cave are similar to those to be seen in collections gathered from the cultivated fields of southern Connecticut. There is, for example, a single banner stone (fig 5); its height is somewhat greater than its spread of wings and along one margin are several tally marks. Banner stones are not very plentiful in the state. The only semilunar knife (fig. 6) has an unusally sharp edge and a plain back. It is made of slate. Two quartz knives of simple workmanship are reproduced in figure 7. At least one of these is chipped from a waterworn pebble, the original surface of which is retained over a portion of one side.

Only one polished celt or tomahawk (fig. S) has thus far been

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reported from the Cave. The surface is smoked and greasy as if it has been about the camp fire a good deal. A tomahawk of nearly the same shape was recently found by Mr. Dwight B. Pangburn, in a field bordering on Konold's Pond, less than two miles northwest of Pine Rock. Both are of greenstone. Very little use was made of trap, the rock that formed the shelter. One of the few trap artifacts to reach the Museum is a rudely chipped pick (fig. 9).

Several grinding stones made of pebbles were secured, the best one of which is seen in figure 10. A crude, partially grooved hammer of granite (fig. 11) is the only one of its kind

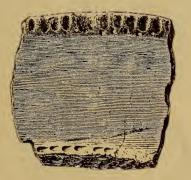


Fig. 27.

FIG. 27. Potsherd showing rim decoration. Natural size.

reported. Equally crude are the large dagger (fig. 12) of schist, and a sinker (fig. 13) of the same material. The schist for these two specimens and the slate for the semilunar knife could have been obtained in the neighborhood of Maltby Lakes.\*

A fine leaf-shaped poniard or spearhead of hornstone is reproduced in figure 14. Of notched spearheads, also hornstone, figure 15 is a good example. The arrowheads include the notched and triangular types. In two cases there is but a single lateral notch at the base; one of these is reproduced in figure 16. Quartz and varieties of hornstone were chiefly used by the arrow-makers (figs. 17–21). There is one arrowhead of quartzite (fig. 22) with a very sharp point and finely retouched margins. Of flints there are but one or two cherty specimens (fig. 23). Drills were scarce. Two types are represented in figure 25. The one with narrow base is of hornstone and the other of trap.

The scarcity of bone artifacts recovered is due in part perhaps to the fact that they did not attract the attention of

\* Rock determinations are by Professor Joseph Barrell.

the collectors so readily as did the stone artifacts. Only three \* specimens, all three bone points, were secured (fig. 26); as two of these were found by our Museum staff, the probability is that many more were carted away with the refuse.

Of pottery a good many fragments were noted by the Woodcocks. Neither they nor the other collectors thought it important to save the potsherds. The sherds preserved belong to two varieties, one of rather fine quality with decorated lip and neck (fig. 27), the other crude. Unfortunately it is not known at what level the pottery was encountered, or whether the two kinds were at the same or different levels.

American archeology has always been handicapped by the lack of chronological data. These can never be supplied by surface finds. Among the possible sources of such data, caves and rock shelters should rightly be counted. The destruction therefore of a cave record like that at Pine Rock is nothing short of an archeological calamity.

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The Cave at Pine Rock as it appeared on the occasion of the author's first visit.

### ART. XLVII.—The Succession of Faunas at Lévis, P. Q.;\* by PERCY E. RAYMOND.

IN spite of the fact that Point Lévis, on the south side of the St. Lawrence River, opposite Quebec, is the typical locality for the cosmopolitan and widely known early Ordovician graptolites, the distribution of the species and the succession of faunas at that locality have remained entirely unknown. The description of the graptolites collected by James Richardson in 1854 and the two following years was intrusted by Sir William Logan to James Hall, and Hall described the species, first without figures, in the Report of Progress of the Geological Survey of Canada for 1857 (1858), and later with very full and beautiful illustrations in a Decade of the same Survey in 1865. Many of the species there described have since been found to have a world-wide distribution, and thanks to the labors of distinguished British and Scandinavian paleontologists, very orderly successions of graptolite faunas have been worked out for Great Britain, Scandinavia, and Australia.

After Hall's description of the fauna from Lévis, almost nothing was done with American early Ordovician (Canadian) graptolites until 1902, when Ruedemann worked out the succession of faunas in the "Graptolite facies of the Beekmantown formation in Rensselaer County, N. Y.,"+ and showed that the general succession of faunules in that section was in substantial agreement with the successions which had been worked out in other countries.

At Lévis itself something has been done between 1854 and the present, but almost nothing which has added to our knowledge of the locality. The original collections were apparently gathered from a number of localities at Lévis, and all put together under one label. Nicholson visited Lévis in 1872 and described some new species from the locality the next year, but as may be seen from his list, the likewise mixed his collections. Gurley does not seem to have visited the locality, but on the basis of collections makes two zones, the main zone in black shale with *Clonograptus flexilis*, and a second higher zone with Diplograpsidæ. He had no way of determining the relations of these zones, but the event has shown that he was correct in making a separation and assigning his "hard, ringing shales" to a higher horizon than the "soft black shale."§

At various times from 1854 to 1888 the officers of the Geological Survey of Canada have collected at Lévis, but they were especially active in 1887 and 1888, when a number of

\* Published by permission of the Director of the Geological Survey of Canada.

Bull. 52, N. Y. State Museum, p. 546, 1902.
 Amn. Mag. Nat. Hist. ser. 4, vol. xi, p. 134, 1873.

§ Jour. Geology, vol. iv, p. 302, 1896.

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collections were made which were reported on by Dr. H. M. Ami in Dr. Ells' "Report on the Geology of a Portion of the Province of Quebec."\* A small number of geographically located collections were listed, but nothing definite was said of the stratigraphic succession.

In commenting on the work of Drs. Ells and Ami, Dr. Ruedemann remarks: "It is, therefore, evident that the complicated stratigraphic conditions under which the Lévis beds are found in the Quebec region do not invite or permit an establishment of the succession of their faunal zones."<sup>†</sup>

Dr. Ruedemann's perfectly justifiable deduction from the previous work in the vicinity of Lévis is happily not in accord with the actual stratigraphic conditions. The structure is certainly complicated enough, but there exists at least one good section sufficiently complete to permit the establishment of the relations of the principal faunas, and if time enough were spent in collecting it is probable that all of Hall's species could be definitely placed as to horizon. In spite of the close folding and the considerable faulting at Lévis, the strata are in general not crushed or metamorphosed, and the fossils are well preserved.

The best section is in the bluff which faces up the river about one-half mile below the station at Lévis, at the point where the street car line climbs to the upper level. It is known locally as Begin's Hill. On this bluff about three hundred feet of strata are exposed, all dipping steeply to the southeast. The following is the section, beginning at a layer of conglomerate exposed in the river at low tide:

#### Section at Begin's Hill.

1. Massive conglomerate with large pebbles of limestone and sandstone. The matrix is largely limestone, but with abundant rounded sand
grains. The whole mass weathers to a rusty yellow color
2. Shale, mostly concealed by the river and rail-
road tracks
3. Hard, dark gray to black shale, some bands of
which weather to a rusty yellow $\dots 60$ ft. = 172 ft.
4. Thin-bedded rather blacker shales with unde-
terminable fragments of graptolites all through.
Good specimens of <i>Didymograptus nitidus</i>
and others have been found seven feet below
the top
5. Thin-bedded limestone with shale partings.
Didymograptus similis and minute trilobites
and ostracods 11 $ft = 232 ft$ .
*Ann. Rept. Geol. and Nat. Hist. Survey Canada, pt. K, for 1887, 1888, pp. 50 K et seq.

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6.	Hard, dark green clay shale. No fossils seen.	9  ft. = 241  ft.
	Banded green and gray shale with very	
	numerous graptolites and brachiopods. The	
	most fossiliferous layer is seventeen feet above	
	the top of No. 5. Lowest bed with Didymo-	
	graptus bifidus	19  ft. = 260  ft.
8.	Dark gray shale band	6  ft. = 266  ft.
9.	Similar shale, weathering yellow. Contains	
	graptolites, Didymograptus bifidus (90° va-	
	riety) and <i>Phyllograptus anna</i> being most characteristic	3  ft. = 269  ft.
10	Dark gray shale	
	Similar shale weathering yellow. Graptolites	<i>J</i> 10 <i>210</i> 10.
11.	present. Top of range of <i>D. bifidus</i>	4  ft. = 282  ft.
12.	Alternating bands of shale which weathers	1 10 202 IU.
	gray or yellow. No fossils seen	51  ft. = 333  ft.
13.	Limestone conglomerate. 4 inches	
	Dark shale above, and yellow weathering	
	shale with Tetragraptus serra below	12  ft. = 345  ft.
15.	Limestone conglomerate with 4 inches quartz	
	sand at top	4 ft.= 349 ft.
	Dark gray shale	30  ft. = 379  ft.
17.	Thin bedded blue limestone, without fossils	3  ft. = 382  ft.
18.	Dark gray shale	12  ft. = 394  ft.
19.	Thin-bedded limestone with a bed of con-	
	glomerate at top and bottom. Zone of Shu-	
	mardia granulosa and Diplograptus dentatus	
20.	Dark shale, weathering yellow	14  ft. = 422  ft.
	Top of bluff.	

In the lower layers of the above section below the street, no fossils have so far been found. Above the street, the lower strata (No. 4) are very thin-bedded, break into small pieces, and though graptolites are present, as is shown by fragments, it has not so far been possible to collect them. The really fossiliferous part of the section begins therefore about 215 feet above the base. Throughout the next 57 feet fossils are fairly abundant, extremely so in zone 7. This entire thickness is characterized particularly by species of *Didymograptus*, the lower 24 feet by the "horizontal" types (*D. nitidus*, etc.), and the upper 33 feet by a "dependent" species. Brachiopods are exceedingly abundant, and the originals of *Elkania desiderata* (Billings), *Acrothele levisensis* Walcott, and *Lingulella irene* (Billings) undoubtedly came from this zone.

Above this zone the strata appear to be almost barren till the limestone at the top of the bluff is reached. In the intermediate strata only a single fossil has been found, a specimen of *Tetragraptus serra*. The limestone at the top of the bluff is exceedingly fossiliferous, in certain layers, and about forty species have been identified, one-half of them graptolites, the remainder brachiopods and trilobites. The most diagnostic graptolite is *Diplograptus dentatus* (Brongniart), but the most abundant ones are species of *Dictyonema*. The striking trilobites are *Shumardia granulosa*, *Endymionia meeki* and *Holometopus angelini*, all of which were described by Billings from this locality and horizon. This layer was called by the late T. C. Weston the "Shumardia limestone," a name which it well deserves. It is not easy to get the fossils in place, but many can usually be obtained from pieces of the limestone which have fallen to the base of the cliff.

About half way between Begin's Hill and the railroad station at Lévis there is a flight of steps by which one may ascend to the upper part of the town. At the base of these steps, at the right hand side of them as one faces the bluff, one may see thin-bedded, light gray limestone, and at the left hard green shale with thin black seams. This limestone contains *Shumardia granulosa*, and the shale above it is full of *Diplograptus dentatus*, *Climacograptus*, etc., showing that these are the same strata as those at the top of the bluff at Begin's Hill. These strata can be traced in the face of the bluff into the well-known anticline on Davidson Street, where one finds the following section, showing the strata above the top of the section on Begin's Hill:

Section above anticline on Davidson Street. (Numbers and measurements continuous with the preceding.)

19.	Thin-bedded limestone, some conglomerate,	
	and shale partings. Shumardia granulosa	
	and other characteristic fossils present. 30 ft.	
20.	Interstratified limestone and shale, the shale	
	carrying graptolites, Diplograptus dentatus	
	being abundant and characteristic	
21.	Hard black and gray shale	80  ft. = 537  ft.
	Concealed	
	Red and green shale	10  ft. = 567  ft.
24.	Limestone conglomerate with large limestone	
	pebbles	
25.	Red shale	15  ft. = 592  ft.

From this point the section is concealed for a short distance, then follow dark gray shales in which the dip reverses, indicating the middle of the sycline.

These two sections combined include all the strata at Lévis which can at present be definitely placed. The heavy conglomerates west of the cemetery at St. Joseph de Lévis are now thought to belong lower in the section, but the structure is so obscure that it is not possible to be certain till an accurate topographic map is available for plotting the outcrops.

It will be noted that the lower part of the section at Begin's Hill is concealed by the river and the railroad. It is possible, however, to trace the rusty conglomerate, which in this section is numbered 1, for a half-mile north along the railroad, to a small cutting, which may easily be recognized, as it is the only one in this vicinity in which there is a shale on both sides of the track. The rusty conglomerate is not continuous through this half-mile, but is, as is explained by the writer in Guide Book No. 1 of Excursion A1 of the 11th International Geological Congress, twice faulted and pushed to the south. That it is the same conglomerate seems, however, to be quite certain, as it has peculiar lithological characters not shared by the other conglomerates of the region.

In the small cutting above referred to and about 20 feet above the rusty conglomerate, is a fine-grained black shale which contains many beautifully preserved specimens of a few species of graptolites. *Clonograptus flexilis* and *C. rigidus* are the most important species. About 30 feet higher in the section is a hard dark gray shale, in which the long form of *Phyllograptus typus* is particularly abundant. Only a few other species have been found in this zone.

In the guide book referred to above, the writer has stated that the lower of these graptolite zones is about 100 feet below the conglomerate, which in the section on Begin's Hill is No. 15. This is the actual field position, but now that the measured section has been compiled, it becomes evident that the faulting has obscured the real relations. The cross faults above referred to have carried the rusty conglomerate further than the conglomerates above, thus mashing it into the shales and greatly shortening the section. The true position of the zone with Clonograptus rigidus, which may be called A, is probably nearly 200 feet below the thin-bedded limestone which forms zone 5 of the Begin's Hill section. Unfortunately this is the only outcrop of the *Clonograptus* beds now known, and its location with regard to the D. bifidus zone will have to remain a matter of estimate for the present. The Clonograptus zone is, however, considerably below that of *Didymograptus*.

The sections given above show that fossils are distributed through a thickness of nearly 500 feet of strata at Lévis, and that four faunules may be recognized, the lower two confined apparently to a very narrow vertical range, while the upper two range through a (relatively) considerable thickness of strata and are capable of division into sub-faunules. For the convenience of the subjoined table, these zones may be known as A, B, C, and D.

A is the lowest zone with Clonograptus flexilis and C. rigidus, Tetragraptus quadribrachiatus, T. serra and T. approximatus.

B is the next higher zone with *Phyllograptus typus*, *Tetra*graptus quadribrachiatus and *Dichograptus octobrachiatus*.

C is the *Didymograptus* zone, which may be subdivided into three sub-zones:

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C1, the lowest, is characterized by horizontal species of *Didymograptus*, such as *D. nitidus* and *D. gracilis*.

C2, the next higher, contains D. bifidus in abundance.

C3 is a thin zone containing that variety of D. bifidus in which the two branches at an angle of about 90°.

D is the highest zone, characterized by Diplograptus dentatus and other Diplograptids. It may be subdivided into two zones, the lower one being that in which the strata are mostly limestone, and the upper in which the strata are shale. The total range of D. dentatus on Davidson Street is about 80 feet.

D1 is the lower sub-zone with *Shumardia granulosa*, other trilobites, brachiopods, and a great abundance of *Dictyonema*.

D2 is the upper one, with numerous graptolites, Diplograptus dentatus, Cryptograptus antennarius, and Climacograptus pungens being especially abundant.

#### Comparison with the section on Deep Kill, N.Y.

Dr. Ruedemann has described in detail the section on Deep Kill, N. Y., and it will be seen that our section agrees in general with that in New York. Ruedemann found in his section three zones, the upper one with *Diplograptus dentatus* and Cryptograptus antennarius, a lower one with Didymograptus bifidus and Phyllograptus anna, and a still lower one which he called the *Tetragraptus* zone, with "horizontal" species of *Didymograptus*. These zones correspond to our D2, C2 and 3, and C1, but C1 does not appear to be nearly so well developed at Lévis as at the Deep Kill, and most of the large specimens of the "horizontal" species of Didymograptus are, at Lévis, found in the sub-zone of D. bifidus. At Deep Kill, the lower zones, A and B, are not exposed, but Ruedemann predicted that the zone with Clonograptus flexilis and C. rigidus would be found below the Didymograptus zones at Point Lévis. For comparison with the foreign sections, the reader is referred to Dr. Ruedemann's excellent papers.

#### Range of Species.

As will be seen from the subjoined table, some of the species have a long range, *Tetragraptus serra* and *Phyllograptus ilicifolius* being found in almost every zone. It must be understood that the identifications are only preliminary, as the bulk of the specimens have not yet been submitted to experts.

In addition to those forms which the writer has himself collected there have been appended to the list those forms which Ami listed, which can, from their geographical locations, be placed in the present section, and also species which Hall mentions as definitely associated on slabs with species whose horizons are now known. These lists are kept separate from the main one. Species marked with an asterisk (\*) in the table were listed by Hall as coming from St. Anne, Que.

Raymond	l—Succe	ssion of	<sup>2</sup> Faunas	at Lévis.	P. c	$Q_{\cdot}$	529

	A	B		<u> </u>			D	
Graptolitoidea.			1	2		1	2	
Dendrograptus flexuosus Hall							×	
D. fructicosus Hall		×				×		
D. striatus Hall							×	
D. succulentus Ruedemann						×		
Callograptus salteri Hall				×		××		
Dictyonema furciferum Ruedemann						×		
D. irregulare Hall						x		
D. rectilineatum Ruedemann						×		
D. 2 new species						×		
Thamnograptus anna Hall				×				
Clonograptus flexilis (Hall) C. rigidus (Hall)	×	· <b>-</b> · ·						
Goniograptus perflexilis Ruedemann	Â				×	×	×	
Loganograptus logani Hall							×	
Dichograptus octobrachiatus (Hall)		×		×				
D. separatus Elles						×		
Tetragraptus ami Elles and Wood							×	
T. approximatus Nicholson T. fructicosus (Hall)	×	··						
T. headi (Hall)		<u>^</u>					×	
T. pendens Elles					×			
T. quadribrachiatus (Hall) T. serra (Brongniart) T. similis (Hall)	×						×	
T. serra (Brongniart)	×			×		×	×	
T. similis (Hall) Didymograptus bifidus (Hall)				××	×	×		
D. bifidus 90° variety				×	 ×			
D. extensus (Hall)				×				
D. forcipiformis Ruedemann						×		
D. indentus (Hall)			×					
D. nitidus (Hall)								
D. pennulatus (Hall) D. similis (Hall)				×				
Isograptus caduceus (Salter)			<u>^</u>			×		
I. caduceus nanus Ruedemann						×	×	
Phyllograptus anna Hall					×			
P. ilicifolius Hall					×	×		
P. typus Hall Temnograptus noveboracensis Ruedemann		×				 ×		
Diplograptus dentatus (Brongniart)						x	×	
Trigonograptus ensiformis (Hall)						×		
Climacograptus pungens Ruedemann							×	
Cryptograptus antennarius (Hall)	:						×	
Dawsonia monodon Gurley					×			
Brachiopoda.								
Elkania desiderata (Billings)				×	×			
Lingulella irene (Billings)				×	×	×		
Lingulella sp. nov.						×	×	
Acrothele levisensis Walcott								
A. pretiosa (Billings) A. rotunda (Nicholson)					×	 ×		
Acrotreta 2 new species						×		
Lingula quebecensis Billings		×				×		
Eorthis sp. ind.						×		
Paterula sp. nov.						×		

....

	A	В	С			D	
Crustacea.			1	2	3	1	2
Agnostus orion Billings						×	
Agnostus orion Billings A. sidenbladhi Linnarsson						x	
Shumardia granulosa Billings						Ŷ	
S. pusilla (Sars)						x	
S. sp. nov.						×	
Endymionia meeki Billings						×	
Holometopus angelini Billings Triarthrus sp. ind.						×	
Triarthrus sp. ind.						×	
"Arionellus" subclavatus Billings Symphysurus elongatus Moberg and Segerberg.			×				
Symphysurus elongatus Moberg and Segerberg-							
S. sp. ind.						×	
Isotelus sp. ind.							
Caryocaris curvilatus Gurley Ostracoda				×			
Ostracoda			×			×	
Graptolites which can be located in the section							
from the associations given by Hall.		1					
<b>.</b> .							
Dendrograptus divergens Hall							
D. erectus Hall						•	
D. gracilis Hall D. diffusus Hall							
Callograptus elegans Hall							×
Dietvonema murravi Hall			.×				
D quadrangularis Hall	Ŷ						
Dictyonema murrayi Hall D. quadrangularis Hall D. robusta Hall	x						
Ptilograptus geinitzianus Hall			×				
P. plumosus Hall			×				
P. plumosus Hall Clonograptus rigidus (Hall)	x						
Loganograptus logani Hall			×				
Dichograptus octobrachiatus (Hall)			×				
Tetragraptus similis (Hall)			×				
T. denticulatus (Hall)			×				••••
T. quadribrachiatus (Hall)			×				
T. serra (Brongniart) Didymograptus arcuatus (Hall)				×			
D. bifidus (Hall)			×	×			
D. constrictus (Hall)				x			
D. extensus (Hall)				×			
D. nitidus (Hall)							
D. pennalatus (Hall)							
D. similis (Hall)							
Phyllograptus ilicifolius Hall				×			
Diplograptus inutilis Hall							×
Trigonograptus ensiformis (Hall) Cryptograptus antennarius (Hall)							×
Cryptograptus antennarius (Hall)							×
Retiograptus tentaculus (Hall)							×
"Graptolithus" extenuatus Hall							×
Graptolites from Ami's lists.							
÷							
Goniograptus thureani McCoy Dichograptus octobrachiatus (Hall)	×		•				
Dichograptus octobrachiatus (Hall)	×						
D. richardsoni (Hall)	×						
Tetragraptus fructicosus (Hall) Didymograptus furcillatus (Hall)				×			
Daymograpius ruremans (man)		(		^			

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R. L. Moodie-Fossil Frogs of North America. 531

## ART. XLVIII.—The Fossil Frogs of North America; by Roy L. Moodie.

THE present review of the fossil frogs of North America is intended to give all the available data regarding the geological and geographical distribution of the Salientia in this continent.

Frogs are of rare occurrence in all known geological formations and our knowledge of their ancestry and origin is very uncertain. It is my intention to indicate, in this review, the possible presence of the Salientia in the Carboniferous of North America and the possible derivation of the salientian Amphibia from other of the Carboniferous land vertebrates. It is the further purpose of this paper to call attention to the discovery of true toads in the Pliocene of Kansas. This announcement is based on remains collected by Mr. J. B. Hatcher in August, September, October of 1884 near Long Island, Kansas. The specimens have recently been sent me for study through the kindness of Mr. Charles Gilmore of the United States National Museum, to which institution the specimens belong. It is the further purpose of this paper to publish figures of the only known American Jurassic Frog, the *Eobatrachus agilis* of Marsh. Professor Marsh has evidently intended to describe and illustrate the *Eobatrachus* fully, for these drawings were found among his effects in the National Museum. They are here published as he left them.

Remains of Salientia have been found in the following geological formations: Carboniferous (Middle Pennsylvanic) (?); Jurassic (Comanchean) Como Beds; Upper Miocene (Pliocene); Pleistocene.

#### PELION LYELLI Wyman.

This Carboniferous species has been very thoroughly treated in the writer's forthcoming monograph of Carboniferous Amphibia and a detailed description in this place is not needed. The length of the vertebral column was probably considerable, possessing an estimated number of 22 or 23 vertebræ. The vertebral segments of all modern and fossil Salientia is nine, but it is well known that the urostyle is a series of coössified vertebræ. This anyone may demonstrate to his satisfaction by the study of a tadpole cleared by the potash method as outlined by Professor Mall\* and the writer. + The ossifications in the urostyle are definitely segmental and young stages show perichondral ossifications similar in many respects to the ossification of other vertebral centers. The whole subject, however, needs careful study, and these observations, while I

\* Amer. Journ. Anat., 1906. + Amer. Journ. Anat., 1908.

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believe them accurate so far as they go, must be confirmed and extended. If the metameric arrangements of the primitive ossification rings in the urostyle indicate that the Salientia came from ancestors with long vertebral columns, then *Pelion lyelli* from the Carboniferous of Linton, Ohio, may well stand in such an ancestral relation. The species is, however, very little known. The remains were the first discovered in the Linton beds of Ohio and in spite of careful search and among the hundreds of other specimens taken from this interesting locality, there has not turned up a single fragment that resembles *Pelion lyelli*. Whether the Linton fauna will be rediscovered remains to be seen.

The remains of *Pelion lyelli* consist of the impression of the ventral surface of the skull and mandible highly carbonized and the structures obscured; a portion of the vertebral column; the major portion of the pectoral girdle and arms; remains of one leg; and an indication of the pelvis. So far as the form of these elements go they are all strikingly salientian, as was noticed by Wyman and Cope and to which attention has been several times called.

It would be too bold a statement to say that *Pelion* is an ancestral salientian, for our knowledge is such that we can say but little more than that *Pelion* looks like a frog with a characteristic long leg and a long back.

The specimen of *Pelion lyelli* is in the American Museum of Natural History.

The history of the Salientia geologically is an interrupted one and if *Pelion* is a frog then the next indication we find of frogs in America is in the Upper Jurassic (Comanchean), in the Como Beds of Wyoming first mentioned by Professor Marsh in 1887 and more fully described by the writer in 1912.

#### EOBATRACHUS AGILIS Marsh.

Marsh, this Journal (3), xxxiii, p. 328, 1887. Marsh, Proc. Brit. Assoc. Science, Aberdeen Meeting, 1885, p. 1033. Marsh, Monograph U. S. G. S., xxvii, p. 508, 1897. Moodie, this Journal, xxxiv, p. 286, 1912.

The specimens of *Eobatrachus agilis* Marsh seem to indicate a bufonid nature for the species. In fact I think we would be safe in locating the species in the family Bufonidæ. The reasons for placing the species in this family are chiefly on account of the well-developed condition of the lower end of the humerus (fig. 1, a; 2, d), and its apparently calcified condition. The ulno-radial articular surface of the humerus is certainly not the same in *Eobatrachus agilis* as it is in *Rana pipiens* or *Rana catesbiana*, and it does resemble the epiphysial structures of calcified cartilage of some of the toads. The specimens represent two or more individuals. At least there are two different grades of sizes. All of the specimens are from quarry 9 of the Como Bluff in Wyoming; and are now preserved in the Yale University Museum.

The humerus (No. 1862, Yale University Museum) of what I suppose to be the typical specimen is represented by the lower end only, this portion measuring  $6^{mm}$  in length, by  $2^{mm}$ in distal width, by slightly more than half a millimeter in shaft diameter. The well-developed characters of the bone indicate a bufonid nature for the species. The ulno-radial articular surfaces are as distinctly marked as in all modern Salientia with which I am acquainted. The ball is apparently capped with calcified cartilage. Above the ball is a distinct pit for muscular attachment, precisely as in modern frogs. The shaft is quite slender and nearly circular (fig. 1,  $\alpha$ ).

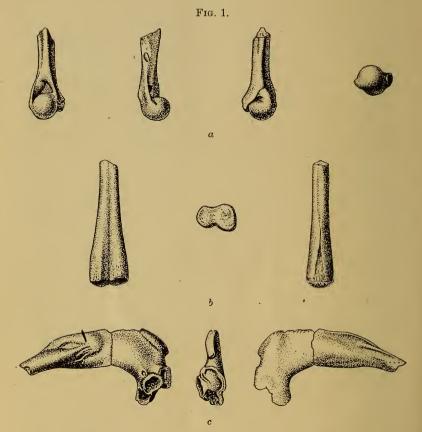
The *ilium* (No. 1568 Yale University Museum) is quite peculiar and will possibly be sufficiently characteristic to sustain the validity of Professor Marsh's genus, *Eobatrachus*. The element is of the right side. It measures  $10^{\text{mm}}$  in greatest length, by  $3^{\text{mm}}$  in greatest width, by  $2^{\text{mm}}$  in greatest thickness on the articular surface. The element is a slender rod, like the modern salientian ilium, with the anterior end greatly narrowed and pointed; the pointed portion occupying one and onehalf millimeters. The shaft of the ilium is flattened laterally. It expands in width from a little less than one-half a millimeter to slightly more than three millimeters. The articular surface is marked by four pits which are the surfaces of the synchondrosteal union of the halves of the pelvis. The element is greatly thickened posteriorly, with a slightly developed, posterior dorsal crest (fig. 1, c).

The *femur* (No. 1862 Yale University Museum) is quite distinctly amphibian of the salientian type. It is a slender rod of bone from which the epiphyses have been lost, leaving in their place pits occupying the ends of the bone; indicating the slight development of the endochondral ossification, as in all Amphibia. The lower end of the femur is divided into two surfaces by an imperfect partition, as in most modern frogs. The upper end is peculiar in having a well-developed crest which, in life, was undoubtedly capped by a large amount of cartilage. In the fossil state it has been preserved as a spine. The femur measures  $12^{mm}$  in length, by  $3^{mm}$  in distal width, by  $1^{mm}$  in diameter of shaft, by  $2\cdot 5^{mm}$  in proximal width.

The *tibio-fibula* (No. 1394 Yale University Museum) is represented by a portion of the lower end including  $S^{mm}$  of the element. Its characters are so clearly those of the modern Salientia that a description is hardly necessary. The lower end is divided by grooves one on either side, indicating the previous

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separation of the tibial and fibular elements, thus plainly showing that the frogs have had a long pre-Jurassic history (fig. 1, b).



- FIG. 1. Professor Marsh's drawings of *Eobatrachus agilis* from the Jurassic of Wyoming.
  - a. From Can 4. Four views of the humerus (1862) collected in the Como beds. × 4.
  - b. Three views of the tibio-fibula (No. 1394) from tray 13 collected in the Como beds.  $\times$  4.
  - c. Three views of the ilinm—the inner, the posterior and the outer. (No. 1568) from Can 1.  $\times$  4.

Another *humerus* (No. 1863 Yale University Museum) is similar to the one already described, although smaller.

The Jurassic frog thus indicated was an animal about the size of *Bufo debilis* Girard of western Kansas and Texas. In

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the writer's previous paper the statement was made that Eobatrachus was the oldest known frog. At the time I was not aware of the species Paleobatrachus gaudryi described by Vidal in 1902 from the Kimmeridge of Spain. Doctor Abel called my attention to this species and kindly furnished

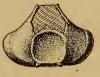
F1G. 2.







a













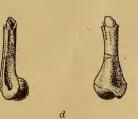


FIG. 2, a.

- *b*.
- Three views of vertebra (No. 1763), Can 42. × 4. Posterior view of vertebra (No. 1763), Can 42. × 4. Lateral, posterior and dorsal views of proximal portion of urostyle (No. 1687), Can 2. × 4. с.
- Four views of humerus (No. 1863). d. × 4.

the references given below.\* The only question now as to the relative ages of the species is that of determining the relative ages of the Kimmeridge and Morrison and of the two the Kimmeridgian is undoubtedly the older,

#### Bufo sp.

The deposit near Long Island, Kansas, had been known for many years as a deposit famous for the production of rhinoceros and other mammalian forms. From these deposits also come the interesting Euphorbia (Tithymalus willistoni Cockerell). The frog remains recently sent me by the United States National Museum were mingled with the Euphorbia seeds, with fragments of small rodents, with small undetermined lizard bones in such a way that they must have been either blown or washed into the same pocket. I have separated out the skeletal elements of several individuals of toads. The elements are chiefly limb bones, vertebræ, urostyles, ilia with scarcely a fragment that can be identified as skull. The humeri especially show well-developed and well-preserved epiphyses which are calcified and are occasionally firmly attached to the cylindrical shaft. In one humerus there is a well-developed deltoid crest which was probably capped by cartilage, this in turn being confluent with the articular cartilage of the head of the humerus. I have had no means of identifying the specimens specifically and I cannot be positive the genus is correct. This must be done by someone connected with an institution containing extensive collections of skeletal elements of the salientian Amphibia. It is not thought desirable to figure the remains, this being left to the one who will discuss the taxonomy of the creatures involved. There is nothing among them which is not found in the modern bufonid.

In the Pleistocene of Pennsylvania and of Arkansas Wheatly and Brown<sup>+</sup> have found remains which they have regarded as Rana, but the elements preserved are very scanty. Professor Lull also reports the finding of remains of Salientia in the Pleistocene deposits at the head of Tule Canyon, Briscoe County, Texas.

Department of Anatomy,

University of Illinois, Chicago.

\* In case others may not have seen the following reference I give it here in full:

Louis Mariano Vidal: Sobre la presencia del tramo Kimeridgense en el Montseih y hallazgo de un Batracio en sus hiladas.

Sur le presence de l'etage Kimeridgien an Montseih (Province de Lerida, Espagne), et decouverte d'un Batracien dans ces assises.—Memorias Real Academ. Cienc. y Artes de Barcelona, iv, 1902, No. 18. (The frog is named Palæobatrachus gaudryi, Vidal, 1902). † Mem. Amer. Mus. Natl. Hist. 1.

G. Torossian-Reduction Test for Tungstic Acid. 537

# ART. XLIX.—Modifications of the Reduction Test for Tungstic Acid; by G. TOROSSIAN.

WHEN acted upon by suitable reducing agents in acid solution tungstic acid is reduced, the solution becoming blue and then brown. Examples of such reductions are the well-known tests with zinc, tin, or aluminium in presence of hydrochloric acid. The test may, however, be made more delicate if the substance to be tested be used in solid (and thus highly concentrated) form and the reduction brought about either by simple friction (in the case of tungstic acid), or, better, with the aid of a very little hydrochloric acid.

#### The Dry Test for Free Tungstic Acid.

When yellow tungstic acid, or tungsten oxide, is rubbed upon a bright surface of iron, aluminium, zinc, nickel, or copper, in the form of sheet or foil, the yellow color is changed to greenish-blue, while the surface of the metal becomes covered with a deep velvet-blue coating. This action serves as the basis of a convenient test for tungstic acid, and, less favorably, for tungstic oxide.

In making the test the powdered substance is placed upon a sheet of paper and simply rubbed with a bright iron spatula or with a strip of bright aluminium. In absence of agents capable of exciting marked oxidizing action upon the lower oxides of tungsten, tungstic acid is reduced and a blue coating will appear upon the surface of the metal. Moistening the rubbing surface by breathing upon it tends to facilitate the coloration. Representative mixtures of tungstic acid with sulphur, calcium fluoride, potassium silicofluoride, alkali chlorides, alkali carbonates, alkali sulphates, tin oxide, or zinc oxide, gave the color in experimental trials; but mixtures of tungstic acid with potassium chromate or dichromate, chlorate or nitrate, or with sodium nitrate, failed to respond to the test.

#### The Acid Test for Tungstic Acid and Tungstates.

The presence of hydrochloric acid facilitates the reducing action of the metal upon the substance to be tested, either tungstic acid, a tungstate or any tungsten compound, and the consequent development of the color, even in presence of an oxidizer. Modifications of this mode of testing and the results obtained are shown in the following concise statement:

<ul><li>Procedure.</li><li>(a) Rubbing the finely powdered substance with an iron spatula and moistening the adherent coating with concentrated hydrochloric acid.</li></ul>	Results. (a) Blue color: developed in absence of oxidizers and higher oxides (e. g. ferric oxide), and without interference by as much as 50% of molybdic acid.
(b) Placing the powdered substance upon aluminium (plate or foil); moistening with a drop or two of water; addition of a drop or two of concentrated hydrochloric acid.	(b) Blue color: developed in pres- ence of oxidizers, ferric oxide, etc.
(c) Placing the powdered substance on aluminium (plate or foil) and touching with a drop or two of concentrated hydrochloric acid.	(c) Wine-red color with superposed layer of blue : developed, in ab- sence of oxidizers, in tests applied to tungstates of calcium, stron- tium, barium, lead, zinc, and rare earths (precipitated sodium tungstate from a solution of rare earth sulphates containing about 26% CeO <sub>2</sub> ).
(d) Placing of water (big drops) in a single globule (not spread) upon sheet aluminium; sprinkling the powdered substance upon the globule; addition of a very small drop of hydrochloric acid to the globule.	(d) Blue color: developed in pres- ence of insoluble carbonaceous material, copper oxide, hematite, lead oxides, sulphur, rare earth oxides, or calcium fluoride.

All the above tests, which are very simple, easily made and rapid, give positive results under different conditions; but the delicacy of the test must necessarily vary with the composition of the substance under test. It was found, for example, that tungstic acid in mixture (fused) with sodium carbonate in the proportion of 1:1000 (0.01 gram.: 10 grm.) was plainly indicated by (c), while the ordinary mode of testing with zinc and hydrochloric acid failed to show any blue coloration; that while tests applied in the ordinary way (zinc and hydrochloric acid, or stannous chloride) to a mixture of sodium tungstate with sodium nitrate in the proportion of 1:50 failed to show the presence of tungstic acid, as did also (a) and (c), the procedures of (b) and (d) gave distinct and good reactions.

The most generally applicable forms of these tests are plainly the second (b) and fourth (d), the essential point of each being the action of a very small amount of dilute hydrochloric acid upon the powdered substance in contact with metallic aluminium.

Cleveland, Ohio.

# ART. L. - The Distribution of the Active Deposit of Actinium in an Electric Field; by A. N. LUCIAN, PH.D. (Yale).

## I. Introduction.

THE observation first made by Rutherford, that the active deposit of radium is to a large extent concentrated on the cathode in an electric field, led naturally to the supposition that the deposit consisted of positively charged particles and that under suitable conditions the concentration could be made complete. The results obtained by Wellisch and Bronson\* and by Wellisch+ separately showed that this supposition is not justifiable. In the second paper cited, it has been shown that the radium deposit atoms consist of neutral and positively charged particles; that even under the most favorable conditions only a definite proportion (about 90 per cent) of the particles is deposited on the cathode; that there is distinct evidence of columnar or initial as well as volume recombination and that in general both effects are much more pronounced for the case of deposit particles and gas ions than for the gas ions among themselves.

The work on the actinium active deposit had been quite inconsistent from the beginning and had given rise to various views in regard to the origin and the sign of the charges carried by the deposit atoms and the mechanism of the transfer in an electric field. Recently, Walmsley; published the results of a series of experiments in which he eliminated the disturbing causes existing in the work of previous investigators, such as presence of dust, moisture, etc. and arrived at the following conclusions: (1) The distribution of the active deposit of actinium between the electrodes is independent of the amount of the emanation, (2) with suitable fields all of the deposit can be collected on the cathode, (3) actinium A and B acquire their positive charge in the process of their creation, (4) in an electric field actinium A and B behave exactly like the positive gas ions produced by their radiations; they recombine in exactly the same way (initial recombination being absent); and the activity on the anode is due entirely to the diffusion of uncharged deposit atoms formed by recombination in the volume of the gas.

The observation that the distribution of activity over a wide range is independent of the amount of emanation and that the activity on the anode is due to the diffusion of neutral particles are in agreement with the results obtained by Wellisch

\* Wellisch and Bronson, Phil. Mag., vol. xxiii, May, 1912.
† Wellisch, this Journal, vol. xxxvi, Oct. 1913.
‡ H. P. Walmsley, Phil. Mag., vol. xxvi, Sept. 1913.

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for the case of radium. On the other hand, some of the above results are in direct contradiction to the experimental facts established by Wellisch for the active deposit of radium, which one would expect to hold in the case of actinium also.

The following investigation was undertaken with a view of distinguishing between the two contradictory sets of results and the corresponding theories, based on them, as to the origin of the charges carried by the deposit particles, their mode of transfer and recombination in an electric field, etc. The main objects of the experiments contained in this paper may be briefly summarized as follows:

(1) Is it possible, under suitable conditions, to collect all the active deposit of actinium on the cathode?

(2) Is columnar as well as volume recombination present?

(3) Does volume recombination between the positively charged actinium deposit particles and the negative ions take place at the same rate as the recombination between positive and negative gas ions?

Before describing in detail the experimental procedure, it is not out of place at this stage to draw attention to a fundamental difference between the method adopted by Walmsley and that followed in the present investigation. In Walmsley's experiments no direct measurement of the activity of the outer electrode (cylindrical vessel with the air-inlet on the side) was made; the total activity was assumed to be equal to the sum of the activities obtained when the central rod was first made the cathode and then the anode. It will be shown later that this assumption is not justifiable. In the present research the activities of both the case and the central electrode were obtained by direct measurement.

#### II. Experimental Procedure.

The source of the actinium emanation employed was a preparation of actinium, which Professor Boltwood kindly placed at my disposal.

The air current, which carried the emanation into the testing vessel, was produced by means of an ordinary water-blower. This gave the desired high velocities of the air current, which could not be conveniently obtained by means of a Mariotte's bottle or a gasometer. In order to obtain constancy of flow three regulators were installed in the system; a water-pressure regulator, in series with the water-blower, and two gas-pressure regulators along with several large capacities. With these appliances the variations in the pressure were reduced to about 1 per cent.

The air current was conducted through a concentrated solution of potassium hydroxide, to eliminate carbon dioxide, through two bottles of concentrated sulphuric acid to dry it and through a train of two or more tubes containing  $P_2O_5$ , plugged at each end with glass wool, to absorb any residual minute traces of moisture. The perfectly dry condition of the last  $P_2O_5$  tube indicated that no trace of moisture was left in the air current. This dry air current was then passed through the tube containing the actinium preparation, which was plugged at both ends with cotton wool. Finally the emanation was led into the testing vessel through another cotton wool plug.

The vessel used in the experiments consisted of a brass cylinder with an insulated central electrode sprung into a split brass rod and very easily detachable from it. This rod in turn was rigidly fixed in the tapered ebonite plug P, which fitted closely into the guard-ring E. By employing sealing wax and stop-cock grease all the joints, shown in the diagram, could be made sufficiently air-tight. The dimensions of the vessel are as follows:

Inner height	=	$25 \cdot 2^{cms}$
Inner diameter		
Diameter of inlet	=	3.8
Diameter of central electrode	=	·151
Exposed length of central electrode	=	23.1
Distance of electrode from gauze	=	1.8

The diagram of connections is shown in fig. 1. H is a spring-brass clip slipped over the brass rod to connect the central electrode with the electrometer system. E is a guard tube, which is always kept earthed to prevent any leakage over the surface of the insulators. F is a brass ring which was employed in order to remove the ebonite plug P and the electrode without the necessity of handling the insulation. G is a piece of fine-mesh gauze placed over the cotton wool in order to prevent an abrupt change in the regularity of the electric field at the bottom of the vessel and also to stop cotton wool particles being blown into the test-vessel. b is a detachable brass piece placed centrally over the gauze in order to make the flow symmetrical, as much as possible, with respect to the case and the central electrode. The vessel was supported on the side by spring-brass clips (not shown in the diagram) which were mounted on ebonite and were connected to a series of highpotential accumulators through the water resistance H and the triple key M.

The wire B in the figure goes to a second vessel, of construction identical with A, except for the bottom, which was a flat brass piece in this case. KR'D is a potentiometer arrangement which was employed whenever it was necessary to charge

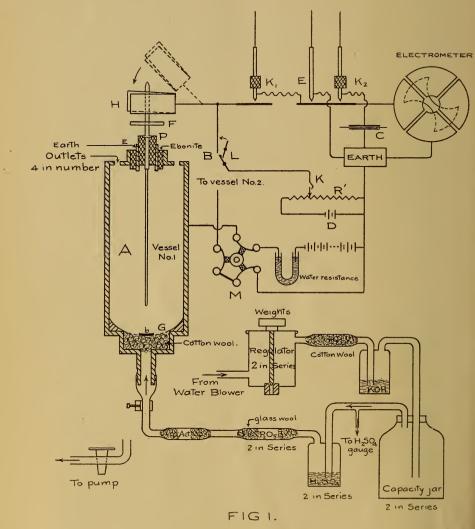


FIG. 1.

DIAGRAM OF CONNECTIONS.

the quadrant system to any desired potential. It might be worth mentioning that the key K was connected with the double-lever system in such a way that by closing K either way simultaneous contact was made at L with the electrometer lead; thus the use of two separate keys was avoided.

The usual electrometer key-system is represented by  $K_1$ , E and  $K_2$ . C is a capacity of tinfoil and mica, which when added to the electrometer system would increase the total capacity of the system 48 1/2 times. The electrometer was of the Dolezalek type with a platinum suspension. The needle was kept charged to a potential of 120 volts; and at this potential the sensitiveness was about 190<sup>mms</sup> per volt on a scale a meter away. The leads, the keys, the capacity and the electrometer were carefully screened from all electrical disturbances.

The potentials used, varying up to 1700 volts, were obtained from a battery of high-potential cells.

The method of procedure in general was as follows :

The air current was first established; the vessel was connected to an air-pump and was exhausted to a pressure of a few mms. of mercury, the outer surface being simultaneously heated moderately in order to expel traces of residual gas. The vessel was then quickly put in connection with the aircurrent, which was made to pass through the actinium tube; the potential was applied and the air current regulated to the desired pressure. This method was followed in all the experiments and evidently insured a perfectly dry and dust-free stream of emanation flowing into a dust and moisture-free vessel. The electrode and the vessel were thus exposed to a steady flow for a period long enough for the emanation to get into equilibrium with its subsequent products. This period of activation was usually three hours and never less than two and a half hours.

When equilibrium was established, measurements were taken of the ionization current passing through the vessel, first with the potential (v) used in the particular experiment and then with a standard potential, which was 600 volts in all cases. These ionization currents are designated by  $I_v$  and  $I_{000}$  respectively. These operations in general disturbed the activity distribution: hence after the ionization readings ample time was allowed for this distribution to be restored. Then the actinium tube was removed, the electric field was switched off and a strong current of dry air allowed to flow for a minute in order to drive out the emanation and deposit particles remaining in the vessel. Time was measured from the instant of the removal of the actinium tube.

The amounts of deposit which settled on the case and the central electrode were measured by the ionization current to which they gave rise, with an applied potential of +200 volts on the case. Although this potential was not sufficient to afford saturation current, later experiments showed that the ratio of the activities thus measured was the same as that obtained by using higher potentials. To measure the case activity, the ebonite plug P containing the central electrode was removed, care being taken that the electrode did not touch the sides of the vessel, the gauze bottom was removed and a clean flat bottom was screwed on, to avoid spurious effects due to deposit particles collected by the cotton wool. Then a fresh electrode held in a stiff brass rod, without the ebonite plug, was introduced into the vessel and held as usual by the brass clip H: and a series of readings of ionization current were taken at definite intervals after the zero of time. It is to be noticed that by avoiding the use of ebonite the ionization current could be measured with great precision. As the case activities were in general small, their exact value was of relatively greater importance than those of the central electrode; hence a greater number of readings were taken with and without the capacity C in order to check the results. It might be mentioned that almost all the readings were taken with the capacity added to the system. From these ionization current readings due to the activity, calculations were made of the maximum activity at the time when the deposit was in equilibrium with the emanation, by means of the table given in Appendix II, p. 147 of Makower and Geiger's Practical Measurements in Radioactivity. Ordinarily three or four readings were taken and these gave for the maximum activity results which were very consistent and well within the limits of experimental errors.

The activity on the central electrode was determined by removing it from its holder and suspending it in the vessel B in the same manner as described above and measuring the ionization current to which it gave rise at definite intervals after the removal of the actinium tube.

In all measurements of the ionization current, the zero of the electrometer was made the center of the swing. This was accomplished by the use of the potentiometer arrangement mentioned above.

The amount of emanation in the vessel was varied by varying the distance of the source of emanation from the vessel, keeping the pressure and hence the velocity of the air stream constant. This method was adopted, in preference to changing the stream velocity, for the reason that in this way the relative concentration of the emanation along the vessel would remain constant, as is evident from the form of the expression,

 $e^{-\frac{\gamma}{v}x}$ , for the concentration at any distance x from the bot-

tom. Varying the distance of the source means simply varying the concentration at the bottom of the vessel or shifting the axis of ordinates of an exponential curve along the X-axis.

The velocity of the air current, which depends upon the pressure and the resistance of the series of tubes and bottles, was roughly measured in the following way:-Exposures were made in the usual manner with different pressures and the activities on different portions of the electrode were measured separately. This measurement was effected by inserting the wire centrally into a long brass tube of small diameter, which had a small window cut at its middle exposing about 6<sup>mms</sup> of the electrode, and placing the tube inside the ionization chamber of an ordinary a-ray electroscope. A large number of experiments were performed and it was found that the distribution of activity along the wire decreased exponentially with the distance from the end; except at the lower extremity where there was an abnormal increase, obviously to be expected when we consider the volume of the emanation to which the end of the electrode was exposed. Curves were plotted for each pressure and from these the distance x, in which the activity fell to half-value, was measured and the velocity v calculated, taking the half-value time to be 3.9 secs. It must be remembered that these determinations of velocity for a given pressure are not absolute, and that any change in the resistance of the line will change the velocity of the flow. This was noticed constantly during the course of the investigation.

The pressure of the air-current finally chosen was about  $14 \cdot 0^{\text{cms}}$  of  $H_2SO_4$ . With this pressure the velocity obtained was about  $5^{\text{mms}}$  per sec. and the concentration of the emanation fell to less than one per cent in a distance of about  $15^{\text{cms}}$ , which is more than one-half the height of the vessel employed. It will be seen that with this velocity more than one-half of the emanation would be found above the first few mms. of the central electrode, the only places where any irregularities may be expected. Thus the velocity chosen gives us a fair degree of approximation to the ideal case where the emanation may be uniformly distributed in the vessel and the deposit made evenly along the length of the electrodes.

As is to be expected, experiments with lower pressures, such as  $9^{\text{cms}}$  and  $5^{\text{cms}}$  of  $H_2SO_4$  gave smaller values of the percentage of cathode activity, due to edge-effect and other causes which helped the case to get more than its share of the activity.

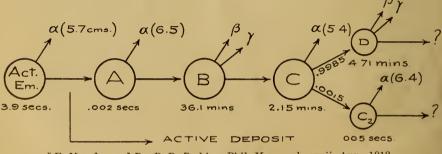
Mention might be made here of one or two experiments in which it was found that the distribution of the activity was perceptibly affected (the cathode percentage activity being increased) in the case where the flow was asymmetrical with respect to the central electrode, three out of four outlet tubes being stopped.

The effect of the irregularities of the field was examined in a separate series of experiments. The variation of the electric intensity in the cylindrical portion of the vessel and in the bottom will not obey the same law, no matter what the construction of the bottom is. As a consequence, we would expect to find discrepancies in the relative number of the neutral particles formed in the body of the vessel and near the bottom, and diffusing to the electrodes. The bottom corner of the vessel was filled in with a curved piece to get rid of the edge effect, and gauze bottoms of various shapes, flat and curved, tried. It was then found that, although discrepancies in the values of the cathode percentage for different shaped gauzes occurred, these never exceeded the limits of experimental error, and did not exhibit any consistent direction, as one would be led to expect from the consideration of the different shapes of the bottoms. Evidently the high velocity of the air stream helped to smooth out the irregularities that would be expected at lower pressures. Finally the curved gauze, shown in the diagram, was adopted in order to match up with the curvature of the corners. It will be noticed that the distance of the electrode from the gauze is adjusted so that the average electric intensity at the bottom of the vessel would not by any chance be smaller than in the body of the vessel.

#### III. Experimental Results.

Before giving the experimental results of this investigation it may be useful to recapitulate the transformations which a quantity of emanation undergoes, according to our present state of knowledge.

The complete scheme of transformation, after Marsden and Perkins,\* is as follows :---



\* E. Marsden and Dr. P. B. Perkins, Phil. Mag., vol. xxvii, Apr., 1913.

All the products after the emanation compose what is known as the active deposit.

It will be noticed that the determining factor in the distribution of the active deposit of actinium is Act. B. Act. A being a short-lived product decays rapidly before any appreciable amount of it reaches the central electrode, for smaller potentials. In fact it may be shown by calculation, using the following expression for the fraction of the Act. A particles that reach the central electrode,

$$\frac{2 Vk}{(b^2-a^2)\lambda\log\frac{b}{a}} \left\{ 1 - e^{-\frac{\lambda\log\frac{b}{a}(b^2-a^2)}{2 Vk}} \right\}$$

where,

V = applied potential,

 $k = 1.54 \frac{\text{cm}^2}{\text{sec. volt}}$ , mobility of the positive ion, assumed to represent approximately the mobility of the deposit particle also.

a = .075 cm., the radius of the central electrode.

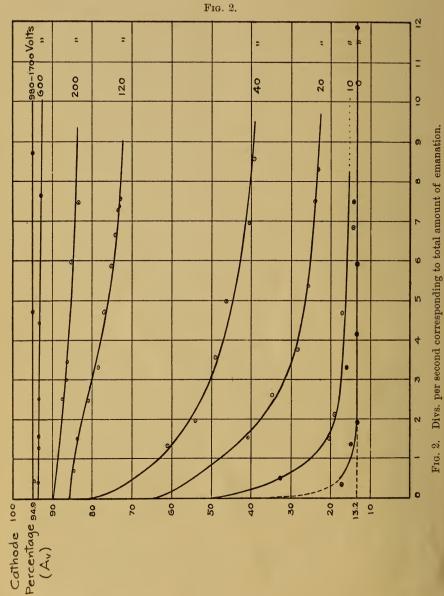
b = 2.45 cms., the inner radius of the vessel.

 $\lambda = 350 \text{ sec}^{-1}$ , transformation const. of Act. A.

that with 600 volts about 25 per cent of the deposit reaches the wire as actinium A, with 1000 volts less than 40 per cent, and with the highest potential used (1700 volts) less than 55 per cent. Since, as will be shown later, no increase of potential difference above 1000 volts appreciably alters the percentage of the cathode deposit, it may be assumed that with increasing potentials the increased amount of actinium A on the central electrode has no effect on the distribution of the deposit; at least, in so far as the final result is concerned. It seems probable, therefore, that actinium A and actinium B are born with the same physical characteristics and exhibit the same peculiarities in an electric field.

The following experimental results were obtained in connection with the three special objects of investigation mentioned in the introduction.

First of all, the dependence of the distribution of activity on the amount of emanation employed claimed attention and was made the subject of investigation. It was found that the cathode percentage, which we shall call  $A_v$  (activity at potential v, referring to the cathode), depended to a great extent on



the amount of emanation used, for values of V up to 600 volts or thereabouts. Above V = 600,  $A_v$  was independent of the amount of emanation used, when the amount was not excessively large. The curves in fig. 2 represent the results of these experiments and give an idea of the ratio of amounts used in these experiments. Very excessive amounts have not been tried, but there are strong indications that the above independence would no longer hold good.

The points on the curves represent the percentage of the total activity which is deposited on the cathode, for a given amount of emanation. As has already been mentioned, the activities on the case (anode) and the central electrode (cathode) were measured separately and from these measurements the above values of the cathode percentage calculated. A condensed table, in which the values have been interpolated from the curves to correspond to given amounts of emanation at points sufficiently near the experimental values, is given below, for purposes of reference :

Am ounts	Percentage Cathode Activity.								
$\frac{\text{in}}{\text{divs.}/\text{sec.}}$	0 volts	10 volts	20 volts	40 volts	120 volts	200 volts	600 volts	980 volts	1700 volts
•50	17 0	32.8			85.1		93.7	94.7	
1.5	14.0	20.3	41.0	59.0	83.9		93.6		
2.0	13.2	189	37.5	54.5	82.4	88.0			
2.5	13.2	18.0	34.5	52.8	81.2	87.5	93.6	94.8	
3.2	15.5	17.0	30.1	49.2	78.8	86.3	93.4		94.9
5.0	13.2	16.5	26.6	45.2	76.5	85.5	93.4	95.0	
8.0	13.2	15.0	24.0	40.0	73.0	83.5	93.0	<b>95</b> •0	94.9

TABLE I.

It is to be noticed that the curves for 600 volts, 980 volts and 1700 volts are horizontal; the last two being coincident.

Owing to the presence of neutral deposit particles, even at the highest potentials employed, it is necessary to correct, for diffusion, all the experimental values of the distribution of activity. This was done by obtaining experimental values for the distribution in the absence of an external electric field (0 volts), so that diffusion alone was operative. It was found that the deposits on the central rod and the case were in the ratio of 1 to 6.6 approximately. This ratio is quite different from the ratio of the areas of the central rod and case, which was 1 to 37. It is evident that if we corrected for diffusion on the supposition that the diffusion distribution was proportional to the exposed areas, we would get higher values for the cathode percentage. All the values given in the present paper refer to distributions for which the proper correction has been made.

The curve for 0 volts in fig. 2 would be expected to remain horizontal for all amounts of the emanation employed. The upward slope of the curve for very small amounts may be due to residual electric fields as well as to molecular agitation and initial diffusion from the recoil-column which are of no effect for larger amounts.

Some experiments of not a very high degree of precision were tried with a negative potential applied to the case, the central electrode being earthed. A typical set of equilibrium values with added capacity for -600 volts on the case is as follows:

Maximum activity on the central electrode	=	•08	$\frac{\text{mms.}}{\text{sec.}}$
Maximum activity on the case	=	10.7	
Total activity Cathode percentage	=	10.78	66 cl
Corrected for diffusion	=	99 <sup>3</sup> 0 94.6	%

The corrected value for the cathode percentage is quite in accordance with the values for +600 volts when the central electrode was made the cathode.

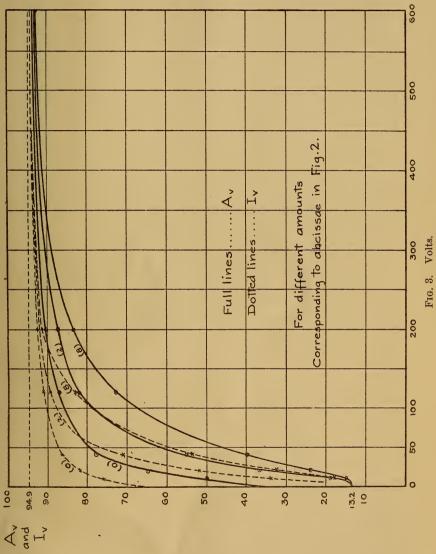
It is now evident that if we followed Walmsley's procedure and obtained the distribution of the active deposit by measuring the activity of the central rod, first as cathode and then as anode, neglecting\* the deposit on the case, we would obtain for large potentials a cathode activity apparently very nearly 100 per cent of the total amount.

The experiments with a negative applied potential show further that the activity deposited on the anode is due entirely to neutral particles; for, if negative particles existed in the vessel, the activity when the central electrode is made the anode should be larger than the amount which settles there by diffusion alone; whereas by a simple calculation, from the value of diffusion on the case, we find that for +600 volts on the case and a total amount corresponding to 10.78 mms./sec. the activity diffusing to the central electrode is .113, which is larger than the value obtained here (.08) for -600 volts on the case. This shows conclusively that no negative particles exist, or at least, take part in the transfer of activity considered.

The above difference between the values of the active deposit that diffuses to the central electrode as anode and cathode can

<sup>\*</sup> A close examination of the figures given by Walmsley in Table I (loc. cit.) seem to warrant the statement here made that he did neglect consideration of the activity which diffused to the case (anode) at high potentials.

F1G. 3.



be explained by considering the different relative distribution of charged deposit particles and negative ions, the different conditions of electric intensity and the consequent different amount of recombination near the central electrode and in the neighborhood of the boundary of the vessel.

The curves shown in fig. 3 are plotted from those in fig. 2 by taking the points in which the curves of fig. 2 intersect a vertical line, corresponding to a given amount of emanation.

The earlier portions of the curves show clearly the increase of volume recombination with the increase of the amount of emanation employed. The gradual rise of the curves after 200 volts shows the presence of columnar or initial recombination. The curves of ionization coincide at about 600 volts; the curves for the distribution of activity coincide at about 1000 volts (not shown in the fig.), and thenceforth, no increase of voltage alters perceptibly the percentage of the cathode deposit. Thus there seems to be a definite limit (94.9) to the value of the cathode percentage; this limiting value for actinium is considerably greater than the value (88.2) found by Wellisch for the active deposit of radium.

The dotted lines in fig. 3 show a number of curves representing the variation with voltage of the ionization current when various amounts of the emanation were in equilibrium with the deposit products. The readings of the ionization current were obtained while the air current was passing and on this account were not of a high order of accuracy as the amount of emanation present in the vessel was subject to slight variations. Hence a large number of these readings were taken for various voltages and for different arbitrary amounts of emanation used, and a set of average curves was plotted. All the ionization curves in fig. 3 were plotted by changing the scale of ordinates to correspond to a saturation value of 94.9. It should be noticed that the ionization current is assumed to attain its saturation value at 600 volts. This is very approximately true; at any rate the qualitative results that will be drawn from the nature of the ionization and activity curves are not invalidated by this assumption. At 1000 volts ionization current readings showed no appreciable difference from the values at 600 volts.

From an inspection of the curves of fig. 3 it will be seen that for any given amount of emanation the "activity" curve lies continually below the ionization curve. In other words, the electric field is able to bring to the central electrode a larger proportion of positive ions than of positively charged deposit particles. For smaller voltages this can be easily explained on the supposition that the deposit particles and negative ions contained in the volume of the vessel combine much more readily than the negative and positive ions among themselves, i. e., volume recombination takes place at a widely different rate for the two cases.

The same remarks hold true in the case of columnar recombination also. The fact that the central electrode receives. even for the higher potentials, a smaller proportion of charged deposit particles than of positive ions shows that the deposit particles are liable to lose their charge by recombination in the columns more readily than the positive ions. The difference in this particular phenomenon may be more strikingly shown by considering the curves of ionization and activity corresponding to an infinitesimal amount of emanation in the vessel. These were obtained by the method used by Wellisch for the case of radium by producing the curves of fig. 2 and of the corresponding figure for ionization currents, so as to intersect the axis of ordinates, and plotting these points of intersection against the potentials, and are marked o in fig. 3; they may be regarded as limiting curves, corresponding to the absence of volume recombination. They show clearly that any given potential is able to prevent columnar recombination of ions much more easily than of active deposit particles. The two curves approach at about 600 volts.

#### IV. Summary and Discussion of Results.

1. When actinium emanation is mixed with dust-free dry air and allowed to come into equilibrium with its active deposit the percentage of the deposit which is collected by the cathode increases with increasing potentials, but even under the most favorable conditions and at the highest potentials applied there seems to be a definite limit to the percentage of the active deposit which settles on the cathode. This limit is 94.9 per cent, or 95 per cent roughly.

2. The remaining five per cent of the active deposit consists of neutral particles which reach the electrodes by diffusion. It was shown also that no negatively charged deposit particles take part in the transfer of activity.

3. For values of the activity distribution which are less than this limiting value, the formation of the neutral particles is explained on the view that the deposit atoms recombine with the negative ions in the volume of the vessel for small applied potentials, and with negative ions formed in the columns for larger potentials. Thus both volume recombination and initial or columnar recombination have to be taken into consideration for a complete explanation of the experimental results.

4. It has been shown that both volume and columnar recombination take place at a greater rate between the deposit particles and ions than for the ions among themselves. This was shown by a comparison of the two sets of curves in fig. 3, one for equilibrium ionization current and the other for the cathode percentage of the equilibrium active deposit. This behavior of the deposit atoms leads one to the conclusion that they are of larger mass and size than the ordinary gas jons.

The ionization and activity curves of fig. 3, marked o, and corresponding to absence of volume recombination, afford further evidence as to the size of the deposit atoms. It will be seen on inspection that the activity and ionization curves cut the axis of ordinates at the points 36 and 66 respectively, corresponding to 38 per cent and 69 per cent of the total number of ions and of deposit atoms. These numbers represent. according to Wellisch and Woodrow,\* the percentage of the total number of ions and of deposit particles which escape from the  $\alpha$ -particle and recoil columns as a result of molecular agitation and diffusion. The above numbers indicate that, roughly speaking, twice as many positive ions on the average escape from the *a*-particle column as positively charged recoil atoms from the recoil column. This relative slowness exhibited by the deposit particles is naturally to be ascribed to their size and mass as compared with the ions.

In all these particulars actinium active deposit seems to behave, qualitatively at least, like the deposit of radium.

A theory has already been advanced by Wellisch in explanation of the behavior of the radium active deposit in an electric field. According to this view, after a deposit particle recoils into the gas, it is subject to the chances of columnar and volume recombination. But when both columnar and volume recombination are avoided by the application of sufficiently high potentials, the distribution of the active deposit on the electrodes is determined by the relative number of charged and uncharged carriers which result from the process of recoil. During the motion of recoil the deposit atom is unaffected by any applied electric field, so that initially the relative number of charged and uncharged recoil atoms is independent of the applied potential. The nature of the charges carried by the deposit particles at the end of their recoil path is determined by the continual process of gain and loss which occurs during the recoil motion of the particles.

This theory is susceptible to modification and further development, especially with regard to the sign of the charges acquired by the deposit particle as a result of and at the end of the recoil motion, by taking into consideration the mechanism of the process of ionization in the following manner. To start with, the recoil atoms at their formation will acquire in general an electric charge as a result of the simultaneous expulsion of an *a*-particle and a number of slow-moving electrons; further, the deposit atoms are at least of ionic order of magnitude and perhaps larger and move with relatively small velocities.

\* Wellisch and Woodrow, this Journal, Sept., 1913.

We may also assume that the recoil atoms effect the process of ionization by some sort of collision with or bombardment of the gas molecules, expelling negative electrons from the molecules with much greater initial velocity than that imparted to the main bulk which forms the positive ion. We may picture to ourselves, therefore, the recoil deposit atom moving all the time in and at the head of a column the core of which consists of an overwhelming majority of positive gas ions and the outer layer is constituted of negative electrons. Now, whatever the charges acquired by the deposit particles at their formation, it is only reasonable to expect that travelling in this core, lined on all sides almost exclusively with positively charged gas ions, they should possess a greater probability of emerging from the recoil columns with a positive charge than otherwise. If the positive charge is acquired by the combination of the deposit atoms with the positive ions of the core, then the resulting positively charged deposit particle assumes molecular dimensions and becomes a cluster under favorable circumstances; this agrees very well with the conclusions arrived at from the discussion of the curves of fig. 3. Further, the more complete the initial exclusion of the negative electrons from the columns, the less will be the number of deposit atoms emerging from the columns as neutral particles and hence the higher the limiting value of the percentage of the cathode deposit. It is also evident that no negatively charged deposit particles, even if they existed initially in great numbers, could emerge as such from the recoil columns.

The supposition here involved is that recoil atoms of different initial velocity impart different amounts of energy to the electrons which they expel in the act of ionization, and as a consequence, for a very short time, during the motion of recoil, a separation of positive and negative columns of ions actually occurs. The fact that the limiting value of the cathode deposit for actinium is higher than that for radium is exactly what would be expected when we consider that the recoil atom from actinium A is expelled with a greater velocity than that from radium A. Moreover, since the recoil deposit atom of thorium has a velocity intermediate between that of radium and actinium, we would expect to find the limiting value for the cathode percentage of the thorium active deposit to lie between 88.2 and 94.9. Experiments on the distribution of the active deposit of thorium are now in progress and will soon be published.

In conclusion I wish to express my gratitude to Prof. E. M. Wellisch for suggesting this problem and for his continual interest and advice throughout the course of the investigation. I am also indebted to Prof. Boltwood for his helpful suggestions.

Sloane Physical Laboratory, Yale University, New Haven, Conn., May 18, 1914.

Am. Jour. Sci. — Fourth Series, Vol. XXXVIII, No. 228. – December, 1914. 38

# ART. LI.— The Amherst Eclipse Expedition; by DAVID TODD.

To observe a total eclipse successfully, one must have suitable instruments, he must get in the path of the shadow, and he should have cloudless skies. In spite of both war and clouds, the expedition secured results of value, though both these sinister circumstances were operant against us. Fortunately we had arrived in the middle of the eclipse belt just as mobilization was beginning.

The instruments taken from the home Observatory were intended mainly for a photographic record of the corona, and were a selection from those that had been found most suitable in previous eclipse expeditions. Unluckily they got stranded somewhere between Libau, the port of entry to Russia, and Kieff in Southern Russia, near which was the location of our eclipse station. And although the officials of the Imperial Railways did everything in their power to locate them, they arrived at the station only the night before the eclipse; too late to be of any use.

Meanwhile, with many days of waiting at Kieff, itself very near the line of central eclipse, though meteorologically not very favorable, I had been successful in getting together an auxiliary outfit for photographing the eclipse, and there was abundant time for adjusting and testing it.

Kieff is a very old city, with more than half a million inhabitants, and every modern necessity. Exploring its interesting shops with Mr. George Martin Day, we very soon found a Dallmeyer 6-inch portrait objective, the back lens of which afforded a fine image of the sun 1.65<sup>cm</sup> in diameter. Professor DeMetz, Dean of the University in Kieff, accorded me every facility of the department of physics, where we had an excellent tube constructed, and fitted with the necessary focalplane shutter (a Thornton-Pickard), and a new Dresden camera. Unfortunately there was no time to supply the farther requisite of clock-work mounting, but everything else was there ; and with the help of Professor Sleusarefsky, the instrument was set up, tested and provisionally adjusted in the south front of the Pedagogic Museum, one of the finest buildings in Kieff, with a clear outlook for the eclipse.

Had it remained there we should have secured nothing, as this region for many miles around was covered under thick clouds all through totality. But a fortunate meeting with Count Andrew Bobrinsky at Kieff led to my acceptance of his invitation to visit his estates in Smala, about one hundred miles southeast of Kieff, where the chances of clear skies were rather better than at Kieff itself. So the instrument was dismounted at the Museum three days before the eclipse; and although Smala was nearer the frontier where battles were imminent, it seemed best to take it there and so increase the chances of getting the corona, especially as Professor Sleusarefsky had been able to replace the Dallmeyer lens at the Museum with a Voigtländer objective of nearly equal power.

At Smala I was farther fortunate in the enthusiastic interest and assistance of Prince Troubetskoy; and with the help of a local carpenter and photographer we got the instrument into perfect adjustment in ample time the day before the eclipse. It was rigidly mounted on the south balcony of Count Bobrinsky's residence, and the necessary practice drill was perfected. The plates on which we got the best pictures were made in Moscow; and greatly to our regret the thin clouds drifting over the sun during the entire time of total eclipse were sufficient to obscure the outer corona completely, although two of the plates give the inner corona very satisfactorily.

Clear night-time skies after the eclipse also enabled me to carry out successfully a plan for fixing on the photographic plate, alongside the corona, a sharply defined line to mark the zero of reference in measuring up the prominences and filaments. This was done in the following manner: leaving the camera in position till night came on, the coronal plate was returned to the camera, and exposed to the trail of  $\propto$  Ophiuchi, for two minutes on the preceding side of the sun and three minutes following. Developing the star-trail and corona together, the trail provides the direction of the "parallel" as an exact zero of position. In the next total eclipse, on the 3d of February, 1916, Sirius will be similarly located, and most helpful in exact adjustment of eclipse instruments, as well as star-trails afterward.

Every courtesy of the officials of the Russian Government and the Imperial Academy of Science was accorded the Expedition; also of Dr. Backlund, director of the Observatory at Pulkowa, who kindly permits our instruments to be stored at Pulkowa till after hostilities.

Returning homeward by the roundabout route through Finland and Sweden, I met at Stockholm Dr. E. Nordenmark, who had got the eclipse with a cinematograph at Solleftea, Sweden, in a perfectly clear sky. This tilm contains many hundred impressions of the corona, at a speed of six to the second; and shows also a fine coronal ring on all exposures just before and after totality. This first complete success of the cinematograph is of great interest as indicating the availability of automatic photography for the portrayal of the swift development of a total eclipse.

Amherst College Observatory, Nov. 6, 1914.

### SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. A New Volumetric Method for the Determination of Cobalt in the Presence of Nickel. ALBERT METZL describes his method as follows: The cobalt solution in a flask should not have a volume of more than 100°c. To this is added, for each 0.1 g. of cobalt, 15<sup>cc</sup> of "10 volume" hydrogen peroxide, 30<sup>cc</sup> of 5 per cent sodium bicarbonate, and 30<sup>cc</sup> of 10 per cent sodium hydroxide. Then it is well shaken and heated over a wire gauze for from 20 to 23 minutes to destroy the excess of hydrogen peroxide. Then it is cooled, potassium iodide and dilute sulphuric acid are added. and the liberated iodine is determined by means of thiosulphate solution. One iodine atom corresponds to one of cobalt, since the latter is oxidized to hydrated Co.O. The author gives very satisfactory results with widely varying proportions of cobalt and nickel. He has devised a modification of the method where the oxidation takes place in the presence of ammonium chloride and ammonium hydroxide, but in this case it is difficult to destroy the whole of the hydrogen peroxide by boiling, so that long boiling and the employment of restricted amounts of ammonia and ammonium chloride were required.-Zeitschr. analyt. Chem., liii, 538. H. L. W.

2. The Hydrogenization of Oils; by CARLETON ELLIS. 8vo. pp. 340. New York, 1914 (D. Van Nostrand Company. Price, \$4 net).—This book deals with a very interesting and important recent development in industrial chemistry which consists in the combination of hydrogen with the oils, thus converting them into more valuable solid fats. The process at the same time often removes disagreeable odors and in addition it lessens the tendency of the fats to become rancid. This "hardening" process is already applied on a very large scale to cottonseed oil, various nut-oils, fish oils, etc., in order to produce fats suitable for lard and butter substitutes, for soap making, and so on. Certain catalytic agents are necessary for effecting the combination of hydrogen with the unsaturated oils, the most important of which appears to be metallic nickel. The book under consideration treats the subject very thoroughly, particularly in connection with the patent literature. The methods of hydrogenation, the various catalyzers, the analytical constants of the products, edible hydrogenated oils and the utilization of the products in soap making are all extensively discussed, while a very elaborate treatment of the technical methods for the production and purification of hydrogen gas is also included. H. L. W.

3 Methods of Quantitative Organic Analysis; by P. C. R. KINGSCOTT and R. S. G KNIGHT. 8vo, pp. 283. London, 1914 (Longmans, Green and Co. Price \$2 net).—This is a useful book for advanced students in organic chemistry. The first chapter deals with the important methods for the determination of molecular weights. The second chapter discusses rather extensively ultimate organic analysis, including nitrogen, sulphur, the halogens, phosphorus and arsenic. Chapter III explains very fully the methods for the estimation of typical groups, including the carboxyl, amido, acetyl, hydroxyl, amino and imino, nitro, and carbonyl groups. The fourth chapter, which is the last and comprises about 140 pages, takes up the estimation of some compounds of technical importance, such as sugars, indigo, fats, oils and waxes, a few alkaloids, alcohols, etc. Some of the descriptions in this last chapter are brief, but here, as well as in the other sections of the book there are copious references to the original literature. H. L. W.

4. Essays and Addresses; by JAMES CAMPBELL BROWN. 8vo, pp. 208, London, 1914 (J. & A. Churchill. Price \$2 net).— The late Dr. Brown, who was Professor of Chemistry in the University of Liverpool, had prepared and read a large number of papers, of which this book gives a selection of a dozen. While they were written from 10 to 28 years ago, they are in most cases of permanent interest. One of the addresses is a translation of Liebig's fascinating short autobiography, another gives very interesting reminiscences of Hofmann, another celebrated German chemist, who went to England in 1845 and taught and carried on investigations there for a period of twenty years. Several of the addresses give advice to students, particularly in regard to education in technical chemistry. H. L. W.

5. Metallurgy; by HENRY WYSOR. 8vo, pp. 391, Easton, Pa., 1914 (The Chemical Publishing Co.).—This book is described on the title-page as "A condensed treatise for the use of College students and any desiring a general knowledge of the subject." This is the second edition, about 80 pages larger than the first, which appeared six years ago. The preface states that the criticisms of the first edition have been carefully weighed, but it appears that there is still room for much criticism in regard to the present edition. It contains many unsatisfactory and even incorrect statements, and many very important facts are not mentioned. However there are many things that are well discussed in the book, and the illustrations are usually very satisfactory. H. L. W.

6. Introduction to Organic Chemistry; by JOHN TAPPAN STODDARD. 12mo, pp. 418, Philadelphia, 1914 (P. Blakiston's Son & Co.).—This book is intended to be used in connection with lectures, recitations, and laboratory work in the first course of organic chemistry in college. Although it is considerably smaller than most texts of similar character, it seems to be well suited for the purpose in view, as it contains most of the essential facts needed by beginners and presents the subject clearly. It appears, however, that brevity has been carried too far in some instances. For example, the chapter partially devoted to dyes comprises scarcely three pages, while uric acid and the related compounds are given but a single page. Also the matter of nomenclature seems to be slighted. On the other hand, it may be said to its advantage that the book contains but little of the unessentials, with which many of the elementary text books are encumbered.

7. An Introduction to the Study of Organic Chemistry; by H. T. CLARK. 12mo, pp. 484. London, 1914 (Longmans, Green and Co.).-In preparing this new text book the author has confined himself to the discussion of the important types of organic compounds, clearly showing their relationships with each other and their important reactions. He has generally avoided giving the details of preparations, as being out of place in an elementary The material included, while being distinctly fundatext-book. mental in character, covers the field quite satisfactorily, and includes some quite modern facts. One of the early chapters of the book is devoted to an interesting and instructive survey of The the classes of compounds derived from ordinary alcohol. book is one which teachers of elementary organic chemistry should find of interest. N. A. SHEPARD.

8. The Relation between Absorption and Wave-length of X-rays.—By making use of the experimental data obtained by Barkla, Darwin, Moseley, and others, M. SIEGBAHN has brought out some important facts concerning the functional dependence of the absorption upon the wave-length of Röntgen-rays. When the logarithms of the wave-lengths of the K type of radiation from calcium, iron, cobalt, nickel, copper, zinc, molybdenum, and silver are plotted as abscissæ with the logarithms of the corre-

sponding values of the ratio  $\left(\frac{\mu}{\sigma}\right)$  of the absorption coefficient ( $\mu$ )

for aluminium to the density ( $\sigma$ ) as ordinates, the points are found to lie on a straight line. In this case the wave-lengths vary from  $3.368 \times 10^{-8}$  cm. to  $0.560 \times 10^{-8}$  cm., or more than two octaves, while the absorption ratio changes from 435 to 2.5 cm<sup>2</sup>/gram. This fact

may be expressed by the equation  $\left(\frac{\mu}{\sigma}\right)_{Al} = A \cdot \lambda^x$ , where A and x

are constants. A depends upon the radiator itself whereas x is a general constant having the value 3, very nearly. When the same kind of diagram is plotted for wave-lengths greater than those of the fluorescent or homogeneous characteristic radiations the same formula with the same value of x is found to hold good. The lines are straight for all wave-lengths outside of the regions of selective absorption. At the regions of selective absorption the straight lines are shifted bodily parallel to themselves. In other words, for a given radiator possessing a band of selective absorption, within the interval of X-rays whose wave-lengths have been determined, the symbol A has one value below the band and another above the same. The values of A for the extreme elements carbon and tin are 1.5 and 81 respectively. Again, the same formula applies to the following gases and vapors, namely;—air, sulphur dioxide, ethyl bromide, and methyl iodide. In brief, the symbol x has the same value (3<sup>-</sup>) for substances whose densities vary from 0.00129 (air) to 10.5 gram/cm<sup>3</sup> (silver).

Owen found that the absorption exhibited by gases for characteristic radiations is proportional to the fifth power of the atomic weight of the radiating element, and Kauffman has pointed out that this relation is also fulfilled by aluminium as absorber. The diagram of Siegbahn shows conclusively that the above relation is incorrect as stated, and that the atomic number (N) is the correct parameter and not the atomic weight. Therefore, it fol-

lows at once that  $\frac{\mu}{\sigma} = \text{const.} \frac{1}{(N-1)^{2x}}$ . Since  $2x \doteq 6$  the fifth

power must be replaced by the sixth in Owen's law.—Phys. Zeitschr., August 15, 1914, p. 753. H. s. u.

9. The X-ray Spectrum of Platinum.—The photographic negatives obtained by Bragg, Moseley and Darwin, and deBroglie with platinum as radiator apparently show continuous bands as well as a few fine, discrete lines. By greatly improving the experimental conditions it has been shown, quite recently, by H. SEEMANN, not only that the bands consist of a relatively large number of sharp lines but also that some of the single lines found by previous investigators may each be resolved into several finer lines. Furthermore the faint, continuous background present in Seemann's negatives may be accounted for as arising from radiation which has been scattered at the crystal surface and elsewhere. Therefore in the case of platinum, at least, reasonable doubt may be entertained as to the existence of any appreciable continuous radiation in the region of extremely short wave-lengths.

A brief account of Seemann's method of experimenting may not be superfluous. The X-rays were caused to pass out of the bulb through a lithium glass window. The chief advantage of lithium glass ("Lindemann-glas") is that it is more transparent to the less refrangible components of the Röntgen ray spectrum than the sodium glass walls of the bulbs ordinarily used. The slit of the spectrograph was placed directly in front of the emergence window and it was given widths from  $0.1^{\text{nm}}$  to  $0.03^{\text{nm}}$ . Slit-widths of the order of  $1^{\text{nm}}$  were used by earlier investigators of this field. A very fine rock-salt crystal was used as "grating." It was situated in the axis of a spectrometer table at a distance of 6<sup>cm</sup> from the slit. Seemann found that rock-salt gave incomparably better results than crystals of fluorite, gypsum, hematite, Iceland spar, iron pyrites, mica, sulphur, and zinc blende. A plane photographic plate was held, at a distance of 10<sup>cm</sup> from the crystal, by an arm which was rigidly fastened to the spectrometer table. This arrangement of apparatus made it possible to photograph, at one exposure, a region of the spectrum only 1°.5 wide. Successive exposures were taken on different plates, the plate-holder and crystal having been moved together through an angle of 1°.5 each time. The final, scientifically beautiful posi-

tive was compounded of separate strips carefully pasted side by side on one sheet of paper. It is thus seen that Seemann's method differs from the more common arrangements in several respects. For example, it is customary to endeavor to obtain good definition by making the distance from the plate to the "reflecting" surface of the crystal equal to the distance between the slit and this crystal surface. Also, the crystal is usually rotated while a photographic film, curved to the proper radius, is kept fixed with respect to the bulb and slit. - Phys. Zeitschr., Sept. 15, 1914, p. 794. H. S. U.

10. The Spectroscopy of the Extreme Ultra-violet; by THEO-DORE LYMAN. Pp. v, 135, with 15 figures and 1 plate. London. 1914 (Longmans, Green and Co.).-The first Part of this book (pages 1 to 28) deals with the ordinary ultra-violet, which is defined as comprising the region between  $\lambda 4000$  and  $\lambda 2000$ . The rest of the text. Part II, is devoted to a detailed account of the Schumann region,  $\lambda 2000$  to  $\lambda 900$ . The five chapters of the second and main division of the volume pertain respectively to the apparatus and methods of investigation in the extreme ultra-violet. absorption of solids and gases, emission spectra of gases, emission spectra of solids, and to photo-electric and photo-abiotic phenomena.

The author has been able to present the subject-matter in a very clear, concise manner because of his extensive and fruitful experience in investigating the Schumann region with his specially designed grating spectrograph. The style is far more satisfactory than is often the case with monographs of this general character in that the author discusses his own brilliant work with dignified modesty, and does not neglect the historic side of the subject and the results obtained by others. It is almost needless to state that the text abounds in important spectroscopic data. At the end of the volume, seventeen tables of wave-lengths are given. These are followed by a general bibliography, a list of papers by V. Schumann, an appendix on the sensitizing of plates, and subject and author indices. The book is undoubtedly an important and authoritative contribution to the special field to which it relates.

H. S. U.

11. Elementary Electricity and Magnetism; by WM. S. FRANKLIN and BARRY MACNUTT. Pp. viii, 174, with 152 figures. New York 1914 (The Macmillan Co.).—This little volume is designed to be used as a text-book in colleges and technical schools. The kind of study of electricity and magnetism contemplated by the authors may very properly be called "electromechanics." In other words, the subject-matter is presented in such a manner as to be independent of any considerations concerning the nature either of the physical action which leads to the production of electromotive force in a voltaic cell or dynamo, or of the physical action which constitutes an electric current in a wire, or of the disturbance which constitutes a magnetic field, or of the stress in an electric field. The first chapter deals with

the effects of the electric current and with magnetism. The titles of the remaining chapters are respectively,-"Chemical Effect of the Electric Current," "The Heating Effect of the Electric Current," "Induced Electromotive Force," and "Electric Charge and the Condenser." In addition to the lucid explanations the ideas are made very vivid and concrete in two ways, first, by placing diagrams of the mechanical or hydraulic analogues side by side with the diagrams of the associated electric or electromagnetic apparatus, and second, by tabulating the statements of analogous laws and facts in parallel columns. The experiment with the "electric doubler" (Art. 108), is especially interesting and instructive. About 120 problems, with answers, are appended to the several chapters. In conclusion it may be remarked that there is a frankness of statement and freshness of presentation which should prove stimulating to the teacher as well as to the student. H. S. U.

# II. GEOLOGY AND MINERALOGY.

1. The Climatic Factor, as Illustrated in Arid America; by ELLSWORTH HUNTINGTON, Assistant Professor of Geography in Yale University; with contributions by CHARLES SCHUCHERT, ANDREW E. DOUGLASS, and CHARLES J. KULLMER. Pp. vi, 341, with 12 plates, 2 maps, 90 text-figures. Carnegie Institution of Washington Publication No. 192, 1914.—This is a volume replete with new data and new points of view, bearing upon the fields of archeology, history, meteorology, and geology. It is divided into three parts. Part I deals with the problem of climatic changes, divided into a discussion of the data which show the nature of the changes during the past 2,000 to 3,000 years, and the hypotheses which are suggested in order to give an adequate explanation of the phenomena. There are twenty chapters. Part II is a single chapter of thirty pages by Professor Schuchert on the climates of geologic time. Part III consists of tables.

To revert in more detail to Part I, the first three chapters give an account of the climatic character of Arizona and New Mexico and its relations to the physiography and vegetation. Then follows Chapter IV on the climatic theory of terraces and the means of distinguishing terraces of climatic origin from those due to crustal movements. This is a most important subject as it is the key to the climatic interpretation of the Pleistocene and recent epochs in regions of piedmont alluvial deposits. It is a relatively new principle which has been but little used and is not as yet widely understood. The fluctuations of the inclosed bodies of water furnish supplemental evidence. Chapters VI to IX inclusive deal with the archeological evidence. Taken in connection with the preceding chapters, they go to show that notable changes in the mean annual rainfall have occurred since man first cultivated the region, and that the ancient people lived in a time when the climate of this southwestern region was less arid than at present and supported a denser population. The subject is then tested by a study of southern Mexico. This is some 1,200 to 1,500 miles south and in a different climatic zone, on the southern instead of the northern margin of the belt of tradewinds. Here the study of lake strands and river terraces shows a similar climatic history.

Chapters XI to XIV inclusive develop a new and most important method of studying the climatic fluctuations of the past 2,000 to 3,000 years, that derived from the variable growth of trees. The inception of this method is due to Professor Douglass, who contributes the first chapter. The basis of the study rests upon the principles that the thickness of the rings of growth measure the food supply and this depends largely upon the amount of moisture, especially where the quantity of moisture is limited and the life struggle of the tree is against drought rather than against competing vegetation. Cycles of years favorable for tree growth can be detected and confirmed by the comparison of stumps. Huntington has followed this method, using especially the stumps of the giant sequoias of California and arrives at a general confirmation of the climatic curve as deduced from studies in Asia.

The next section of the volume deals with the climatic changes which have taken place in the northern part of the torrid zone, as shown in Yucatan and Guatemala. It includes a chapter on "the shift of the storm track" by Charles J. Kullmer. The conclusion is that during a time of coolness and more abundant rain, the trade-wind belts are compressed towards the equator. Consequently regions like southern Yucatan and eastern Guatemala, which now possess tropical forest, would at such a time have had a drier and cooler climate and have been free from heavy forest. As a result the region, as shown by the ruins, permitted a high civilization where now it appears impossible. The argument is in accord with analogy given by the shifting toward the equator exhibited by the trade-wind zone during the winter season.

Chapters XIX and XX take up the problem of explanation of the ultimate causes of the changes determined from the previous studies. It is concluded that the rapid oscillations, both of smaller and larger amplitude, are most probably accounted for by variations in solar radiation. Crust movements with related changes in atmospheric composition seem, on the other hand, to dominate those slower and longer changes which individualize the geologic periods. Both seem to have been in operation through all of geologic time.

Part II of the volume is on the climates of geologic time, and is by Charles Schuchert, Professor of Paleontology in Yale University. A review is given of the various lines of geologic evidence, derived from tellites, aq eous sediments, and fossils. The conclusions drawn as to the variations in climate from period to period are correlated with the record of diastrophism, and the whole is put together on p. 285 into a diagram which shows the curves of coal formation, limestone deposition, aridity, temperature, and diastrophism. Schuchert concludes that the major cause in the climatic changes through geologic time is to be found in the topographic changes of the earth's crust from period to period. There are other causes, perhaps many others, but they are subordinated in importance to diastrophism.

This description of the contents of the volume serves to show its importance to many lines of investigation. It gives a firmer basis to the subject of climatic changes through historic time than had previously appeared. Many meteorologists and historians have insisted that there was no evidence of climatic change, that there was merely an irregular variability from year to year. and that the ruin of ancient empires or the migration of barbarian hordes were of purely human initiation, not the human response to the compulsion of nature. Since both factors would enter as causes most of the evidence could be interpreted in two ways, either for or against climatic change and would not compel a view contrary to that which had been previously believed. Here, however, three independent lines of evidence are assembled which have no causal connection with the human factor. They are lake strands, river terraces, and tree growth. Together they lead to the belief that there have been changes which have had considerable effect upon man in those regions where the supply of moisture is the critical factor in the climate, that is, especially in the arid and semi-arid regions. The changes in mean annual temperature do not seem to have been so material.

Other scientists have held that climatic changes during historic times have taken place but that they were slow and progressive, a part of a drying-up process extending through geologic time and leading ultimately toward lessened oceans and widened deserts. The evidence brought forward in this book shows that such a view has no support.

Huntington's work has gone far toward establishing an intermediate view and yet one which has features not found in either. Climate is subject to pulsatory change ; smaller and larger rhythms are superposed. The changes may go forward very rapidly, so that the population of an arid or semi-arid region may be largely reduced in a single generation. The changes in the past 3,000 years have been small in comparison with the changes which have taken place since the culmination of the last glaciation and yet they are to be regarded as of the same nature, the continuation of the geologic past into the present.

From the standpoint of the geologist the contributions of Huntington as well as Schuchert are of importance; for as Lyell showed that the present is the key to the past in the crustal history of the earth, in a similar manner the key to the climatic history is to be found in the study of the present climates and their fluctuations. Subjects which stand in the middle between a number of sciences are likely to have important bearings upon all, and yet, since their investigation requires the ability to evaluate evidence outside of each specialty, their weight is slow to become appreciated.

As yet, however, the work is largely preliminary. There can be no doubt but that climatic fluctuations measured by centuries have taken place, but just what difference this means in mean annual rainfall, or just how large a factor this is in stimulating the migrations of peoples, is a matter upon which no unanimity of judgment has been reached. But for these very reasons the subject is one of the first importance and demands an extension and intensification of the investigation. Great credit is due to Dr. Huntington for the energy and courage with which he has explored distant regions of the earth, for the direct and varied studies of nature, and for the originality of conceptions which he displays in his work.

It would appear that the investigation of the growth-curve of the sequoias should be followed up in the immediate future. Huntington, in his work, employed a method of averaging together a large number of measurements from stumps. But the sequoia is very sensitive to environment, as shown by its restricted range. Consequently the character of slope exposure, elevation above the sea, depth and quantity of ground water would have marked influence. A slight climatic change toward aridity would affect unfavorably the trees on sunny slopes or low altitudes, while it might affect favorably, or not at all, trees situated at the upper limits of growth, or growing on shaded or better watered tracts. This is probably in considerable part the explanation of the great individual variations shown in the growth. If the stumps were classified according to careful studies of the environment, and only selected stumps used in each, the record would very probably become more clear. Particular cycles of years might be identifiable in different stumps, as Douglas was able to identify them, for the nineteenth century in Arizona. This would not only fix definite time markers by means of individual years and sequences of years, but would give a much closer and more detailed record of climatic conditions in California extending backward to the era of the Trojan war.

Statistical studies of the age of trees in each division of environment should also be made, for during a time of dryness few or no new trees would start to grow on the areas most adversely affected. During times of cold and wetness the opposite limiting areas would be expected to show few beginnings. A progressive regional shift in the optimum would also be expected. It is for the determination of the long and slow progressive changes that such a method if applicable would be most valuable, and it is for just such changes that the individual stumps are of least value, for the growth curves of the trees are affected by the changes in rate due to the passage from youth to age. Furthermore, the tree once established can survive, while in its prime, changes which would disastrously affect very young or feeble trees. There are, of course, other factors such as shading in youth, which can only be eliminated by a method of averages, but it is seen that there is here a priceless record, as yet only partly surveyed. But year by year decay is making it more illegible.

As climate varies in the same direction in similar climatic belts throughout the world, but in opposite direction in belts of opposite character, the record derived from California is of very specific value for the understanding of the historic record of the eastern hemisphere; and further for the understanding of that stratigraphic record of the geologic past which is the parent of the human present. J. B.

2. Connecticut Geological and Natural History Survey. Volume IV, Bulletins 16-21, 1910-1913. 1914.—Volume IV of the Connecticut Survey publications includes the following bulletins previously issued in separate form:

Bulletin 16, Guide to the Insects of Connecticut; prepared under the direction of W. E. Britton. Part I. General introduction by W. E. Britton. Part II. The Euplexoptera and Orthoptera of Connecticut, by B. H. Walden. Pp. 1-31, pls. I-XI, textfigures 66.

Bulletin 17, Fourth Biennial Report of the Commissioners of the State Geological and Natural History Survey of Connecticut, 1909-10.

Bulletin 18, Triassic Fishes of Connecticut, by C. R. Eastman. Pp. 1-77, pls. I-XI, text-figures 8.

Bulletin 19, Echinoderms of Connecticut, by W. R. Coe. Pp. 1-147, pls. I-XXXII, text-figures 29.

Bulletin 20, The Birds of Connecticut, by John H. Sage and Louis B. Bishop, assisted by Walter P. Bliss. Pp. 1-370.

Bulletin 21, Fifth Biennial Report of the Commissioners of the State Geological and Natural History Survey of Connecticut, 1911-1912.

3. The recent Eruptions of Lassen Peak.—The September number of the Bulletin of the Seismological Society opens with an article by J. S. DILLER on the recent eruptions of Lassen Peak in California, about which frequent reports have appeared in the public press. As has been generally appreciated, the violence of these eruptions has been a surprise not only locally, but to the geologists who had worked in the Cascade Range. During the period from May 30th to August 23d, 1914, thirty-two eruptions are included in the list given, of which one-half had an interval of less than a day between them. The most violent eruption took place on July 18th, when ashes, steam, etc. rose to a height of 1100 feet. An interval of twenty-three days followed before another outbreak took place and this was of minor character. The paper is accompanied by several plates giving striking views of the eruption of June 14th, at successive intervals of five minutes each, from 9.45 to 10 A. M.

4. West Virginia Geological Survey, I. C. WHITE, State Geologist. Preston County, by RAY V. HENNEN, and DAVID B. REGER, Assistant Geologists. Part IV, Paleontology, by W. ARMSTRONG PRICE, Paleontologist. Pp. 566, maps I-III, in separate case, pls. I-XLIII, figs. 1-10. 1914 .- The ambitious scheme of the West Virginia Survey to publish a detailed geologic and soil report for each county in the state is being carried out with unusual speed. Reports covering twenty-eight counties, about half the state, are now either published or in preparation. Work on base maps for the remaining portions of the state are progressing satisfactorily. The report on Preston county, accompanied by maps showing topography, general and economic geology, and soil, follows the plan of previous reports and includes chapters on historical and industrial development, structure, stratigraphy, mineral resources, and paleontology. H. E. G.

5. The Production of Platinum. - The peculiar conditions now existing abroad give special interest to the recent report by DAVID T. DAY on the production of platinum and the allied metals in 1913 (Min. Res., U. S. Geol. Survey). During that year, the supply from the placers of Russia was declining somewhat, as it had been previously. The continued high prices, ranging from \$43.45 to \$45.50 (per troy ounce), had stimulated prospecting in the United States, but without marked increase of The total amount obtained from California and production. Oregon in 1913 was valued at about \$18,500, and the writer believes that this could be increased if the demand justified it. He remarks: "The greater part of the California platinum came, as usual, from the large gold-dredging operations in Butte, Yuba, Sacramento, and Calaveras counties. The question of a larger yield of domestic platinum depends principally upon working the Oregon and California beaches, including the old beaches now several miles inland and elevated considerably above sea level."

A new discovery of platinum in Nevada is noted as follows: "In August, 1914, while this chapter was in proof, a new discovery of platinum in lode deposits was reported to the United States Geological Survey, and efforts were made by the Survey to obtain some reliable preliminary data for inclusion herewith in view of the threatened shortage of Russian supplies due to the European A geologic investigation of the occurrence during the war. present field season is in prospect by the Survey. The property upon which the discovery was made is located about 10 miles west of Goodsprings, and development work has disclosed a considerable body of siliceous ore, carrying copper, gold, silver, and platinum, occurring along a fractured zone in limestone and adjacent to a large intrusion of quartz monzonite porphyry. Some very rich ore has been reported, and at least 2,000 tons of ore carrying 1 ounce of gold to the ton, with associated silver and platinum, were estimated to be in sight in August. Numerous assays indicated that the high-grade gold ore carried as high as 65 ounces and the low-grade about 1 ounce of platinum per ton."

# III. ASTRONOMY.

1. On the Theory of the Moon's Motion.-The address of Professor E. W. BROWN before the sub-section of cosmical physics at the Australian meeting of the British Association starts with a brief review of the history of the problem of the lunar motion. He points out that for the past two hundred years there has been a constant effort for the theory to account for the observed path. The success which has been obtained up to the present time is the main object of his address. His theory was completed some seven years ago, and since that time the chief object has been to compare it with the observations so as to secure the best values of the arbitrary constants and to find out in what respects the Moon deviates from its computed position. There are two great series of observations, one consisting of occultations gathered from observatories all over the world by Simon Newcomb, the other the Greenwich meridian observations recorded almost without a break since the year 1750. Newcomb's results from the occultations were published not long ago and the amount of work necessary to compare it with the latest theory has been quite small. The reduction of something like twenty thousand Greenwich observations has been partly done by Airy and P. H. Cowell. Professor Brown has taken their results and corrected them in every possible way so as to get a direct comparison with the new theory. The net result is very satisfactory. The agreement with Newcomb's values has been unexpectedly close and the differences which do occur are neither very large nor very important. On the whole, the meridian observations give better results in most cases than the occultations. The great value of the latter series is that it gives us a criterion which enables us to say that certain deviations of the Moon from its theoretical orbit are not due to errors in the observations.

The principal deviations consist first of the great inequality discovered by Simon Newcomb having a period of some 270 years and amplitude of about 12 seconds of arc. This is a deviation of the Moon in front of and behind its theoretical position. Superposed on this are smaller deviations which appear to have a main period of between 60 and 70 years and a coefficient of 3 or 4 seconds. But it is pointed out that this is not a periodic change in the proper sense, for it has been found impossible to analyze it. It is these deviations which have formed the subject of a number of hypotheses. It appears now to be fairly certain that they cannot be accounted for by any gravitational cause; the effects of all the bodies in the solar system have been very carefully computed and the observed fluctuations are very large in comparison with most of the gravitational effects which come from distant bodies. At the end of his address Professor Brown examines a number of hypotheses which have been advanced to explain either or both of these deviations. He rejects many of

those which at first sight seem possible; for example, a planet inside the orbit of Mercury or a swarm of small bodies near the Bottlinger's hypothesis of the shading of gravitation by Sun. interposing matter is attractive, but the curve he gets does not fit the observed deviations and according to theory it should not be able to account for them. The motion of the magnetic field of the Earth has also been mentioned, but it is to be rejected because this hypothesis would require changes in other parts of the Moon's orbit which cannot be admitted. A diagram is given which seems to indicate that there are changes in the motions of the Earth and Mercury similar in their nature but smaller in magnitude than those in the Moon. If this correlation turns out on further examination to be real, it would appear that there is some kind of a surge spreading through the solar system affecting planets and satellites in the same way but to different degrees. A suggestion that this surge is in some way connected with the well-known changes in the frequency of the magnetic storms on the Earth is brought forward by presenting in the diagram the well-known sun-spot curve which follows closely the magnetic storm-frequency curve. Professor Brown lays little stress on the somewhat doubtful correlation. He believes, however, that it is the only hypothesis which has some chance of receiving confirmation or the reverse from sources other than that furnished by the Moon's motion.

Certain other results are obtained from an examination of the observations of the Moon. In three directions the number 1/294 is obtained for the ellipticity of the Earth. This agrees with Clarke's value obtained from geodetic measures (1/293.5) but differs from Helmert's determination (1/298). Professor Brown believes that the evidence for 1/294 is sufficiently strong to require its adoption for astronomical purposes. Finally it appears from a series of terms in the motion that the inequalities of the Moon's limb have a systematic character. Roughly speaking, the edge of the southern half of the Moon is farther away from the Moon's center of mass than the northern half. It is concluded that the density of the crust of the former is less than that of the latter in accordance with the principle of isostasy. The analogy to the case of the Earth with its marked land and sea hemispheres is pointed out. This result was obtained a short time previously by Professor Bakhuysen from the examination of a smaller series of observations. The larger quantity of evidence and the explanation were obtained by Professor Brown independently.

In the course of his address Professor Brown also gives a brief description of the tables of the Moon's motion which are being formed and makes a plea for the establishment at some government observatory in the southern hemisphere of the Harvard method for obtaining the Moon's position by photograph.

An interesting statement as to the degree of accuracy of the Newtonian law is made. From the agreement of the theoretical and observed motions of the perigee it is concluded that the index which the inverse square law contains does not differ from 2 by a fraction so great as 1/400,000,000.

# IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The Antiquity of Man in Europe; by JAMES GEIKIE. Pp. xi, 328; 4 maps, 21 plates, and 9 text-figures. New York, 1914 (D. van Nostrand Co.).—The volume includes ten lectures and some twelve pages of notes. The author is especially known in this country through his work entitled "The Great Ice Age" (1894). Of the ten lectures now published, one is devoted to Pleistocene Faunas and Floras, two to the Caves, one to the River-Drifts, three to the Glacial Formations, one to the Interglacial Formations and two to the Pleistocene Period.

In the preface the author states that the result of recent investigations has been to confirm the view that the so-called Chellean culture-stage dates back to the second Interglacial epoch, and to prove that Mousterian man flourished during the third Glacial and the succeeding Interglacial epoch. This view is held by other well-known authorities, including Penck. On the other hand Boule and Obermaier would place the Chellean in the third Interglacial, and the Mousterian in the fourth Glacial.

Geikie's principal contribution is in his treatment of the successive glacial and interglacial phases and their bearing on the antiquity of man as well as on the fauna and flora in general. His views concerning the Ice Age correspond with those of Penck, although he makes use of a different terminology. Instead of the Günz, Mindel, Riss, and Würm glacial epochs and the alternating Günz-Mindel, Mindel-Riss, and Riss-Würm interglacial epochs, we have the Scanian glacial and Norfolkian interglacial, the Saxonian glacial and Tyrolian interglacial, the Polonial glacial and Dürntenian interglacial, and the Mecklenburgian glacial.

The warm phase following the fourth or Mecklenburg glaciation Geikie calls Lower Forestian interglacial (probably corresponding to the Achen retreat). Then came in succession: a recrudescence of glacial conditions, to which is given the name the Lower Turbarian glacial epoch, the Upper Forestian interglacial epoch, the Upper Turbarian glacial epoch, and finally the Recent and Present epoch. The author would seem to be in error in regarding the Lower and Upper Turbarian as the equivalents of the Gschnitz and Daun stadia of Penck (p. 293). They should correspond with Penck's Bühl and Gschnitz stadia.

While the absolute duration of Pleistocene time cannot be determined, a "careful estimate of the geological work done during the several interglacial epochs may enable us to form some conception of the time involved." The author is inclined to accept Penck's estimate of half a million to a million years as being a fair approximation.

For Geikie the Chellean industry dates back to at least the middle Pleistocene, 250,000 to 500,000 years ago. From recent discoveries, however, he believes that man may have been living in Europe during the first Interglacial epoch, if not still earlier, thus greatly increasing our estimate of his antiquity.

GEORGE GRANT MACCURDY.

AM. JOUR. Sci. — Fourth Series, Vol. XXXVIII, No. 228. — December, 1914. 39 2. Award of the Medal of the Royal Society of London.— The announcement has been received by the cable that one of the Royal Medals of the Royal Society of London has been recently awarded to Professor Ernest W. Brown of Yale University in recognition of his investigations in astronomy.

3. The National Academy of Sciences.—The autumn meeting of the National Academy will be held this year in Chicago and at a somewhat later date than usual, namely on Dec. 7, 8 and 9. The sessions will be, by invitation, at the University of Chicago.

It is to be noted that with the opening year the Academy will begin the publication of monthly *Proceedings*. It is planned that these shall "present in the form of brief original articles a comprehensive survey of the more important scientific researches currently made by American investigators." Up to this time the Academy has given to its members no opportunity for a prompt announcement of the results of their investigations. It has, however, issued occasional extended papers as a series of Memoirs in quarto, and an octavo series of Biographical Memoirs; volume VII of the latter has recently appeared.

4. The American Association for the Advancement of Science. —The American Association for the Advancement of Science will hold its next convocation-week meeting in Philadelphia, Pa., from Dec. 28, 1914, to January 2, 1915, under the presidency of Dr. Charles W. Eliot, President Emeritus of Harvard University. The usual affiliated Societies will also hold meetings at the same time; some thirty organizations are now included in this list.

5. The British Association for the Advancement of Science.— The annual meeting of the British Association was held this year in Australia and was attended by numerous scientists from England notwithstanding the unfortunate conditions existing in Europe. The president, Dr. William Bateson, delivered the first part of his address at Melbourne on August 14, and the second part at Sydney on August 20. An abstract of the address by Prof. E. W. Brown before the section of Cosmical Physics is given on an earlier page.

6. Food Products; by HENRY C. SHERMAN. Pp. ix, 594. New York, 1914 (The Macmillan Co.).—This is a timely and useful book by a writer thoroughly conversant with the subject. It is not merely a compilation of analyses or a description of the technical processes of food manufacture, but differs from most of the works on the same topic in the emphasis which is either explicitly or indirectly given to the bearing of each chapter upon the problems of nutrition. Unique nutritive virtues such as are now commonly believed to be associated with certain foods like milk and butter, the relative value of polished and unpolished rice with its story of the "vitamines," the physiological as well as the legal aspects of the question of the various food preservatives, digestibility and utilization of the nutrients—these are illustrations of the sort of novelty which Sherman has introduced freely. An appendix dealing with the rules and regulations for

# Obituary.

the enforcement of the Federal Food and Drugs Act, Food Inspection decisions, important Laws and Regulations pertaining to the distribution and sale of foods are also useful innovations. An elaborate table of the composition of foods in 100-calorie portions, including the unique feature of quantitative data on their acidand base-forming properties, conclude the book. L. B. M.

7. The Sarawak Museum Journal. Vol. II (part I), No. 5, June, 1914. Issued by the Sarawak Museum under the authority of His Highness the Rajah.—This number includes the following papers: Die Tenebrionidenfauna Borneos. Part I, by Hans Gebien; Two New Species of *Pheretima* from Borneo, by W. Michaelsen; Sea-Shells and their makers, by A. J. Jukes-Brown; Notes on collecting Ferns, with particular reference to certain Bornean Ferns of considerable interest, by D. H. Campbell; Some notes on Birds in Sarawak, by R. B. Williams.

8. The Mining World Index of Current Literature. Vol. V. First Half Year, 1914; by GEORGE E. SISLEY. Pp. i-xii, 237, xiii-xxix. Chicago, 1914 (Mining World Co.).—This fifth volume of the "Mining World Index" covers, as in previous volumes, the world's literature on mining, metallurgy and kindred subjects and embraces all references of any importance to the literature of the field it exclusively represents. The convenience of use has been increased by the employment of a larger type than heretofore.

# OBITUARY.

DR. THEODORE NICHOLAS GILL, the distinguished zoologist, for many years connected with the Smithsonian Institution and the National Museum at Washington, died on September 25 at the age of seventy-seven years. His scientific activity is attested by the publication of upwards of five hundred papers upon zoological subjects, but he was noted also for the breadth and thoroughness of his knowledge and the profound influence that he exerted upon those with whom he was associated ; he leaves a large number of personal friends.

DR. HENRY GANNETT, president of the National Geographic Society, chairman of the United States Geographic Board, and geographer of the United States Geological Survey, died on November 5 at his home in Washington. D. C., at the age of sixty-eight years. He began his geographic work as topographer for the Hayden Survey, and in 1882 became the chief geographer of the newly established U. S. Geological Survey. He was geographer of the Tenth, Eleventh, and Twelfth Censuses, and was also one of the leaders in the organization of the National Geographic Society.

DR. AUGUST WEISMANN, the celebrated zoologist, professor in the University of Freiburg since 1867, died on November 6 at the age of eighty years.

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