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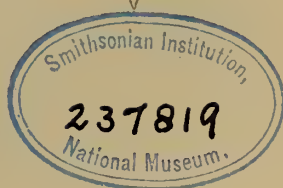
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WITH PLATE I.

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1916.



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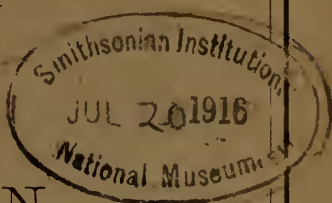
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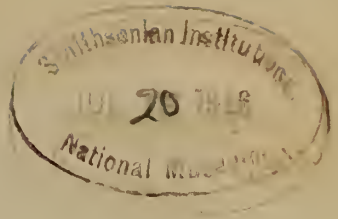
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THE

# AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. I.—*On the Discovery of Fossil Human Remains in Florida in Association with Extinct Vertebrates*; by E. H. SELLARDS.

A NEW and very important locality for vertebrate, invertebrate, and plant fossils was found in 1913 at Vero on the Atlantic Coast in Central-Eastern Florida, the occurrence of fossils at this place having first become known as a result of the construction of a drainage canal made by the Indian River Farms Company. Throughout the greater part of its course this canal, which extends from the coast several miles inland, cuts through the surface materials including sand, marl, and muck beds, and into marine shell marl. In the marine marl, invertebrates are found in abundance and in an excellent state of preservation, while in the sands, fresh-water marls, and muck beds, vertebrates and fresh-water invertebrates are not infrequently preserved. The chief locality for vertebrate and plant fossils, however, is at the public road crossing one-half mile north of Vero, where the canal cuts into an old stream bed. The canal enters the stream bed about 500 feet west of the crossing, and follows it while passing under the bridge and for 500 or 600 feet beyond, or for a total distance of about 1,000 feet (Sketch map, fig. 1).

Although this locality has been known and collected from for nearly three years, it has now acquired a new interest by the discovery, during the past year, of human remains in association with the vertebrate, fresh-water invertebrate, and plant fossils. The results obtained at this locality are of exceptional value since in addition to a record of early man in America, there are here preserved the fauna and flora with which man was then associated.



*Acknowledgments.*—Notice of the occurrence of fossils at Vero was brought to the writer's attention in November, 1913, by Mr. Isaac M. Weills, the presence of fossil bones in the canal having been reported to him by Mr. F. C. Gifford. Mr. Weills, with the assistance of Mr. Frank Ayers, has constantly watched the canal banks and has thus obtained the fossils as they were exposed. Among others, who have contributed fossils from this locality, are Messrs. F. C. Gifford, E. J. Wood, J. McCullers, N. F. McCall and J. W. Welch. To Messrs. Weills and Ayers in particular are due the very important results that have been obtained, Mr. Ayers' close watch of the canal bank having been rewarded by the fortunate discovery of the human remains while they were still in place in the undisturbed walls of the canal. Additional collections at this locality have been made by H. Gunter and the writer. Acknowledgments are due the officials of the U. S. National Museum, and especially to Mr. J. W. Gidley, assistant Curator of Mammals, for facilities afforded in consulting the collections of the Museum. The turtles of the Pleistocene of Florida contained in the Florida State Geological Survey collection, including those found at Vero, have been identified, and subsequently will be described, by Dr. O. P. Hay of the Carnegie Institution. The photographs included in this paper, except that of text-figure 7, were made by E. P. Greenc. The chemical analyses have been made by L. Heimberger, under the direction of R. E. Rose, State Chemist of Florida.

#### *The Geologic Section at Vero.*

It is desirable, before describing the human remains, to consider the general geologic section at Vero, as well as the late geologic history of this part of the Atlantic Coast. The marine shell marl into which the canal cuts, number 1 of the section shown in text-figure 2, is a part of the extensive series of marine marls which border the Atlantic Coast, beginning on the north near St. Augustine, where the marl is known as "Coquina" rock, and extending south to the Everglades of Florida, beyond which the shell marls give place to the shallow-water limestones of extreme southern Florida. These marls and limestones are known by their invertebrate fauna to be of Pleistocene age.<sup>1</sup>

The sands which as a rule overlie the shell marls are in part of marine origin, having accumulated in shoal waters, or as

<sup>1</sup> Florida State Geol. Survey, Second Annual Report, 1909.

beaches and dunes, at the time the sea withdrew from the land; and are thus contemporaneous in age or nearly so with the marine shell marls. However, in ponds, streams and lakes, fresh-water marls, sand and muck deposits accumulated which rest upon and hence are of somewhat later age than the marine marls, and it is in deposits of this kind chiefly, as would be expected, that the land and fresh-water fossils are preserved. A more detailed account of a section through a stream bed at Vero will be given in connection with the description of the fossil human remains.

### *Geologic History of the Florida East Coast.*

The geologic history of the Florida East Coast will be considered in this paper only in so far as it affects the locality under discussion. It is known that the early Pleistocene included a period of great submergence during which the extensive marine marls and limestones of eastern and southern Florida were deposited. Following the accumulation of these early Pleistocene formations the peninsula was lifted in relation to the strand-line to a level somewhat above its present elevation. This period of probably slight emergence was followed by a depression, proof of which is derived from many sources and is conclusive. Shaler long ago noted the fact that the important harbors of Florida are flooded river valleys.<sup>2</sup> Vaughan likewise has called attention to the submerged channels of both the Atlantic and the Gulf coasts which, together with other evidence, lead him to conclude that both the mainland and the Keys of the Florida East Coast stood at the time of maximum Pleistocene emergence as much as 30 feet above the present strand line.<sup>3</sup> The existence of a Pleistocene cypress swamp in Hillsboro Bay, 20 feet below the present sea level, and of a peat bed at the same depth near the Florida Keys on the Atlantic Coast, has been noted by the writer. Additional evidence of changes of level may be adduced from physiographic features in the interior of the State, particularly from the lakes of the "Lake Region" of Florida, the basins of which probably originated through sinkhole formation at a time when the land area stood higher than at present.<sup>4</sup> The

<sup>2</sup> The Geological History of Harbors, U. S. Geol. Surv., 13th Ann. Rept., pt. 2, pp. 190-192, 1893.

<sup>3</sup> Sketch of the Geologic History of the Florida Coral Reef Tract and Comparisons with Other Coral Reef Areas, Washington Acad. Sciences, vol. iv, p. 30, 1914.

<sup>4</sup> Florida State Geol. Surv., Seventh Annual Report, p. 56, 1915; *ibid.*, Sixth Annual Report, p. 155, 1914.

land fauna found in the stream beds and ponds of the Atlantic Coast of Florida, therefore, represents that part of the Pleistocene following the deposition of the marine shell marl and the subsequent emergence of the land. In some of these ponds deposits have probably accumulated continuously from the Pleistocene to the present time.

The excavations as well as the timber growth show that the old stream-bed or valley at Vero had a width of from 350 to 500 feet for a distance of about three-fourths of a mile from the Indian River, which is itself an inlet from the ocean. The stream valley, however, is very shallow, the material which fills it having at the present time a thickness of not more than from four to six feet. At the time the canal was cut, a sluggish stream, known as Van Valkenburg's Creek, following an ill-defined channel, flowed through the valley which had been aggraded to within three or four feet of the surrounding land level. The fill in the stream valley includes, as shown in the accompanying sketch (fig. 2), two successive fluvial deposits. From the sketch map (fig. 1) it will be seen also that the broad valley is formed, near the place where the fossils are found, by two tributaries which enter, one from the north and one from the south. These streams originate only a few miles inland and their course is controlled by the Pleistocene beaches and dunes which here parallel the coast. The position of the original stream may have been determined by a natural depression or inlet from the ocean which possibly accounts for the great width as compared to the shallow depth of the valley. The possibility of the stream having in former times been fed by a spring also suggests itself, especially as the number of vertebrates found in this locality seems to imply some kind of a fresh-water resort.

#### *Section through the Stream Bed.*

The section through the stream bed, as exposed in the banks of the canal at the place where the human fossils are found, is represented by text-figure 2. The section as here shown does not extend directly across the stream, but as will be seen by referring to the sketch map (fig. 1), runs approximately parallel to the general course of the valley, from the union of the two tributaries to the crossing of the Florida East Coast Railroad, a distance of 512 feet. Number 1 of the section represents the marine shell marl which is common to this part of the state, and is cut into by the canal here as elsewhere.



The material next following the marl, number 2 of the section, includes cross-bedded river-wash sand, partially decayed wood and muck, sand stained brown by organic matter, and at places fresh-water marl rock. The distinctly cross-bedded sands of this stratum are found near the base, and it is here chiefly that the decayed wood and muck occur lying in stream channels in the shell marl. The brown sand contains in places many fresh-water shells, and at the top grades into the fresh-water marl which in places reaches a thickness of as much as two feet. Vertebrates and fresh-water invertebrate fossils occur throughout this bed from the cross-bedded sands at the base to the marl rock at the top. It is from this bed also that the first human fossils found at Vero were taken.

Resting upon this sand and marl bed and in places cutting into it is an alluvial deposit consisting chiefly of vegetable material intermixed with sand, grading at the top in places, as is true also of the bed beneath, into a fresh-water marl. The average aggrading of the stream valley by this alluvial material amounts to about two feet, although locally where the stream cut deeply into the underlying bed this deposit reaches a maximum thickness of five or six feet. This alluvial deposit contains vertebrate and plant fossils and in the fresh-water marl occasional invertebrates. Human fossils are found in this deposit also, their place in the section being indicated in text-figures 1 and 2.

#### *The Human Remains.*

Fossil human bones from two skeletons have been obtained at Vero. Of the two individuals represented one is from the older deposits of the stream valley, number 2 of the section shown in text-figure 2, while the other is from the base of the next overlying bed, number 3 of the section.

#### *Human Remains from the Older Stream Deposits.*

In October, 1915, Mr. Ayers, while examining the stratum which contains the vertebrate fossils, found some bones in place which seemed probably to belong to a human skeleton. In order to verify the place of the bones in the section he then called Mr. Weills, and together they removed the bones. The parts of this skeleton obtained include the right and left femur, lacking the extremities; right patella; left tibia and fragments of the right; right fibula; right calcaneum, right and left astragalus; left navicular; external cuneiform of the right

FIG. 1.

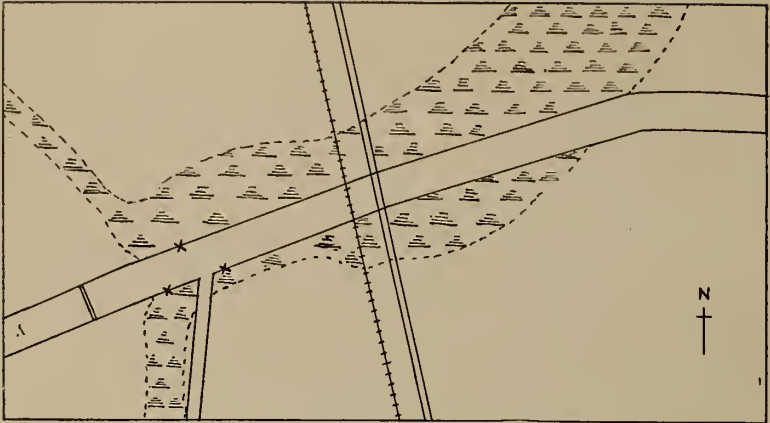


FIG. 1. Sketch map showing the locality at which human fossils were found at Vero. Scale, 1 inch equals 300 feet. The location of the human remains in the canal bank is indicated in the sketch by a cross. The margins of the broad valley are indicated by the dotted lines, and the canal by the conventional character. The canal follows the stream valley while passing under the Florida East Coast Railroad and the public road. The modern stream in this valley followed an ill-defined, anastomosing and frequently changing channel.

FIG. 2.

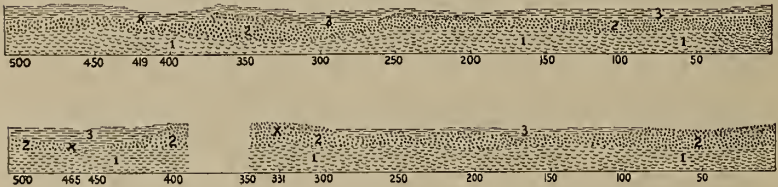


FIG. 2. Sketch showing the section of the canal banks from the Florida East Coast Railroad bridge west to the entrance of the lateral streams. Horizontal scale, one inch equals 125 feet; vertical scale, one inch equals 40 feet. The base line is drawn at water level in the canal which at that time stood 18 feet below the top of the railroad track. The break in the sketch indicates the entrance of the lateral canal from the south. (1) Marine shell marl found generally throughout this part of the state and cut into by the canal here as elsewhere. (2) River deposits consisting near the base of cross bedded sands with inclusions at places of muck and vegetable material; at a higher level the sand is prevailing of a brown color, fairly well indurated, and contains many fresh-water shells; at the top the sand at places grades into a fresh-water marl which reaches a maximum thickness of two feet. Vertebrate fossils are found throughout this deposit from the marl at the top to the muck inclusions at the base. The first human bones obtained are from this bed, the location in the canal bank being indicated in the sketch by a cross. (3) Alluvial deposits having an average thickness of about two feet. The second human skeleton was obtained from the base of this bed at a place where it reaches a maximum thickness of about five feet. The location of human bones in this bed is also indicated in the sketch.

foot; right metatarsals one to four; left metatarsals three to five; a part of the shaft of the left humerus; right os magnum; three metacarpals; and three phalanges. All of these bones pertain apparently to the same specimen, representing a small individual, probably a female. From the lower margin of the lesser tuberosity to the upper margin of the inner condylar notch, the femur measures 29 cm., the corresponding measurement on the femur of a large modern adult being as much as 32 cm. The extremities of the larger limb bones of this skeleton are but poorly preserved, a condition common to many of the bones in this sand, although the bones found in muck in this bed are as a rule more nearly complete.

The section of the bank at the place where these human bones were found is as follows:

	FEET	INCHES
Sandy hard marl rock .....	1	3
Sand stained brown by organic matter .....	3	9
Marine shell marl to water level in the canal .....	5	9

The marl rock and the brown sand beneath represent stratum number 2 of the general section (Text-figure 2), the alluvial bed, no. 3 of the section, being absent at this place. The human remains were imbedded in the brown sand about three feet from the base or two feet from the ground surface as it existed previous to the construction of the canal.

That the sands in which the human remains are found represent a continuation of the stratum holding the other vertebrate fossils there can be no question, as the section is continuous along the canal bank and the deposits identical in appearance. *Elephas columbi*, *Equus leidy* and other extinct species are found at an equal or higher level in the beds on either side of the human remains. From the marl rock which lies at the top of the section the writer obtained within six feet of the place where the human skeleton lay, a premolar tooth of a fox, representing not the common gray fox of that region, but either an extinct species, or possibly the red fox, *Vulpes pennsylvanicus*, which at present is not known in Florida. In immediate association with the human bones were the scapula and astragalus of a deer which is also found elsewhere in the sands, being one of the common fossils of the bone bed. In addition a hyoid bone of the sloth, *Megalonyx jeffersoni*, and pieces of the teeth of the mastodon, *Mammot americanum*, have been collected from the canal bank at the place where the human bones were found.

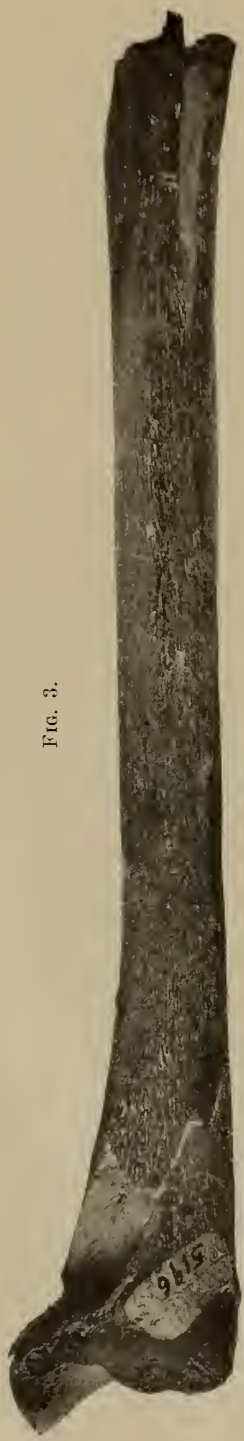


FIG. 3.

FIG. 4.

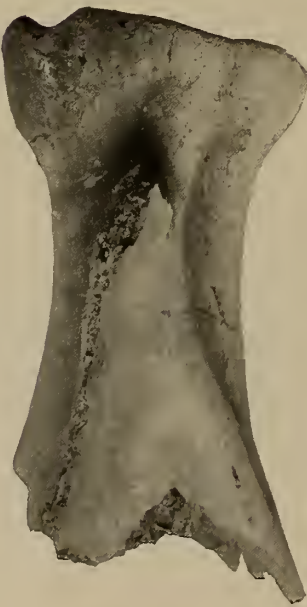


FIG. 5.



FIG. 6.



FIG. 3. Left tibia of man found in place in the older stream deposit (no. 2 of text-figure 2), at the place indicated by a cross, 331 feet west of the railroad bridge. Seven-tenths natural size. Fla. Survey Coll. No. 5196.

FIG. 4. Scapula of deer found in immediate association with the tibia and other human bones. This deer is one of the common fossils of this and the succeeding stream deposit at Vero. Natural size. Fla. Survey Coll. No. 5199.

FIG. 5. Astragalus of deer found in immediate association with the human fossils. Natural size. Fla. Survey Coll. No. 5218.

FIG. 6. Hyoid bone of the sloth, *Megalonys jeffersonii*, found near the human remains. Natural size. Fla. Survey Coll. No. 5212.



*Preliminary List of Mammals from the older Stream Deposits at Vero.*

In the following list those species that have been found in place in the older stream deposits at Vero are indicated by the use of the dagger. All others have been taken not in place and are here referred provisionally to the older bed as their probable source, although some may prove to have been derived from the next overlying deposits. In addition to the mammals, which include those best known and most characteristic of the North American Pleistocene, there have been found in this bed, vertebræ and teeth of a large and probably extinct crocodilian, some bird, fish and batrachian bones, and a considerable variety of turtles, including two very large extinct land tortoises, the whole vertebrate fauna obtained including probably not less than twenty-five species. This fauna affords conclusive proof of the Pleistocene age of the deposits in which it is found.

Megalonyx jeffersonii†	Bison sp.
Myiodon sp.	Mammot americanum†
Chlamytherium septentrionalis	Elephas columbi†
Equus leidy†	Hydrochaerus sp.
Equus complicatus	Smilodon sp.†
Equus litoralis	Canis sp.†
Tapirus haysii?†	Edentate, indt.
Peccary, indt.	Procyon sp.
Cameloid, indt.	Vulpes pennsylvanicus?†
Odocoileus sp.†	

*Chemical Analysis.*—The chemical analysis of fossil bones is usually considered as affording important contributory evidence of age. In the present instance the opportunity for comparative analysis is particularly good, since it is possible on the one hand to compare the fossil human bones with recent human bones from the Indian mounds, and on the other with the bones of animals, known to be of Pleistocene age, found in the same bed as the human bones. Accordingly, analyses have been made at the writer's request in the State Laboratory under the direction of the State Chemist. The results of the analyses are presented in the following table. All of the analyses included in this table were made at the same time and by the same methods.

## ANALYSIS OF RECENT AND FOSSIL BONES FROM VERO, FLORIDA.

	No. 1	No. 2	No. 3	No. 4
Specific gravity .....	2.0627	2.8357	2.6293	2.7505
Moisture at 100° C. ....	10.72	2.07	4.09	3.89
Volatile matter .....	19.59	8.92	8.22	10.30
Phosphoric acid, P <sub>2</sub> O <sub>5</sub> .....	27.24	32.27	30.88	32.00
Calcium oxide, CaO .....	39.75	46.80	45.69	48.31
Insoluble matter, silica, etc. ....	0.60	1.11	3.61	1.39
Iron and aluminum oxides .....	0.13	3.71	1.85	0.76

No. 1 is from a recent human tibia taken from an Indian mound near Vero. Fla. Surv. coll. No. 5537. No. 2 is from the right tibia of a man taken in place in the Pleistocene bed at Vero. Fla. Surv. coll. No. 5200. No. 3 is from the femur of *Canis* sp. from the stream bed at Vero. Fla. Surv. coll. No. 5449. No. 4 is from the front part of the jaw of *Megalonyx jeffersonii*, from Vero. Fla. Surv. coll. No. 4374.

The specific gravity was obtained from the finely powdered bone by the pycnometer method. The moisture, taken at 100° C., includes, as will be recognized, any other constituents sufficiently unstable to be driven off at that temperature. Volatile matter, likewise, represents the constituents driven off when the sample is maintained at red heat in a muffle for several hours, and necessarily includes carbon dioxide, and possibly other constituents in addition to the organic matter. The phosphoric acid, calcium oxide, and iron and aluminum oxides were determined by standard methods. The analyses show, as may be seen from the table, that the fossil human bones are quite as well mineralized as are the associated bones of the Pleistocene animals.

Since the stratum holding the bones lies near the surface the possibility of the human bones having been placed in it by burial must be considered, although in case of a burial it seems probable that more of the skeleton would have been found. Since being dug the canal has gradually widened by the eaving of the banks, and at the place where the human fossil was found the rock at the top of the section had broken from the ledge and lay inclined on the canal bank, having moved somewhat from its original position. When in place, however, this rock rested above the human bones. The sand in which the bones were imbedded had not been disturbed. Moreover, the human bones are thoroughly mineralized, and it is highly improbable that a recent skeleton, if placed in these beds, would have become equally as well mineralized as the much older Pleistocene bones. Without doubt the mineralization of the bones is the result of the slow chemical changes by which bones are altered while being fossilized, a process which at this

locality has affected alike, although in a slightly varying degree, all of the bones of the deposit. The fossil wood in this bed, on the contrary, has apparently undergone but little change, having merely become water soaked and softened. No implements have been taken in this part of the section, although a fragment of bird bone and the tip of the tusk of a proboscidian taken in place at the base of this bed, show markings which apparently

FIG. 7.



FIG. 7. Photograph of the bank showing the human remains in place in bed no. 3 as shown in text-figure 2. The ulna lies at (1); the humerus at (2); and the radius at (3). The human bones, although found at slightly different actual levels, lie at the same place in the section, at the bottom of the alluvial bed.

were made by tools. Charcoal is found in this as well as in the later bed at this locality.

#### *Human Remains from Bed No. 3 of the General Section.*

In February, 1916, Mr. Ayers obtained a human right ulna which, although not found in place, was recognized as having been derived from the bank, since the degree of mineralization was similar to that of the associated vertebrate fossils. The skeleton from which this bone came, however, was not located

FIG. 8.



FIG. 9.

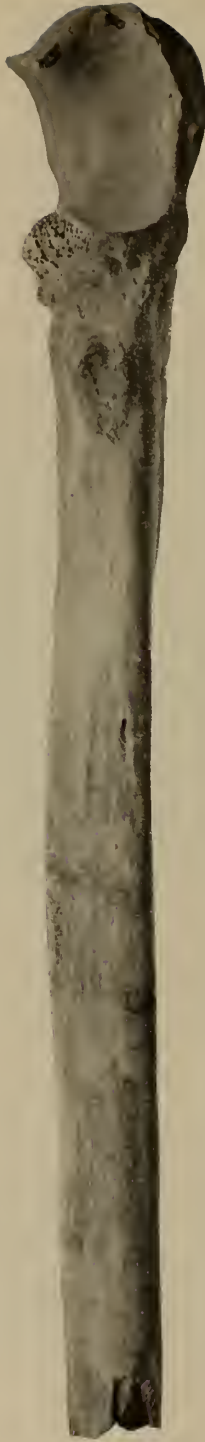


FIG. 10.





at that time. Again in April, 1916, Mr. Ayers found the distal end of a humerus, which, although not in place, had recently fallen from the bank. The discovery of this bone led to the location of the second human skeleton to which belongs also the ulna found three months earlier.

At the place where these bones were found, the stream had cut into the earlier river deposits, making a narrow channel with abrupt slopes at the sides. At the center this channel cuts through to the shell marl and the first foot or more of deposits in the channel includes coarse sand mixed with broken shell from the marl beneath. This is followed by alternating layers of muck and sand. A soft fresh-water marl, which in places reaches a maximum thickness of two feet, is found at the top of the section.

This second human fossil was taken from the bank by Weills, Ayers and Sellards. In addition to the ulna and humerus, there were obtained from cavings from the bank a part of a sphenoid bone, scapula, and a left first upper incisor; and in place in the bank the left ulna, a femur, radius, base of a jaw, parts of the skull and two metatarsals. Subsequently a toe bone was found on the opposite side of the canal in the same bed and at the same level. The first bone found in place was the left ulna, of which the proximal part only was present, although the distal part lacking the extremities was later obtained a few inches farther back in the bank. The bone next

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FIG. 8. The right ulna lacking the distal one-fourth; exterior view, very slightly reduced. Actual length of specimen as preserved 20 cm. Fla. Surv. coll. No. 5895. On the exterior side of the bone at the union of the olecranon process with the shaft is a deep pit or excavation through which a nutrient canal enters the bone. Just posterior to this pit may be seen a pronounced line or ridge which passes from the posterior margin obliquely outward and becomes confluent with the outer margin of the greater sigmoid cavity at the base of the olecranon process. The angle which separates the superior from the posterior side of the olecranon process is gently rounded, not being as pronounced as in most modern skeletons. Although not taken in place this ulna was subsequently found to belong with the skeleton from bed no. 3 of the section, as it agrees in all details with the left ulna found at that place.

FIG. 9. Same bone, anterior view.

FIG. 10. Right ulna of a large wolf, *Canis* sp., included to illustrate the identity of preservation of the human and other Pleistocene fossils from this deposit. Seven-tenths natural size. Fla. Surv. coll. No. 5451. The canid found in this deposit, no. 2 of the section, is of the size of *Canis dirus* and the limb bones, when isolated, are scarcely to be distinguished from those of that species. The skull, however, is longer and more narrow, the snout in particular being narrow. The teeth likewise are not crowded in the jaw as are those of *C. dirus*. The canid obtained from bed no. 3 of the section, referred to in the text, represents a smaller and more stocky species.

found, the femur, of which only a part of the shaft is preserved, was lying near the ulna and at about the same level. The radius, of which the proximal part only was obtained, was found five feet north of east of the ulna, and at the same place in the section, that is at the bottom of the bed of sand and alluvial material. Owing to the slope of the bed at this place, however, this bone lay at an actual level fully two feet lower than the ulna. The jaw and the parts of the skull were found chiefly between the ulna and the radius and from a few inches to two feet farther back in the bank. One of the foot bones, a fifth metatarsal, was taken about eight feet east of the ulna and at an actual level, owing to the change in slope, above that of the radius and approximately the same as that of the ulna. Above the human skeleton four feet of alluvial material are found at this place, consisting of alternating layers of sand and muck, which in places grade into soft fresh-water marl having a thickness of as much as two feet. Fossil plants including leaves, stems and seeds are found in the muck bed. The plants, apparently, are but little changed from their original condition.

In this deposit were found also numerous pieces of pottery, fragments of charcoal, and a few implements. Of the implements three are of bone, one of wood, and one of flint, possibly the tip of an arrow point.

#### *The Associated Vertebrate Fossils.*

The position of this skeleton and the conditions of preservation are such as to exclude definitely the possibility of its representing a human burial. In discussing the human remains it is well, therefore, to pass at once to a consideration of the associated fossils. The stream bed at the place where the human fossils were found, as already noted, cuts through the older stream fill and into the marine shell marl. Under these conditions it becomes necessary to carefully exclude any fossils that may have washed in from the older bed beneath. It is by no means unusual for fossil bones and teeth to wash from an older and lodge in a newer formation, although such bones are very sure to betray their true origin by their rounded and worn condition. It is a significant fact, therefore, that the bones found in association with the human fossils, as well as elsewhere in this alluvial bed, are sharp cornered and entirely unworn. The associated bones are frequently broken, but no more so than are the human bones. The fact that delicate jaws and teeth are here preserved is conclusive proof that the animals represented were actually contemporaneous with man at this place.

Of mammals found in association with the human bones twelve species may be recognized. Of these five or six are extinct, the remainder being identical, so far as can now be determined, with existing species. Of the extinct species, one, an armadillo, is referable to the extinct genus *Chlamytherium*, while another, a rabbit which is quite unlike any rabbit now known in the United States, is probably to be referred to a new extinct genus having affinities possibly with the genus *Romerolagus* of Mexico or *Pronolagus* of South Africa. In addition to mammals there are found in this bed bones of crocodilians, fishes, birds, and a variety of turtles, as well as plant and insect remains. The human fossils are mineralized and in all respects preserved in the same manner as the associated vertebrate fossils.

LIST OF MAMMALIAN SPECIES FROM BED No. 3.

*Chlamytherium septentrionalis*. This extinct armadillo-like animal is represented by dermal plates taken from the muck and sand layers about one foot above the human remains. The articulating margins of the plates, although very delicate, are uneroded.

*Lynx* sp. Represented by a tibia and a lower jaw lacking only the incisor teeth. This lynx differs from the modern lynx now found in Florida by a large canine which crowds upon and reduces the space available for the incisors; the diastema between the canine and the premolars is reduced, the jaw as a whole is thicker, and the teeth more closely crowded than in the modern species.

*Rabbit* Gn., sp. nov. Represented by right and left jaws, taken from the muck eighteen inches above the human radius. In the structure of the first molariform tooth this rabbit differs from any known from the United States and resembles in this respect the aberrant *Romerolagus* known only from the west side of Mt. Popocatepetl in Mexico, and the South African rabbit, *Pronolagus*.

*Vulpes pennsylvanicus?* Represented by a part of the lower jaw with two premolars preserved.

*Neofiber alleni*. Represented by the front part of the skull and two lower jaws.

*Canis* sp. Represented by a scapula, humerus, radius and tibia, indicating a canid of more stocky build than the coyotes.

*Sigmodon* sp. Represented by a right lower jaw.

*Odocoileus* sp. Represented by a part of the lower jaw and various parts of the skeleton.

*Lutra canadensis*. Represented by humerus, femur and tibia.

*Didelphis virginiana*. Jaw, humerus and ulna.

*Neotoma* sp. Lower jaw.

*Procyon lotor?* Ulna and radius.

*Ursus* indt. Part of crown of molar tooth.

*Elephas columbi* and *Equus leidyii* (?) have also been obtained from this deposit, but as these two species are represented only

FIG. 11.



FIG. 11. Photograph showing plant remains from bed no. 3 of the section at Vero. The plant remains are found from one to two feet above the human bones. In addition to the plants the slab illustrated shows the scale of a fish and the tibia of an insect. Natural size.

by broken teeth from near the bottom of the bed, they are not at present included as a part of this fauna.



Summary.

That the human bones found in the older stream deposits at Vero belong with and are a part of the fauna with which they are associated, and were not placed in the bed by human burial is supported by the following observations: A part only of the skeleton was present; the sand in which the bones were imbedded had not been disturbed, nor had the overlying covering of hard rock been removed; the human bones are thoroughly mineralized, agreeing in this respect with the bones of the associated Pleistocene vertebrates; the scapula and astragalus of a deer common to this and the succeeding river deposits were found in immediate association with the human bones; bones of the sloth, *Megalonyx jeffersonii*, and teeth of the mastodon,

FIG. 12.



FIG. 12. Fragment of a bird bone showing markings which were apparently made by a tool. Natural size. A tip of a proboscidian tusk obtained at the same place shows markings which by their regularity of spacing may indicate design. Both specimens were taken in place at the base of bed no. 2 of the section as shown in fig. 2.

*Mammut americanum*, have been found in the canal bank at this place showing, together with evidence based on the texture and appearance of the sand, that there is no break in the continuity of the stratum holding the Pleistocene fossils.

That the human bones found in the newer fluviatile deposits in this valley do not represent a human burial, but are contemporaneous with the fauna with which they are associated, is shown by the entire similarity in the manner of deposition and preservation of the bones; that the associated fossils were not washed in from some older deposits is shown by the fact that the bones are not in the least eroded, rounded or water-worn.

Aside from the change in the fauna the time interval since the human skeletons became lodged in the stream bed is measured by the accumulation of the overlying fluviatile deposits. The aggrading of the stream valley as a whole since the later of the two skeletons became entombed includes an accumulation over the whole valley of an average of about two feet of vegetable material and sand. Inasmuch as the streams tribu-

tary to this valley originate only a few miles inland, and the valley in recent times has been occupied merely by a small sluggish clear-water stream, the aggrading of the stream valley must have progressed very slowly. The fact that the fresh-water marl which overlies the alluvial bed amounts in places to as much as two feet in thickness is further evidence of the considerable length of time that has elapsed since this deposit was accumulated.

The mammalian fauna contained in the older stratum holding human remains at Vero, No. 2 of the section, makes it certain that this bed was deposited during the Pleistocene period. That the overlying bed, No. 3 of the section, is likewise of great antiquity is established by the fact that it contains a number of extinct mammalian species, as well as by the fact that the human and other bones which it contains are well mineralized. However, further discussion of the place of this bed in the geologic time scale will be deferred until a more complete determination has been made of the associated fauna and flora. This is the more desirable since the collections from this very important locality are being rapidly increased, thus affording additional data with which to determine the age of the deposits.

Florida Geological Survey, Tallahassee, Fla.

ART. II.—*A New Cyprinid Fish, Leuciscus rosei, from the Miocene of British Columbia*; by L. HUSSAKOF.

SOME time ago Dr. B. Rose, of the Geological Survey of Canada, sent me for examination four fossil fishes which he had collected while investigating the geology of the southern part of British Columbia in 1912. The specimens are from a formation known as the Tranquille beds, probably of Miocene age, on Kamloops Lake, B. C.\* Each specimen consists of a more or less complete fish about 6 inches in length, represented by its skeleton in a layer of stratified light brown tuff. The fishes apparently represent a new species.

*Leuciscus rosei*, n. sp.

*Type*.—Impression of a complete fish lacking only the lower lobe of the caudal. Total length, 127<sup>mm</sup>. In the collection of

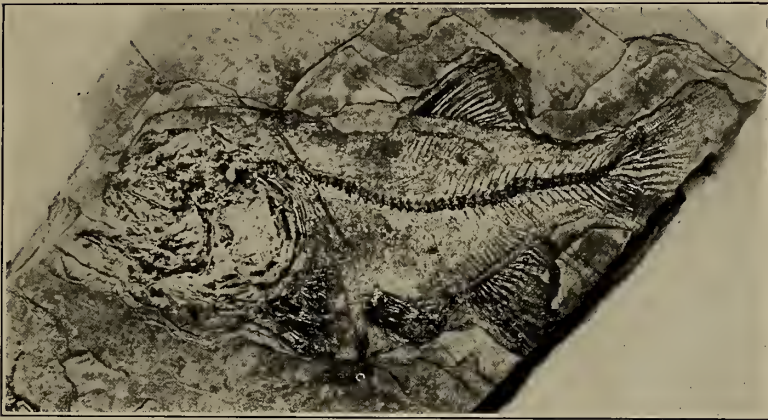
\* A brief description of the geology of the region in which the specimens were collected was given by Dr. B. Rose in his paper, "Savona Map-area, British Columbia." Summary Report, Geological Survey Canada, for the Calendar year 1912 (1914), 151-155.

the Geological Survey of Canada. Locality: Red Point, on Kamloops Lake, B. C.

Head  $2\frac{1}{2}$  in length to base of caudal; depth  $2\frac{3}{4}$ . Dorsal 14; anal 18 or 19. Vertebrae about 40.

Fish rather short and deep, with large head and projecting lower jaw. Dorsal triangular, its front rays the longest, half again as long as the dorsal base. Origin of dorsal behind that of ventrals, at about middle of the total length;  $\frac{1}{3}$  of dorsal base

FIG. 1.



*Leuciscus rosei*, n. sp. Type,  $\times \frac{2}{3}$ . Tranquille beds (probably Miocene); Kamloops Lake, British Columbia.

in front of anal. Anal larger than dorsal, its anterior rays elongated, its base separated from the caudal by a distance slightly less than the depth of the peduncle. Origin of ventrals about equidistant between origins of pectorals and of anal. Peduncle rather deep, equal to base of dorsal. Caudal not completely preserved, but obviously forked as shown by the elongation of the upper rays and the shortness of the middle ones in the type specimen.

*Remarks.*—The Cyprinid fishes are distinguished into genera largely by the character of their pharyngeal teeth, and since these are not preserved in the present specimens one cannot be absolutely certain as to the generic determination. However, a comparison with figures of various genera would indicate from the proportions of the fish, the position and size of the

fins, and the projection of the lower jaw, that the species most probably belongs in the genus *Leuciscus*.

It is interesting to note that the fossil has considerable resemblance to *Leuciscus balteatus* (Richardson), a species now living in the same region and said to be "generally abundant everywhere in the Columbia Basin, and very variable."\* It differs, however, in being deeper, in having a larger head, and a longer dorsal, with 14 rays as against 10. The anal in *Leuciscus balteatus* is given by Jordan and Evermann as "11 to 22, usually 16," so that the anal of the fossil species falls within this range of variation.

Six other fossil species of *Leuciscus* have been described from North America,† but only one is known by a complete fish, the other five—from the Pleistocene of Idaho—being based on pharyngeal teeth. The complete fish is *Leuciscus turneri* Lucas,‡ from the Miocene of Nevada. From this species the present one differs in proportions, position of the fins and other details.

Besides the type, I have in hand three other specimens (paratypes) from the same locality, and also collected by Dr. Rose. One is a fish as large as the type but with the fins in less perfect condition and lacking the upper margin of the body. This specimen also belongs to the Geological Survey of Canada. Secondly, two imperfect fishes in the American Museum collection: one, an impression lacking the snout and the lower margin of the body including the pectorals, one ventral and the front portion of the anal; the other, a poorly preserved mold of a fish about as large as the type with the bone completely weathered away but showing part of the outline of the body and tracings of the opercular region and of the dorsal and caudal fins.

The species is named for Dr. Bruce Rose, of the Geological Survey of Canada, who collected the specimens, and kindly placed them at my disposal for study.

\* Jordan and Evermann, *Fishes of North America*, Pt. I, 238; and Pt. IV, pl. xlii, figs. 105, 105a.

† O. P. Hay, *Bibliogr. and Catal. Fossil Vertebr.*, N. Amer., 1902, 396.

‡ F. A. Lucas, A New Fossil Cyprinoid, *Leuciscus turneri*, from the Miocene of Nevada. *Proc. U. S. Nat. Mus.*, xxiii, 1901, 333-334, pl. viii.



ART. III.—*A Cycadophyte from the North American Coal Measures*; by HARVEY BASSLER.

ALTHOUGH the remains of fronds of indubitable cycadophytes have long been known from the European Paleozoic none have heretofore been known from the North American Paleozoic.

During the summer of 1915 the writer, while collecting from the so-called Four-foot Coal Seam opposite Barnum, W. Va., discovered a single characteristic specimen of the genus *Plagiozamites*.

The importance attached to the finding of this genus in the Paleozoic of North America and the possible significance of the occurrence of such a well-known Permian type as low in the coal-measures as the middle of the Conemaugh formation warrants the publication of the present announcement in advance of the publication of the detailed account of the flora which is now approaching completion.

The genus *Plagiozamites* was established in 1894 by Prof. René Zeiller\* to include cycadean fronds with oval-lanceolate leaflets resembling in their general form those of *Zamites*, but inserted obliquely on the common rachis, the leaflets differing, further, from those of *Zamites* in that they do not display at the base the callous thickening that always or nearly always characterizes the latter. The Maryland specimen is not, however, specifically different from *Plagiozamites Planchardi* (Renault) Zeiller† of the Lower Permian of Trienbach in Alsace, and this makes the discovery of peculiar interest, for the American material comes from a horizon in the Middle Conemaugh 410' ± below the Pittsburg seam of coal, which marks the base of the superjacent Monongahela Formation, and nearly 700' beneath what has been considered to be the base of the Permian in this region. This fact, however, is in perfect accord with other evidence tending to show an interesting relationship between the middle Conemaugh of the Appalachian province and the Permian of other regions.

The appearance in the Conemaugh for the first time since the close of the Mississippian of inherently red sediments has for some years‡ been considered significant of some important geologic change such as might mark the passage from the true Coal Measures to the Permian-Carboniferous and this found confirmation in 1908 when in the Annals of the Carnegie Museum, vol. iv, pages 234–241, Prof. E. C. Case described a small collection of vertebrate fossils made by Dr. Percy E. Raymond in

\* Zeiller, 1894, Bull. Soc. Geol. France, 3e Serie, xxii, pp. 174, 177.

† Zeiller, 1894, *ibid.*, p. 174, pl. viii, figs. 1–5, pl. ix, fig. 1.

‡ White, I. C., 1903, West Virginia Geol. Survey, vol. ii, pp. 165, 226, 227.

the middle Conemaugh at Piteairn about fifteen miles east of Pittsburg, Pa. The determinable specimens of this collection, to the number of about twenty, are distributed among the reptilian genera *Naosaurus* and *Desmatodon* and the amphibian genus *Eryops*, and are declared to be distinctly of the same character as those from the Permian beds of northern Texas. These bones came from a horizon in the Pittsburg Red Shale about 35 feet beneath the Ames or Crinoidal Limestone which in turn lies 315 feet beneath the base of the Pittsburg Coal Seam and marks the last paleozoic marine invasion of this general region. Further, Dr. I. C. White, in Vol. II (A) of the West Virginia Geological Survey (1908), page 623, mentions the discovery near Salt Lick Bridge, Braxton Co., W. Va., a few feet above the horizon of the Ames Limestone, of what appears to be a perfect cast of the tibia of a large reptile allied to the Permian-Triassic *Parciasauria*. In this connection it is interesting to recall that Scudder in 1896 (Bull. U. S. G. S., No. 124, p. 12), in discussing a collection of insect wings made near Steubenville, Ohio, from a horizon "a little above the Crinoidal" or Ames Limestone, states that this insect fauna closely resembles one from the Lower Permian of Weissig in Saxony.

The reference of each of the above faunal horizons to the Ames marine horizon raises the question of the relation of the "Four-foot Seam" at Barnum to this marine limestone. This coal-seam is the same as that at Barton, Md., 9 miles to the northeastward in the Georges Creek Valley which is known in the literature of the region as the *Bakerstown Coal* and which at Barton is about 135' above the uppermost known marine fauna—*Brush Creek* of the literature—but this so-called Brush Creek horizon on the evidence of a considerable marine fauna is considered by Drs. C. K. Swartz and W. A. Price as probably that of the Ames Limestone.

In addition to the occurrence of *Plagiozamites Planchardi* at Teufelsbrunn in Alsace it has been found also in France, in the Tranchée de Forêt, in shales associated with the Grand Couche of the Commentry Basin\* and in shales associated with the upper seam of coal at the mines of Longpendu in the Blanzly Basin,† in both cases at practically the same horizon (slightly older than the one in the Vosges) which Zeiller‡ considers

\* Renault, 1890, Flore Foss. terr. houill. de Commentry, 2e part, p. 615, Atlas, pl. lxxvii, fig. 8.

† Zeiller, 1906, Flore foss. bass. houill. et Perm. de Blanzly et du Creusot, page 193, pl. xlvi, fig. 2.

‡ Zeiller, 1894, Sur l'âge des dépôts houill. d. Commentry, Bull. Geol. Soc. France, 3e ser., t. xxii, p. 275 et seq., also Zeiller, 1906, loc. cit., pp. 237, 247.

uppermost Stephanian and which Sterzel\* and Potonié† both consider referable to the lowermost Autunian or Rothliegendes (Permian). This horizon will be referred to as Permo-Carboniferous in the sense that it probably occurs in the narrow zone of passage from the Stephanian to the Autunian.

The material from Maryland falls well within the limits of this species as described by Zeiller, for, while the leaflets are rather less bluntly terminated than is the case with the Alsatian specimens or with the one from Longpendu, they are distally somewhat less attenuate than that from Cominentry. The rachis of the Maryland specimen, unlike the rather poorly preserved rachises of the material figured by Zeiller, instead of being terete as these appear to have been, is flattened above, is rather coarsely but somewhat indistinctly lineate and is traversed longitudinally by a shallow median channel. The manner in which the base of the pinnales obliquely half encircles the rachis and the evidence near the base, of the torsion of these leaflets during fossilization, out of the plane they occupied during life, is well seen in the accompanying figures.

The better to show the nervation with its rather infrequent dichotomies and the spinulose denticles into which the nerves are produced, I have added a somewhat diagrammatic line drawing. The nerves occur to the number of 10 to 13 in each half centimeter.

Associated with *Plagiozamites Planchardi* in Europe are two species of Pteridosperms—*Linopteris Germari* (Geibel) Potonié and *Odontopteris genuina* Grand'Eury—which I believe do not anywhere range lower‡ and it is a matter of considerable interest to know that these three species are likewise found associated in Maryland.

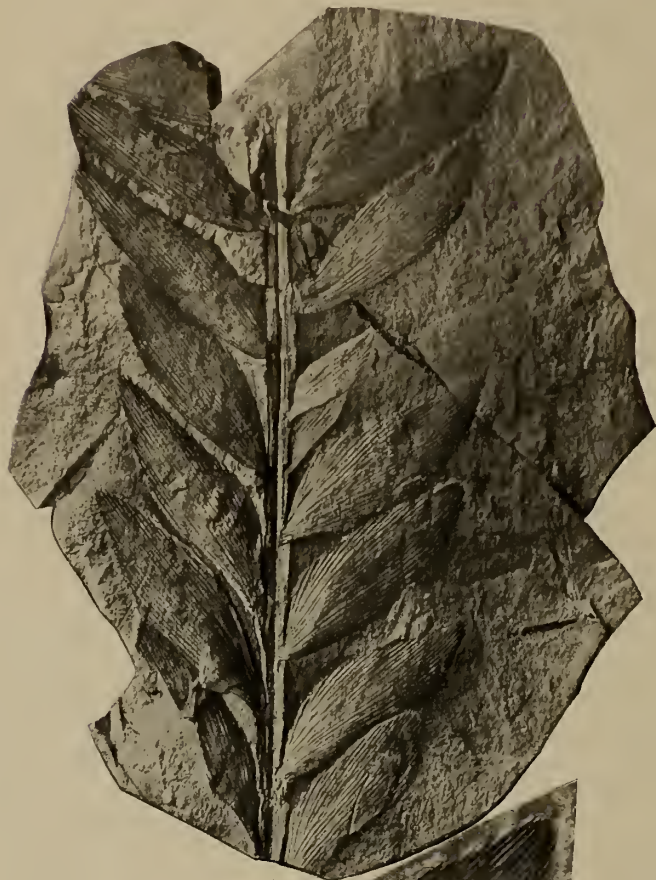
If we are not yet prepared to correlate the beds of the middle Conemaugh of the Appalachian basin with the Permo-Carboniferous of Europe, then the horizon which has yielded the plant here considered is lower than any other from which zamitoid cycadophytean fronds have yet been collected. The

\* Sterzel, 1899, Flora des Rothl. von Oppenau, Mitth. d. grossherz. Badisch. Geol. Landesanst., Bd. 3, p. 340 et seq., also Sterzel, 1893, Flora d. Rothl. in Plauenschen Grunde bei Dresden; Abhandl. k. Sächs. Gesell. Wiss., vol. xix, pp. 157, 159.

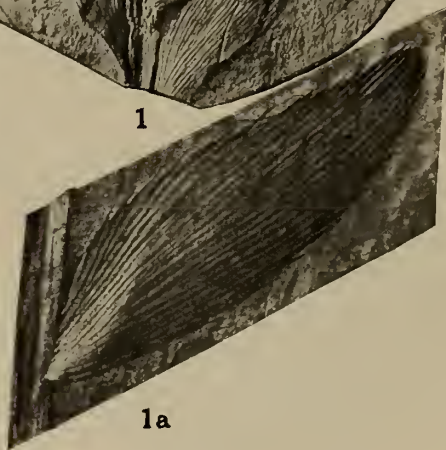
† Potonié, 1893, Die Flora des Rothl. von Thüringen; Abh. kgl. Preuss. Geol. Landesanst., neue Folge, Heft 9, Theil ii, p. 224.

‡ To the species *Odontopteris genuina* Grand'Eury I would assign only material the pinnales of the more distal pinnae of which are obliquely ovate-triangular in shape with the upper margin straight or slightly concave, thus excluding the plant figured under this name by Kidston in 1901, in Flora Carb. Period, Proc. Yorksh. Geol. and Polytech. Soc., vol. xiv, pt. ii, pl. xxviii, fig. 1, from the Middle Coal Measures of England and that by Potonié in 1904 in Abbild. u. Beschreib., Lief. ii, No. 22, fig. 1, from the Westphalian of the basin of the Saar, forms which appear to have more in common with *Odontopteris brittanica* Gutbier.

FIG. 1.



1

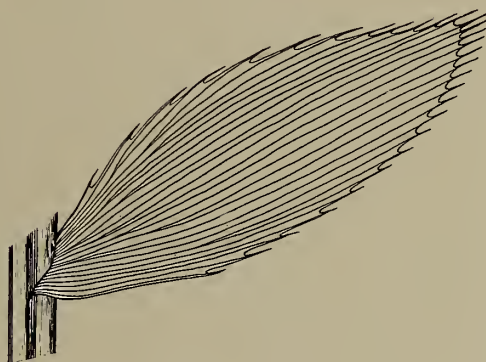


1a



present known distribution of Paleozoic cycadophycean remains, the nature of which is reasonably above suspicion, may prove of interest in this connection. This material gives representation to three genera—the zamitoid genera *Plagiozamites*, confined to the Paleozoic, and *Sphenozamites* which ranges from the Permian to the top of the Jurassic, and the encephalartoid genus *Pterophyllum* which ranges from the Westphalian (Carboniferous) to the Wealden (Cretaceous), but is most extensively developed in the Kenper (Triassic).

FIG. 2.



In addition to *Plagiozamites Planchardi* there are five other described and figured species of this genus.\* *Plagiozamites carbonarius* (Renault) Zeiller occurs in the Permo-Carboniferous, at the Tranchée de Forêt in the Commeny Basin and in the Lower Rothliegenden (Gehrener Schichten) at Stockheim in Thuringia,† while *P. minieri* Renault sp., *P. acicularis* Renault sp., *P. regularis* Renault sp., and *P. Saportanus* Renault sp. have not yet been reported outside of the Commeny Basin, where they also occur in the Permo-Carboniferous at Tranchée de Forêt.‡

The single Paleozoic representative of the genus *Sphenozamites* is *S. Rochei* Renault§ from the (Lower Permian) Autunian shales at Lally in the coal basin of Autun in France;

\* In Erläut. z. geol. Spezialkarte d. k. Sachs. Sect. Zwickau 1901, p. 135, in a list of the more important Middle Rothliegenden plants of Saxony, Sterzel gives *Plagiozamites Liebeanus* which in Pal. char. d. ober Steink. u. Rothl. im erzgeb. Beck (Ber. d. nat. Ges. z. Chemnitz) 1881, he had described, without figure, as *Cordaites Liebeanus* from the lower tuff in Helene-Schachte near Ölsnitz in Saxony.

† Potonie, 1893, loc. cit. p. 210, pl. xxix, fig. 5.

‡ Renault 1890, loc. cit., p. 614-618, pl. lxxvii, figs. 7-19.

§ Renault, 1896, Flore foss. bass. houill et perm d'Autun et d'Epinae, p. 327, pl. 81, fig. 1.

*Pterophyllum*, on the other hand, is well represented, with *P. cottæanum* Gutbier from the Lebacher Schichten (Middle Rothliegende) at Reinsdorf near Zwickau, Saxony,\* from the lower Porphyrtuffe (Middle Rothliegende) at Bernsdorf near Chemnitz, Saxony† and from the Lower Permian (Middle-Rothliegende) at Zbeschau near Rossitz, Moravia,‡ *P. blechnoides* Sandberger, from the Middle Rothliegende at Holzplatz near Oppenau in the Black Forest of Baden,§ and from the Middle Rothliegende at Weissig near Pilitz, Saxony;|| *P. Fayoli* Renault, from the Permo-Carboniferous at the Tranchée de Pochin in the small coal basin of Montvicq a short distance northeast of Commentry, France;¶ *P. Grand Euryi* Saporta et Marion, from the 'upper zone' (Permo-Carboniferous) at the mines of Montehanin and Montmaillot in the Blanzey Basin, France;\*\* *P. Cambrayi* Renault from the Upper Autunian shales immediately overlying the Boghead of Thèlot in the Basin of Autun;†† *P. inflexum* Eichwald, from the indurated red slate at Socolowa near Afonino in the coal basin of Kouznetzsk which lies in the central part of the province of Tomsk, on the northern slope of the Altai Mts., Siberia,‡‡ and from the red slates in the valley of the Inia River in the same region§§—both Permian||| of what has been called the northern type—and finally the unique occurrence of an unnamed species of *Pterophyllum* from the Transition Coal Measures (Westphalian) at Barfreston in the Kent Coal-field of Great Britain reported in 1912 by Prof. E. A. N. Arber,¶¶ which marks the earliest occurrence thus far recorded of the plant group here considered.

Geological Laboratory,  
Johns Hopkins University,  
March 31, 1916.

\* Gutbier, 1849, Die Versteinerungen d. Rothlieg. in Sachs., p. 21, pl. vii, fig. 7.

† Sterzel, 1907, Mitth. d. grossherz. Bad. Geol. Landesanst., Bd. v, p. 380.

‡ Hofmann u. Ryba, 1899, Leitpflanzen, p. 103, pl. xx, fig. 3.

§ Sandberger, 1864, Flor. d. ober Steinkohl. im bad. Schwarzwald, p. 34, pl. ii, figs. 1-4.

|| Geinitz, E., 1873, Brandschiefer von Weissig, p. 701, pl. iii, fig. 9, including *P. cottæanum* E. Geinitz (non Gutbier), p. 701, (excl. syn.) pl. iii, fig. 8.

¶ Renault, 1890, loc. cit., p. 619, pl. lxxviii, fig. 1.

\*\* Zeiller, 1906, loc. cit., p. 194, pl. xlvii, fig. 1.

†† Renault, 1896, loc. cit., p. 322, text fig. 64.

‡‡ Eichwald, 1860, Lethæa Rossica, vol. i, p. 215, pl. xv, figs. 5, 6.

§§ Geinitz, 1871, in Cotta's Der Altai, p. 172, pl. iii, fig. 7.

||| Zeiller, 1902, Nouv. observ. sur la flore foss. d. bass. de Kouznetzsk; Compt. rend., t. cxxxiv, p. 887.

¶¶ Arber, 1912, Geol. Mag., Dec. v, vol. ix, p. 98, pl. v, figs. 2, 4.

ART. IV.—*The Pleionian Cycle of Climatic Fluctuations*;  
by HENRYK ARCTOWSKI.

As we observe changes of weather from one day to another, so we observe climatic fluctuations from one season to another, from one year to the following year. Persistency of given weather conditions may frequently be observed. In the case of climatic fluctuations, also, there may be a series of years abnormally dry or abnormally rainy, or we may have groups of years offering some other particularities such as a late spring for example, or an unusually warm winter, and such exceptional conditions, recurring for a succession of years, give the impression of a radical change of climate.

In reality, therefore, we may consider the study of these changes or fluctuations just as important and as having a far more practical value than the study of the so-called normal climatic conditions.

Considering ten-yearly means of atmospheric temperature as representing quasi-normal values, I inscribed the annual departures from these means on maps. For each year so far taken into consideration the departures are never positive all over the world, or negative; in each case some regions are characterized by an excess of heat, whereas in other regions temperature is in deficiency. The areas of positive departures have been called thermo-pleions and those of negative departures anti-pleions. The anti-pleions do not necessarily compensate the thermo-pleions. The year 1900, for example, was a year of an excess of pleions and the year 1893 was a year of deficiency of pleions. The difference of the world's temperature, for such exceptional pleionian and anti-pleionian years, may reach  $0.5^{\circ}$  C. or perhaps even more.

Taking barometric measurements into consideration, one also finds that for each year some centers of abnormally high and abnormally low atmospheric pressure are conspicuous.† These baro-pleions and anti-baros displace themselves from year to year, and evidently influence atmospheric circulation very greatly.

These changes must have an effect on the distribution of storm frequency‡ and on rainfall. Of rainfall data, I have studied extensively the ombro-pleions observed in Europe during the years 1851–1905, but the results of these researches have not been published.

\* An address before Section IIb of the Second Pan-American Scientific Congress, on December 29th, 1915.

† Bull. Amer. Geogr. Soc., v. xlii, p. 270, 1910.

‡ Month. Weath. Rev., v. xliii, p. 379, 1915.

In order to investigate these phenomena more thoroughly, the monthly means of temperature, atmospheric pressure, rainfall, sunshine duration and thunderstorm frequency have been taken into consideration and the changes from one year to another have been studied by the method of overlapping means.

Among other results it was found that at many stations, particularly in equatorial regions, temperature rises or falls practically simultaneously and that the pleions disappear and reappear more or less periodically at intervals of 2 to 3 years.\* The records of the Harvard Observatory station at Arequipa, in Peru, have been taken as a standard of the occurring pleionian fluctuations,† and the results of the comparisons made induced me to search for the cause of this cycle of climatic variations.

After it was demonstrated that the cause of the formation of pleions could not be attributed to the presence or absence of volcanic dust-veils in the higher levels of the atmosphere,‡ it was but natural to search for their origin in the variations of the solar atmosphere.

It seems obvious that, if changes in the vertical circulation of the incandescent solar clouds exist, these changes must produce oscillations of the quantity of thermal energy radiated into space.

A few words of explanation are necessary.

Although it is difficult to imagine how the heat of the solar atmosphere originates, or where it originates, we must admit that the amount of heat is greater below the incandescent photospheric clouds than above,—simply because these clouds are a phenomenon of condensation, due to loss of heat, and because condensation could not take place if the temperature below the clouds was not higher than the temperature above. In consequence, we must admit that, just as in the case of terrestrial atmospheric conditions, the radiation into space, from below, must be a question of cloudiness. This radiation is not necessarily constant. If the vertical currents producing the ascending clouds are intensified, the loss of heat must be greater. For the sake of comparison, our terrestrial Cu-Ni clouds, with their panaches of false-cirri, may serve as an example.

I imagined that the solar-faculæ, which always accompany the formation of sunspots, might have an origin similar to the false-cirri, and this vague analogy led to the supposition that perhaps the faculæ would give some information concerning possible changes of the intensity of the output of solar energy.

\* *Annals N. Y. Acad. Sc.*, v. xxiv, p. 39, 1914.

† *Bull. Am. Geogr. Soc.*, v. xliv, p. 598, 1912.

‡ *Annals N. Y. Acad. Sc.*, v. xxvi, p. 149, 1915.



Faculæ are indeed merely a product of the solar atmospheric circulation. Faculæ occur often independently of sunspots, but more often they accompany the spots. Some connection exists also between the frequency of spots and the formation of faculæ. When sunspots are numerous, larger areas of the solar surface are occupied by faculæ. For the average characteristic outbursts of sunspots, the accompanying faculæ reach their maximal development about nine days after the spottedness has reached its maximum.\* The faculæ are evidently one of the phases of the phenomenon that produces the formation of spots.

Admitting that a sunspot is the center of violent descending currents in the solar atmosphere, we must admit that the vapors slide sidewise from the spot when they reach the lower levels and reascend, at a certain distance from the spot, more quietly and overheated. It is to these ascending currents that the formation of faculæ must be ascribed. Faculæ must, therefore, radiate into space a quantity of heat larger than the quantity of heat radiated by the spotted area. If so, the ratio of the surfaces occupied by faculæ and sunspots must equal or be proportional to the ratio of radiation.

If, therefore, the pleionian cycle of terrestrial temperature is to be ascribed to solar fluctuations, we may presume that the quotient of the areas of faculæ and sunspots is not constant, and we may suppose that the changes of this quotient vary in harmony with the pleionian cycle. And the fact is, that not only this ratio of faculæ and spots varies extensively, but also that these variations present some striking similarities with the Arequipa or standard type of thermo-pleionian fluctuations.

The figures I have utilized† are those of the Greenwich photo-heliographic measurements. In order to eliminate the shorter fluctuations, and to obtain numbers comparable to annual means of temperature, I have formed the totals of the areas of umbræ and faculæ for every consecutive solar 10 rotations. I have used the figures given for the rotations 275 to 805, or the results of the measurements made during the years 1875 to 1913. Then I divided the faculæ numbers by those for umbræ. The quotients thus obtained express numerically how many times the areas of faculæ exceeded those of umbræ. The curve representing these figures graphically, compared with the curve of sunspots, shows an unmistakable correlation with the 11-year period. The curve may indeed be characterized as follows :

\* Mem. Soc. Spettr. Ital., Ser. II, vol. iv, p. 181, 1915.

† Ibid., p. 185, 1915.

Well-pronounced minima preceding by approximately 12 rotations (or more or less 9 months) those of spots; less pronounced minima coinciding or preceding by a few rotations the maxima of sunspots; then, in each 11 years' cycle, another minimum between the minimum and maximum of the curve of sunspots and two minima between the maximum and the following minimum. And so, in the period of more or less 11 years' duration there are 5 maxima of the ratio of faculæ and umbræ; the first coincides with, or closely follows the minimum of spots, the second occurs between the minimum and the maximum and the three others occur between the maximum and the minimum of the sunspot curve.

It may be useful to mention that the range of these variations is well pronounced. The highest observed ratio of 10 consecutive rotations is 73·74, while the lowest figure is 2·42. But these are extreme values. The average ratio of the 15 observed crests is 26·93 and the mean of the corresponding depressions is 11·47, or less than one-half. Such are the facts.

To come back to hypothetical considerations, it may be asked how these fluctuations of the ratio of faculæ and sunspots can be explained?

Let us say that the depth to which our terrestrial storms extend is limited by the surface of the earth crust or the surface of the sea. Evidently the sun does not present similar conditions and *à priori* we may admit the possibility of variations in the depth to which the circulation of the solar atmosphere may extend. If so, the proportion of faculæ to spots must vary, and when the faculæ are more predominant, we may suppose that the ascending columns of vapors come from greater depths and that, in consequence, the radiation is increased. Some sort of tidal movements making the solar atmosphere more or less expanded would explain the possibility of changes of depth to which the vertical circulation extends.

Now, since the maxima of solar faculæ-umbræ ratios reoccur—just like the terrestrial thermo-pleions, ombro-, helio- and baro-pleions,—at intervals of 2 to 3 years, and since some striking time coincidences exist, I shall call these maxima of solar fluctuations, horne-pleions,—which simply means pleionian impulses.

I say expressly horne- and not arche-pleions, because this last name must be reserved for the solar, or planetary, or cosmical relations which cause the changes of the solar atmospheric vertical circulation, changes for which the horne-pleions are simply numerical expressions.

In the foregoing considerations I have spoken of solar clouds. This expression may displease some of the students of solar phenomena. But what difference does it make if condensation

of calcium for example can or cannot take place at the very high temperatures of the photosphere? For my considerations it is absolutely indifferent if the faculæ are formed of incandescent dust or of metallic vapors condensed into liquid drops or whether they are simply gaseous vapors.

Again, another objection may be raised against the conception of the circulation in and around the solar spots that I have adopted. But in this case also, theory has no importance since the fact is that umbræ radiate less heat than the average photospheric surface and that faculæ seem to radiate more heat.

Speaking of heat, it would also be preferable to avoid that expression entirely and use the words radiation, or energy, or radiant energy of the sun.

But all such objections have nothing in common with the fact of the existence of a horne-pleionian variation, a fact which is a result of the Greenwich measurements and of my calculations. And now, in order to establish a theory of the terrestrial pleionian fluctuations, more calculations are necessary.

The first effort to be made is to find out whether atmospheric temperature varies proportionally to the ratio of the faculæ and umbræ, or, if such a law cannot be established, because of the complexity of meteorological phenomena, it will be necessary to show at least some striking correlations between the variations of one and the other. Up to the present, a lack of time has prevented me from making more than one single attempt, which has been successful, and I wish to show now how the horne-pleionian maximum of the solar rotations 772-781 found its repercussion in the temperatures observed on our earth-surface during the years 1911 and 1912.

In order to have figures corresponding exactly to the same time-intervals as those of temperature, monthly means of the areas of faculæ and umbræ were calculated, for the years 1909 to 1913, and then the ratios of the overlapping yearly totals were formed.

These figures expressed graphically on a diagram show a well-pronounced crest of the horne-pleion corresponding to the mean of June 1911 to May 1912. But before this maximum is reached we notice two steps, one at the mean of April 1910 to March 1911 and the other corresponding to the mean of November 1910 to October 1911. In 1912 the ratios decrease till a minimum corresponding to the mean of March 1912 to February 1913 is reached, and from then on the ratios again increase and form the ascending branch of a new horne-pleion. To simplify comparisons, we may call 1911:2 the mean of February 1911 to January 1912; 1911:3 that of March 1911 to February 1912, and so forth. The figures for 1910:4,—1910:11,—1911:6 and 1912:3 are therefore conspicuous.

For the same years 1909-1913 I have prepared more than 150 curves of overlapping temperature means of stations from all parts of the world. This amount of already computed data is very respectable, but of course I am anxious to obtain more data, and I do not think that the difficulties one encounters in collecting the results of meteorological observations made in some countries or the shocking mistakes that may be found in the tabulations of official publications of some other countries, will prevent me from trying to make my research as thorough as possible.

If my reasoning is correct, it follows that at the time of the occurrence of the horn-pleionian maximum of 1911:6, or shortly afterwards, we should observe thermo-pleionian crests on the curves of overlapping means of the observed temperatures. Or, since it has been found that in no case studied so far, temperature was above the average all over the world, that, on the contrary, anti-pleions always compensate the pleions, more or less, it will be necessary to find at least a predominance of thermo-pleions synchronal with the solar maximum.

And so it seems to be.

Of the records studied so far I may say that an abnormal increase of temperature during the latter part of 1911 and 1912 is a striking feature of the curves of meteorological stations in Alaska, British Columbia, Vancouver Isl., Oregon, and, to a certain extent, California, then of Mexico, Panama, the West Indies and Bahamas, British and French Guiana, Matto Grosso, Parana, Peru,—the Färoö Isls., Holland, Northern Germany, Switzerland, Italy, Gibraltar,—Algeria, Morocco, the Canary Isls., the Sahara, Egypt, Senegambia, the French Congo, the Transvaal,—Aden, Quetta, India, Ceylon, Mauritius and Seychelles Isls., the Strait Settlements, Cochinchina, China, Japan, Eastern Siberia,—Australia, and the Touamotou Isl. in the Pacific.

The records of a certain number of stations show a retarded pleionian effect. I will cite those of Greenland, Iceland, Carolina, Florida, Cuba,—the Caucasus and Russia,—Southern Nigeria, Togo, German South Africa, Madagascar,—Palestine, Mesopotamia, some stations of India, Christmas Isl., the Philippines, and New Caledonia. Even in the Antarctic regions the records of Cape Evans station, under  $77^{\circ} 38' S.$  lat., show that during the months of May to September, or during the South polar winter, the mean temperature in 1912 was  $10^{\circ} F.$  higher than in 1911.

In striking contrast with these results most stations of the United States, as well as Wellington and Auckland in New Zealand, and some stations in Russia, show a well pronounced depression of temperature corresponding in time with the



occurrence of the horne-pleion and the greatest development of thermo-pleionian conditions in so many countries in different parts of the world.

The American anti-pleion is of particular interest, because of the pleions observed in the Northwestern states, Alaska, Canada and Greenland, as well as in the Southeastern states, the West Indies and Mexico. In North America temperature conditions were evidently in conformity with the horne-pleion, except in the greatest part of the central portion of the continent. Moreover, it was precisely at the time of occurrence of the horne-pleionian maximum, or soon afterwards, that the greatest lowering of temperature was observed in the Middle West from North Dakota down to Texas.

Evidently the supposition that these abnormally low temperatures were due to the veil of volcanic dust produced by the Katmai eruption of June 6th, 1912, is completely out of the question. If that had been the case, temperature would have decreased from that date on, whereas it was decreasing for more than a year before that date in order to reach the minimum at the time of the occurrence of the horne-pleionian maximum and accidentally at the time of the Katmai eruption. The conclusion to be drawn from these facts is that the American anti-pleion of 1911-1912, corresponding in time with practically universally observed pleionian conditions, must have been mechanically produced by abnormal pressure distribution and the resulting abnormal winds. In other words, it seems most probable to me that the anti-pleion observed in the United States was simply due to changes of atmospheric circulation due to the exceptionally well-developed pleionian conditions in the North as well as in the South of the States. The same must have been the case of the other anti-pleions in New Zealand and in Russia, and perhaps in some other countries. But precisely because these anti-pleions are to be considered as an effect of dynamical reaction against the predominant pleionian conditions, it is evident that they could not compensate the action of the horne-pleion.

The direct effect of fluctuations of solar activity upon atmospheric temperature can also be observed in some of the details of the horne-pleionian crest. The steps of the ascending branch, corresponding to the means 1910:4 and 1910:11, as well as the minimum of 1912:3, may easily be distinguished on many of the overlapping temperature curves. But even in more minute details some of the curves present such similarities with the solar curve, that a simple chance circumstance can hardly be presumed, and that forcibly, we must admit that the cause of these temperature fluctuations is really a question of ratio between solar faculæ and umbræ.

Hastings-on-Hudson, December, 1915.

ART. V.—*The Geodes of the Keokuk Beds*; by FRANCIS M. VAN TUYL.*Introduction.*

PROBABLY nowhere else in America do geodes attain such an exceptional development as in the Keokuk beds of the Central Mississippi Valley, and representative specimens of geodes from this region are now found in the mineral cabinets of many of the museums of the world. Apart from Professor Brush's preliminary examination and description of a few select specimens submitted to him in 1865 by A. H. Worthen, then director of the Geological Survey of Illinois, no study of these remarkable geodes has ever been made in spite of the fact that they bear a variety of metallic sulphides and promise to throw some light upon the origin of more important deposits of these minerals in sedimentary rocks showing no signs of igneous influence. The following brief report on their characteristics may therefore seem justified.

*Occurrence.*

The typical geode area is located in Southeastern Iowa and adjacent parts of Northeastern Missouri and Western Illinois. The most famous localities for geodes in this region are Keokuk and Lowell in Iowa; Wayland and St. Francisville in Missouri; and Warsaw and Niota in Illinois.

The age and stratigraphic relations of the geode-bearing beds are shown in the accompanying table:

System	Name of Formation	Thickness in feet
Pennsylvanian	Des Moines sandstone	0 - 50
	...disconformity.....	.....
Mississippian	Pella limestone	0 - 30
	...disconformity.....	.....
	St. Louis limestone	30 - 60
	...disconformity.....	.....
	Salem limestone	0 - 35
	...disconformity.....	.....
	Warsaw shale and limestone	40
	Keokuk	Geode bed
	Keokuk limestone	50
	Burlington limestone	75
	Kinderhook beds	150



The geodes attain their maximum development in the Geode bed but some layers of the Keokuk limestone are geodiferous locally.

The Geode bed consists in its typical development of an impure, siliceous, dolomitic limestone at the base, usually containing large and well-developed geodes, followed by an argillaceous shale with more numerous but less perfectly developed geodes. Each subdivision is about twenty feet in thickness.

The composition of the lower subdivision of the Geode bed where it contains large and well-formed geodes at Keokuk, Iowa, is as follows:

Insoluble matter (largely free silica).....	33.80%
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .....	2.80
CaCO <sub>3</sub> .....	39.99
MgCO <sub>3</sub> .....	12.50
Moisture and carbonaceous matter.....	7.70
Undetermined.....	3.21
	<hr/>
Total.....	100.00

In size the geodes range from about .2<sup>cm</sup> up to 75<sup>cms</sup> in diameter. But well-developed geodes of either extreme are rarely found. In general, the geodes of a given layer do not vary greatly in size at a given locality, but there may be considerable variation in this respect at different levels in the same exposure. Moreover, there may be marked changes in their dimensions at the same level at different localities. Often geodes of similar size are arranged roughly in bands parallel to the stratification. They usually lie with their longest diameter parallel to the bedding-planes, and at some localities they are closely associated with calcareous concretions of similar shape and size.

The abundance of the geodes in the geodiferous phase of the Keokuk formation is quite variable both laterally and vertically. At times they are so numerous in a given layer that their freedom of growth has been interfered with, and they are thus of very irregular shape. At other times, they may be so sparsely distributed through the rock that none may appear in an outcrop embracing several square yards. Again they may be absolutely wanting at some localities. The proportion of well-developed geodes in the beds varies greatly at different localities ranging from less than ten per cent at some places to more than ninety per cent at others.

As to the mineralogical relationship of the geodes to the containing rock, it is found that at any given locality each geodiferous layer as a rule bears geodes which are closely related among themselves, but which may be mineralogically

unlike those from other layers. But sometimes closely placed specimens in the same layer may bear very different minerals.

The contact relations of the geodes with the containing rock are not such as to indicate appreciable expansion during their formation. At no place is the inclosing rock found to be under any strain, nor is there any evidence of deformation of the layers at the contact. Rather the layers end abruptly where they abut into the geodes or exhibit a thinning where they pass immediately over or under them. The calcareous concretions which occur in the beds at some localities exhibit a similar relationship.

The extent of the geodes in the rock back from the outcrop is worthy of consideration. Bassler,\* in his discussion of the geodes of the Knobstone shales of Kentucky and Indiana, calls attention to the impervious nature of shale and inclines to the view that the geodes of that formation are confined to the surface or the immediate neighborhood of joint planes or rifts in the strata through which water had easy access. Such a relationship does not seem to hold for the geodes of the Keokuk beds.

#### *Mineralogy of the Geodes.*

Mineralogically, the geodes are almost invariably siliceous but a few calcareous geodes have been found. The siliceous types are characterized without exception by a thin outer shell of chalcedony and this is usually followed inwardly by crystalline quartz, but calcite may succeed the chalcedony. In some instances, however, the interior is lined with botryoidal chalcedony and no crystalline quartz nor calcite appears. At other times these minerals may all occur in a single geode, but usually only quartz and calcite or chalcedony and calcite are present. In addition the interior linings of the geodes are frequently studied with dolomite or ankerite, and one or more metallic sulphides are often represented. Moreover, some hollow siliceous geodes contain water, and in the vicinity of Niota, Illinois, many specimens are filled with black viscous bitumen. Finally others contain kaolin in the form of flocculent, white powder.

The primary minerals found in the geodes are: quartz, chalcedony, calcite, aragonite, dolomite, ankerite, magnetite, hematite, pyrite, millerite, chalcopryrite, sphalerite, kaolin, and bitumen. The alteration products represented are: limonite, smithsonite, malachite and gypsum.

With reference to the paragenesis, or order of deposition of the primary minerals, no constant order of succession holds for

\* Proc. U. S. Nat. Mus., vol. xxxv, p. 133 ff.

all geodes, and the same order of deposition may not obtain in two adjacent specimens.

For the purpose of illustrating the variations in the succession of the primary minerals in the geodes, the order of deposition in a number of typical specimens is given. The chalcedony of the shell is listed first in each case.

1. Chalcedony, quartz.
2. Chalcedony, quartz, chalcedony.
3. Chalcedony, quartz, chalcedony, quartz, chalcedony, pyrite, calcite with included pyrite.
4. Chalcedony, quartz, chalcedony, pyrite, calcite.
5. Chalcedony, quartz, chalcedony, pyrite, sphalerite.
6. Chalcedony, quartz, dolomite, calcite.
7. Chalcedony, quartz, magnetite, hematite
8. Chalcedony, calcite, calcite.
9. Chalcedony, calcite, millerite.
10. Chalcedony, quartz, ankerite, calcite, aragonite.
11. Chalcedony, quartz, calcite, bitumen.
12. Chalcedony, calcite with included chalcopyrite.
13. Chalcedony, quartz, pyrite, magnetite.
14. Chalcedony, chalcedony, sphalerite.

First, then, in the development of the siliceous geodes there was formed a thin chalcedonic shell. Upon this is superimposed quartz, either in the crystalline or chalcedonic condition, or calcite. It is a remarkable fact that when calcite and quartz appear in the same specimen the calcite is normally subsequent to the quartz, which rests directly on the siliceous shell. This relationship, first pointed out by Professor Brush,\* has been found to hold in every instance by the writer, but A. H. Worthen claims to have found a single specimen at Keokuk "in which large crystals of calcite are partly covered with smaller crystals of quartz."†

The alternation of crystalline quartz and chalcedony in some of the geodes is difficult to account for. If the layers were all formed during one period of growth as seems probable, changes in the condition and amount of silica supplied may have given rise to the phenomenon. Changes in temperature or pressure cannot be appealed to, because adjacent quartz geodes in the strata frequently do not show the same alternations.

The position of calcite in the geodes is subject to many variations. At times it succeeds the chalcedonic shell directly, but more often it rests upon an inner lining of quartz or chalcedony. In some of the geodes, calcite of two generations appears. The earlier calcite is often discolored brownish, and is frequently associated with or directly followed by sphalerite,

\* Geological Survey of Illinois, vol. i, p. 90, 1866.

† Idem, p. 90.

millericite, chalcopyrite or pyrite. Intervening between this calcite and that of younger age, crystals of dolomite or ankerite are also sometimes found.

#### *Origin of the Geodes.*

The origin of the geodes of the Keokuk beds has long been a disputed question, and, although there has been considerable speculation upon the subject, no one theory of their development has, as yet, been widely held.

The existence of perfectly developed geodes in strata often very impervious to underground circulation furnishes a problem which is exceedingly difficult to solve. The containing rock in the Keokuk region is often highly argillaceous and no structures which might serve as passage ways for mineralizing solutions are to be seen.

It was formerly believed that the geodes were formed by the deposition of mineral matter on the walls of cavities formed by the solution of sponges imbedded in the rocks. Thus, Dana states :\*

“They have been supposed to occupy the centers of sponges that were at some time hollowed out by siliceous solutions, like the hollowed corals of Florida, and then lined with crystals by deposition from the same or some other mineral solution.”

This theory has had many followers and S. J. Wallace has even gone so far as to coin a generic name for the sponge whose solution is supposed to have afforded the cavities in which the geodes were developed.† To this genus, called *Biopalla*, eight species were referred upon the basis of difference in size, shape, and surface markings of the geodes. The sponge hypothesis, however, is not now widely held. No evidence of sponges capable of giving rise to geodes have ever been found in the Keokuk beds. Moreover, the geodes vary widely in size and shape, a fact which argues strongly against any theory which presupposes such an origin. Many specimens are nodular and irregularities of the greatest variety characterize their exterior form. It may safely be said that no two of them assume exactly the same proportions.

Professor Shaler, in a paper entitled “Formation of Dikes and Veins,”‡ also devotes some space to the development of geodes and, although his studies were based upon geodes known to be of fossil origin which occur in the Knobstone shales of Kentucky, his conclusions may well be considered at this point :

\* Manual of Geology, 4th ed., pp. 97, 98, 1895.

† This Journal (3), vol. xv, p. 366 ff., 1878.

‡ Bull. Geol. Soc. Am., vol. x, p. 253 ff., 1899.



“Normal geodes are hollow spheroids and are generally found in shales. They clearly represent, in most cases, a segregation of silica, which has evidently taken place under conditions of no very great heat, brought about by deep burial beneath sediments or other sources of temperature. It is difficult in all cases to observe the circumstances of their origin, but in certain instructive instances this can be traced. It is there as follows: Where in a bed in which the conditions have permitted the formation of geodes the calyx of a crinoid occurs, the planes of junction of the several plates of which it is composed may become the seat of vein-building. As the process advances these plates are pushed apart and in course of time enwrapped by the silica until the original sphere may attain many times its original diameter and all trace of its origin lost to view, though it may be more or less clearly revealed by breaking the mass.

In the process of enlargement which the geodes undergo they evidently provide the space for their storage by compressing the rock in which they are formed. In the rare instances where I have been able to clearly observe them in their original position they were evidently cramped against the country rock, the layers of which they had condensed and more or less deformed. Although when found upon the talus slopes or the soil these spheres usually contain no water in their central cavities, these spaces are filled with the fluid while they are forming and so long as they are deeply buried. There can be no doubt that this water is under a considerable though variable pressure.

The conditions of formation of spheroidal veins or geodes clearly indicate that an apparently solid mass of crystalline structure may be in effect easily permeated by vein-building waters, and this when the temperature and pressure could not have been great. It is readily seen that the walls of these hollow spheres grow interstitially while at the same time the crystals projecting from the inner side of the shell grow toward the center. We, therefore, have to recognize the fact that the siliceous water penetrated through the dense wall. In many of these spherical veins we may note that the process of growth in the interior of the spheres have been from time to time interrupted and again resumed. These changes may be due to the variations in pressure to which the water in the cavities is necessarily subjected as the conditions of its passage through the geode-bearing zone are altered.”

More recently Bassler has written\* on the formation of the Knobstone geodes. He says:

“The majority of geodes in the Knobstone group may be traced directly or indirectly to a crinoidal origin for the simple reason that these strata are often crowded with the fragments of this class of organisms. Probably next in order as a geode maker is the common brachiopod *Athyris lamellosa*, but no class of

\* Proc. U. S. Nat. Mus., vol. xxxv, p. 133 ff., 1908.

fossil is exempt from replacement by silica when the proper conditions obtain."

Bassler is of the opinion that the Keokuk geodes may have the same mode of origin as those of the Knobstone. But he disagrees with Shaler as to the details of geode development. Thus:

"Returning to the suggestion in Dana's Manual of Geology that the Keokuk geodes are hollowed out sponges lined with crystals it seems more reasonable, in view of the absence of such sponges in that formation and the presence of numerous specimens indicating the origin described above, that the latter is nearer the truth. Prof. Shaler's idea that this class of geodes is formed when deeply buried is not in accord with the facts, nor does there appear to be any necessity for the water of formation to be under a considerable though variable pressure. Ordinary surface waters charged with silica seem to be sufficient."

This generalization in so far as it relates to the geodes of the Keokuk beds in the region studied, would seem to be too broad. Out of several thousand geodes examined from the Keokuk beds only one, which had plainly been formed by the enlargement of a specimen of the crinoid *Barycrinus*, showed evidence of this method of geodization.

The origin of the Keokuk geodes in the region studied is believed by the writer to be related to the calcareous concretions which originally must have been very abundant in the beds and which are still preserved at some localities. These nodules, being more soluble than the inclosing rocks, have been in large part removed, thus affording cavities in which the geodes could be formed. Where still preserved, the concretions have exactly the same relationship to the containing rock as the geodes and possess analogous shapes. They were obviously formed on the sea-bottom while the strata were being deposited, since lines of stratification do not pass through them and no evidence of expansion is encountered about their borders. The process of solution seems to have started in the interior and proceeded outwards. That this was the method of removal is indicated by the occurrence, in the beds, of some geodic nodules whose interiors were only partially hollowed out when deposition began. Carbonic acid and sulphuric acid, of which the latter must have been generated by the decomposition of the pyrite so common in the beds, were probably the most active solvents.

The white powder of kaolin found in some of the geodes is thought to represent, at least in part, a residual product resulting from the leaching of the original argillaceous content of the nodules. That kaolin can be so formed is clearly indicated



by the presence of this mineral so related to impurities in some of the nodules that its derivation cannot be questioned. The more common occurrence of kaolin in the geodes from the more argillaceous portion of the beds is significant in this connection. Moreover, the great majority of the geodes which contain kaolin are imperfectly developed and the calcite of such specimens invariably includes the white powder of this mineral. These facts strongly support the idea that the kaolin must be a residual product.

Concerning the time of formation of the geodes, little is definitely known. The removal of the calcareous nodules which, it is assumed, preceded the geodes, implies an interval of solvent action during which the Keokuk beds were above ground-water level. Such a condition must have obtained during the period of denudation which succeeded the deposition of the St. Louis limestone. Some solvent action must also have been inaugurated during the pre-Salem and post-Salem emergences but these were of limited duration. The growth of geodes, on the other hand, undoubtedly took place below ground-water level.

In the development of the geodes at least two periods of mineralization are involved. The first period of development was by far the most important. During this period of growth the quartz, chalcedony dolomite, and a considerable amount of the calcite together with almost all of the metallic sulphides were deposited. This period of mineralization possibly took place during the interval which just preceded the Pennsylvanian inundation. The region was certainly near base level at this time and the Keokuk beds must have been below ground-water level. The occurrence of geodes, supposedly derived from the Keokuk beds, in the basal Pennsylvanian conglomerate in Indiana, where similar conditions probably prevailed, supports this view.

Of the minerals of the second period of growth, transparent crystals of calcite and slender, untarnished flakes of pyrite are by far the most important. The minerals of this class are doubtless much younger than those of the former as suggested by the fact that in the same geode the pyrite associated with the newer calcite is often perfectly fresh while the earlier pyrite is badly decomposed.

The secondary minerals of the geodes such as limonite, gypsum, smithsonite, and malachite are for the most part of much more recent origin. They have resulted from the alteration of the primary sulphides as shown by their association with the partially decomposed members of this group.

The bitumen which occurs in some of the geodes must have been introduced sometime after their formation, since it has not interfered with the normal geode development.

The process of geodization evidently consisted of the inward growth of crystals upon the inside walls of cavities left by the solution of the imbedded concretions. The growth was necessarily accomplished by deposition from a solution which filled the interior completely. As this solution became depleted in its mineral content, more was introduced by some process of diffusion and a continuous deposition resulted. In some instances a very impervious wall was developed and growth must have been extremely slow. But in the majority of geodes numerous feeding channels in the walls afforded ready passage to the solutions after they penetrated the siliceous shells.

The mineralogical variation of geodes which may occur in close proximity to each other is difficult to account for. It must either be assumed that the process of geodization was a very local one and that each individual geode possessed only a small sphere of attraction, or that a peculiar localization of conditions favored in some instances the deposition of mineral matter more widely diffused through the mineralizing solutions.

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ART. VI.—*The Berea Formation of Ohio and Pennsylvania*; by WALTER A. VERWIEBE.

[Paper read before Section E, A. A. A. S., at its 68th meeting.]

ONE of the most important formations of Ohio geology, not only for economic reasons, but also for stratigraphic reasons, is undoubtedly the Berea sandstone. It has long been known as the source of some of the finest building stone as well as most of the abrasive stone in the United States. As a reservoir of oil and gas it has brought many millions to the commonwealth of Ohio and adjacent states. Its stratigraphic importance consists in the fact that it is the first prominent and persistent sandstone horizon above the Devonian limestones, and thus serves as an excellent and reliable datum plane. Furthermore evidence is accumulating that its irregular base and thickness are due to a disconformity with the subjacent Bedford; and this diastrophic break corroborated by strong evidence of a faunal break, point to the conclusion that the Berea is the basal formation of the Carboniferous system.

The following table of formations in Ohio and Pennsylvania will give the reader a perspective of its stratigraphic position. (The Roman numerals are the ones used in fig. 1.)

Ohio.	Pottsville	Pennsylvania.	
		----- (unconformity) -----	
Logan	IV	Shenango shale	} Burgoon (Butts)
&		-----	
Black Hand*	III	Shenango sandstone	
		-----	
Cuyahoga		Meadville	
	II	Sharpville	
Sunbury		Orangeville	
		-----	
Berea	I	Corry	} Oil Lake group (White)
		Cussewago	
		-----	
Bedford		Riceville	
&	VI	Venango	} Conewango (Butts)
Ohio		Chemung	

\* Hyde considers the Black Hand a local facies of the Cuyahoga. See his "Stratigraphy of the Waverly Formations of Central and Southern Ohio," *Jour. of Geol.*, vol. xxiii, p. 655 ff., 1915.

It can readily be understood that students of geology have devoted much time and thought to the proper stratigraphic relations of such an important member of the Ohio section. As early as 1838, C. Briggs, Jr., in the first report of the state geologist, described it as part of the 'Waverly Sandstone Series' and pointed out its value as a building stone. When after a lapse of thirty years the work of the State survey was again taken up, J. S. Newberry added a good deal of detailed information regarding the character and distribution of the Berea. To him also is due the credit for the name it bears.\*

Careful and valuable work on this formation was also done by Edward Orton. In volume VI of the Ohio geological survey publications, he added many details as to the character and distribution of the Berea. The most important contribution, however, was furnished by Charles S. Prosser in Bulletin 15 of the State survey reports. This work contains detailed sections showing the thickness and character of the formation from the Roeky River on the west well into Crawford Co., Pa., on the east, across the northern part of Ohio.

Summarizing briefly the results obtained by these investigators, the Berea formation of Ohio may be described as follows: A sandstone of prevailing buff color, where seen above drainage, having a rather persistent uniform texture which varies locally from a very fine grain to a medium-coarse grain. Locally also it may be replaced by shales which are generally arenaceous and bluish grey to buff in color. Toward the east these shales become more prominent, so that the formation takes on a tripartite character, the shales occupying the center. The upper part continues into Pennsylvania, where it is called the Corry sandstone (I. C. White) and the middle shales and lower sandstone are called the Cussewago shales and Cussewago sandstone. Whereas the Corry phase of the Berea retains its typical lithology practically across Ohio and well into Pennsylvania, the Cussewago sandstone phase begins to show a strong tendency to increasing coarseness when followed eastward, although nowhere in Ohio does it become a true conglomerate.

The correlation indicated above has called forth a good deal of discussion among geologists. The first to make an attempt at correlation was perhaps J. S. Newberry,† who seems to have regarded the Shenango sandstone of northwestern Pennsylvania as the equivalent of the Berea. Curiously enough he also states that it does not exist along Oil Creek as a prominent layer and on this basis deduces the derivation of the sediment for the formation from the northwest. Some confusion was

\* Geol. Surv. Ohio, vol. i, p. 186, 1873.

† Geol. Survey of Ohio, vol. ii, p. 90, 1874.

also created by M. C. Read in his report for Ashtabula and Trumbull counties.\* On the map accompanying this report the Berea is shown as splitting into two parts near the Pennsylvania line. Neither of these, however, represented the true Berea; the upper one being the Shenango sandstone and the lower the Sharpsville sandstone (Warren sandstone of Cushing). As a result of this, no doubt, White at first correlated the Sharpsville with the Berea.† Later White reached the conclusion: "It certainly looks as if . . . the Berea grit of Ohio and my Oil Lake group in Crawford and Erie counties occupied the same horizon."‡

About twelve years later, Edward Orton, in a summary of the geological formations of Ohio, says that "his (White's) Corry sandstone appears to be none other than the Berea grit."§ George H. Girty states (1905) that in his opinion "The Berea grit of Ohio is White's Cussewago sandstone, together with probably the Cussewago flags and Corry sandstone,"|| though four years earlier he was inclined to limit its equivalence to the Cussewago sandstone only.¶ Other investigators, including notably Stevenson\*\* and Cushing,†† regarded only the upper part of White's Oil Lake group (Corry) as the equivalent of the Berea in Pennsylvania.

Thus it develops that considerable difference of opinion existed in regard to the correlation of the Berea in Ohio and Pennsylvania; due, no doubt, to the fact that the conclusions were largely based on the literature, instead of precise and careful field-work. Consequently, the credit for solving this perplexing problem should go to Dr. Prosser, who first presented convincing evidence, based on numerous detailed sections. His conclusion on this point is stated as follows: "It is evident from the description of sections in this bulletin, extending from Cuyahoga Co., Ohio, into Crawford Co., Pa., that Dr. White was perfectly correct if he intended to correlate the Oil Lake group of Pennsylvania with the Berea formation of Ohio."‡‡

In Pennsylvania the Berea has been studied in Crawford and Erie counties by I. C. White,§§ and along the Allegheny River by Chas. Bntts.||||

\* Geol. Survey of Ohio, vol. i, pp. 483 and 505-508.

† Pa. 2d Geol. Survey, Q3, p. 124, 1881. See also Prosser, C. S., Devonian and Mississippian: Geol. Survey of Ohio, Bull. 15, p. 355 ff. for a discussion of this.

‡ Penn. 2d Geol. Survey, vol. Q4, p. 91, 1881.

§ Geol. Survey of Ohio, vol. vii, p. 33, 1894.

|| Proc. Wash. Acad. Sci., vol. vii, p. 6, 1905.

¶ Science, N. S., vol. xiii, p. 664, 1901.

\*\* Bull. Geol. Soc. Amer., vol. xiv, p. 41, 1903.

†† Proc. Amer. Ass. Adv. Sci., vol. xxxvi, p. 215, 1888.

‡‡ Geol. Survey of Ohio, Bull. 15, p. 394, 1912.

§§ Pa. 2d Geol. Survey, Q4, 1881.

|||| Rept. Topog. and Geol. Survey Comm. for 1906-08, p. 190.



The former described it under the heading of Oil Lake group, which consists in descending order of the Corry sandstone, Cussewago shales and Cussewago sandstone. Mr. Butts published a continuous section along the Allegheny River from the New York state line to Emlenton in the southern part of Venango Co., Pa. (See fig. 2.) In discussing the section he states: "The Berea sandstone lying 300 feet above the Salamanca can be identified by its characteristic fossils in every section down to the bend of the river 2 miles south of Tionesta, where it passes below the railroad grade. About 160 feet above the Berea and separated from it mainly by blue shale, is a rather thin-bedded, generally fine-grained, sandstone. This was traced with a good degree of certainty from two miles south of Tidioute to a point about one mile south of Hunter, from which point it is exposed at many places near railroad level and was traced continuously to Oleopolis. A similar and probably the same sandstone is exposed at Oil City at railroad level and dips below the railroad about one and one-half miles south of Oil City."\*

From the above it will be seen that the literature covered pretty thoroughly the correlation of the Berea in Ohio and Pennsylvania, as well as the extent of the formation in northeastern Ohio, Crawford and Erie counties in Pennsylvania, and apparently along the Allegheny River. There remained simply to fill in the gap between Crawford Co. and the Allegheny River, involving a survey of parts of Venango, Forest and Warren counties. (Compare fig. 2.) This part of the work was undertaken by the writer during the summer of 1915. After a careful study of the Berea in Ohio it was traced continuously from the boundary line of Ohio and Pennsylvania across Crawford Co. to the Allegheny River. Many sections were made along this line, the most important of which will be found in fig. 1, and in greater detail at the end of this discussion. As a result of this work the following conclusions were reached:

1. The Berea formation is represented in Pennsylvania by the Corry sandstone, and the Cussewago shale and sandstone of I. C. White.

2. The Corry sandstone increases in thickness when followed eastward from the state line, attaining a thickness of about 50 feet along the Allegheny River. (See fig. 1, section E and following sections.)

3. The Corry sandstone becomes gradually coarser toward the east, changing from a rather fine-grained, even-textured rock along the state line to a coarse-grained, pebbly sandrock (at least in its upper part) on the Allegheny River.

\* *Idem*, p. 192.



4. A limestone layer (Cussewago limestone) is practically always to be found immediately underlying the Corry, or separated from it by a few inches of shale. This varies in thickness from 8 inches to 1 foot 10 inches. (See sections E, F, and I.)

5. The Cussewago sandstone thins out and disappears from the section about longitude  $80^{\circ} 5' W.$ ; though it may be represented farther east by a part of the shales and sandstones underlying the Corry.

6. The Corry sandstone is represented along the Allegheny River by the sandstone indicated on Mr. Butts' diagram as lying about 160 feet above the sandstone labelled "Berea (Corry)." See the quotation above and compare the sections K, L, and M in fig. 1.)

7. The Berea is absent along the Allegheny River north of Tidioute. The sandstone, regarded by Butts as the Berea, north of this point, is probably the Venango first oil sand.

The evidence for the conclusions enumerated above is based on paleontology, lithologic character, and on stratigraphic position. It is a well-known fact that clean sandstones are not adapted to the preservation of life forms. It occasions no surprise therefore to find that fossils are very rare in the Berea formation. It is true that some have been reported by Orton, White, and others; however, for practical stratigraphic purposes the formation may be considered unfossiliferous. Still this very fact proves itself an important factor in the identification of the formation, inasmuch as the sandstones above and below, viz., the Shenango sandstone and the Venango first oil sands are not unfossiliferous. Hence the paleontologic evidence, though negative, is considered of importance.

The lithologic character is rather more valuable. For this purpose the Corry phase is most consistent. It is almost always a fine to medium-grained sandstone, of very uniform texture, and very compact. Also its color is a very persistent characteristic, being a bluish-grey in the unaltered rock, and almost invariably a buff in the weathered rock. The Cussewago shales, on the other hand, are very unreliable, inasmuch as they may be arenaceous or argillaceous, bluish-grey, drab, olive-grey or buff; and are frequently ferruginous and micaceous. In addition they may be largely replaced by flaggy sandstones of a similarly varying nature. The Cussewago sandstone phase when typically developed is unmistakable. It is a coarse, loosely-cemented, much discolored sandstone, breaking down readily into an incoherent mass. However, its extent is very limited, and it seems to be more or less lenticular, which is well illustrated by the sections in fig. 1. So far as the writer is aware it does not occur west of longitude  $81^{\circ}$  nor east of longitude  $80^{\circ} W.$

Stratigraphic position was considered most helpful in tracing the Berea. It is overlain in Ohio and to a certain extent in Pennsylvania by a black shale, which is, in addition, rather fossiliferous, containing numerous Lingulæ and Discinæ. This is the Sunbury shale of Ohio, and is equivalent to the lower part of the Orangeville shale in Pennsylvania. It gradually loses its black color when traced into Pennsylvania, but it can always be identified by its characteristic fauna. In addition to this the Meadville limestones are excellent horizon markers, being very persistent and of a peculiar lithologic character. Finally, the Shenango sandstone, if it can be found, is of great value in interpreting the section. It is a rather coarse, siliceous sandstone, weathering a deep brown by the alteration of iron, scattered abundantly through its mass in the form of concretions, secretions and veinlets; it is also quite uniform in thickness.

In this manner the upper part of the Berea or the Corry was traced, it is felt with certainty, as far as the Allegheny River. The determination of the base of the formation was not so easy. Where the Cussewago sandstone is present in typical development the succession and correlation are perfectly clear, but where it is missing it is somewhat difficult to draw the line marking the base. The Cussewago shales are very similar to the underlying Devonian shales; however, in this region buff sandstones occur in the former but are absent in the latter; also the Cussewago shales are quite barren, whereas the Devonian shales are not, and contain a *Spirifer disjunctus* fauna (Chemung) practically to the top. The section secured at Miller Farm is a typical one to illustrate this point. It will be seen that the Corry is underlain by 30 feet of buffish sandstone and bluish-grey shale and sandstone, which in turn rests upon a 6-inch layer of calcareous sandstone containing fossils. This layer is therefore chosen to mark the base of the Berea, partly because it is fossiliferous and partly because below it no prominent buff layers occur. It is more than likely that the Cussewago sandstone is represented in this section by a part of the 30 feet mentioned. In that case it would seem to be but a horizontal variation of the lower buff sandstones of the Berea, in Pennsylvania, exactly as it has proved to be in Ohio. A bit of evidence which may perhaps substantiate this view is the fact that the well drillers in this region call the Berea the "Forty-foot." A typical well drilled (section M in fig. 1) less than three miles east of Miller Farm, where section I was secured, illustrates in excellent fashion the character of the formations underlying the Berea. It appears from this record that the drillers would include a good share of the 30-foot interval in their "Forty-foot," which thus indicates the sandy

nature of the material and a difference from the material below when encountered by the drill.

It has been suggested that the sandstone in the section along Oil Creek is not the Corry but the Cussewago sandstone.\* However, the presence of the Cussewago limestone under it in typical development and the excellent exposures of the Orangeville shale immediately above it point to the conclusion that it is the Corry.

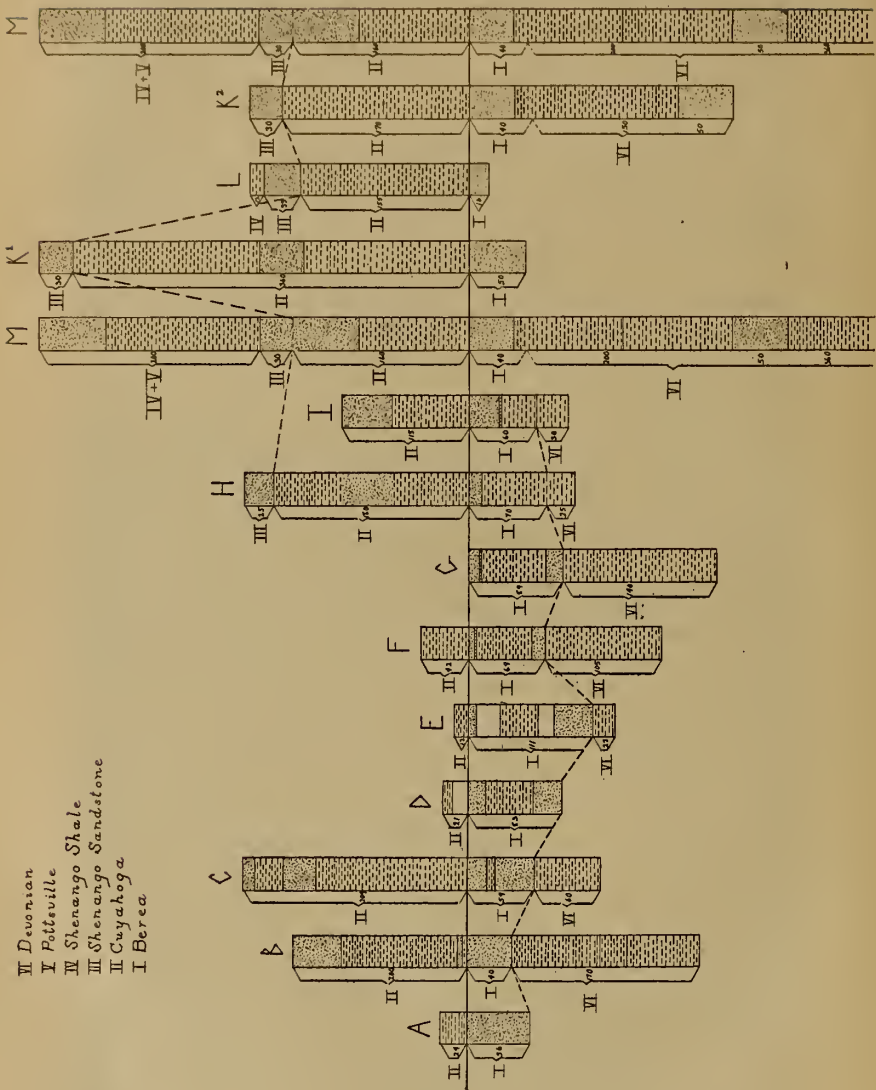
Farther to the east, as shown in the sections at President and Hunter, the Corry becomes still thicker and also rather coarser. The superjacent Orangeville also undergoes much the same change, becoming more arenaceous and containing more sandstone layers. At the base of the Corry, which may be traced for miles along the Allegheny from President northward, the Cussewago limestone occurs. It may be seen to good advantage at Baum (almost on the line between Forest and Venango counties) where it is two feet thick and lies about 20 feet above the railroad tracks.

Northward, along the Allegheny River, the Corry sandstone has been traced in excellent fashion by Butts; however, from a careful study of the stratigraphy of the region the writer is unable to accept his correlation with the Venango first oil sand. The evidence noted above to indicate that the formation is equivalent to Butts' middle Cuyahoga sandstone is further corroborated in a graphic manner in fig. 1. A section was taken from Butts' diagram at a point about midway between Tionesta and Hunter (section K in fig. 1). This is inserted between sections M (Miller Farm; 9 miles N.W.) and section L (Oil City: 12 miles S.W.), first using the nomenclature of Butts (section K<sup>1</sup>), and again between the same two sections, but considering his middle Cuyahoga sandstone as the Berea (section K<sup>2</sup>). The base of the Shenango sandstone is used as the datum plane. It will now be seen that the interval between the Shenango and the Corry is suddenly increased from 160 feet (section M) to 360 feet in a distance of less than 10 miles if the section K<sup>1</sup> is correct. However, if the section be interpreted as at K<sup>2</sup> the base of the Shenango sandstone will be seen to vary but slightly, and the interval between it and the Corry will be practically the same as in sections L and M.

A correct correlation of the Berea sandstone should have a far-reaching effect in clarifying the stratigraphy of the whole of western Pennsylvania, for it has been used as a key horizon not only in the extensive oil and gas fields, but also in the difficult northern area underlain mostly by Devonian shales. The oil and gas field extends roughly southwest from the district studied into West Virginia, Ohio and Kentucky. It has been

\* White, I. C., Pa. 2d Geol. Survey, vol. Q4, p. 93, 1881.

FIG. 1.





thoroughly studied and the productive formations described in many Federal and State publications. Of course it must be granted that many difficulties are encountered by the geologist in attempting to unravel the stratigraphy of rocks totally concealed. However, the many accurate and detailed well records now available enable a person, thoroughly familiar with the formations on the outcrop, to make rather satisfactory correlations.

Of the formations involved in this discussion the following in descending order are locally important as oil or gas horizons: Shenango sandstone, Berea (Corry), and the Venango 1st and 2d sands. Of these the first is generally identified with the "Big Injun" of well drillers. No doubt it frequently includes, besides the Shenango sandstone, also the Shenango shale as well as some of the overlying Pottsville (where the Mauch Chunk is absent) and some of the upper Meadville (as in section M). Beneath this, and with an interval varying from 150 feet in the northern part of the field to about 350 feet in the southwestern part, occurs the Berea sandstone. It carries oil and gas in some parts of the Pennsylvania field, but is rather unimportant in other parts. For this reason it does not always have a prominent place in the well records. However, the 1st Venango oil sand, which is widely known as the Hundred-foot sand in Armstrong, Butler and Beaver counties, or as the Gantz and Fifty-foot sands in Washington and Green counties, is a very important source of oil as well as gas; and this furnishes a very reliable datum plane when accurately determined. By using the latter in addition to the base of the "Big Injun," it is possible to trace the Berea sandstone with considerable definiteness, southwest, from its outcrop on the Allegheny into southern Pennsylvania, and also into Ohio and West Virginia.

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*Explanation of fig. 1.*—The sections in fig. 1 (opposite page) were chosen to illustrate the character and thickness of the Berea formation along an east and west line, from its type locally east to the Allegheny River. Their relative location is indicated on the accompanying map (fig. 2). Sections A, B, C, and D are taken from Prosser's report on the Devonian and Mississippian (Geol. Survey of Ohio, Bull. 15) and may be found in detail on pages 485, 125, 321, 433 respectively. Sections G and H were taken from White's report on Erie and Crawford counties (Pa. 2d Geol. Survey, vol. Q4, p. 164 and 182). Sections E, F, I, L and M were made by the author and the last three will be found in greater detail at the end of the paper. Section K is taken from Butts' work as explained in the above pages.

The top of the Berea (Corry) was used as the base line in plating the sections. The symbols used are the conventional ones. The legend in the upper left hand corner gives the equivalents of the Roman numerals used. For the correlation of these, see page 43. (The scale is 175 feet = 1 inch.)

A rather interesting feature brought out by this figure is the irregular thickness of the Berea, which may be construed as evidence of a disconformity at the base. Another fact well shown is the lenticular character of the Cussewago sandstone.



If this is done it will soon appear that there is a considerable difference in the correlation of the Berea on the one hand and the limits of the Pocono (which is nearly universally accepted as the basal member of the Mississippian in eastern Pennsylvania) as a result of this on the other. Years ago Carll\* established the equivalence of the 1st Venango oil sand and the Hundred-foot or Butler 2d sand. This correlation is still accepted by all who have worked on the problem. Therefore, in the stratigraphy of the quadrangles more recently described and published since Butts' article appeared, his conclusions regarding

FIG. 2.

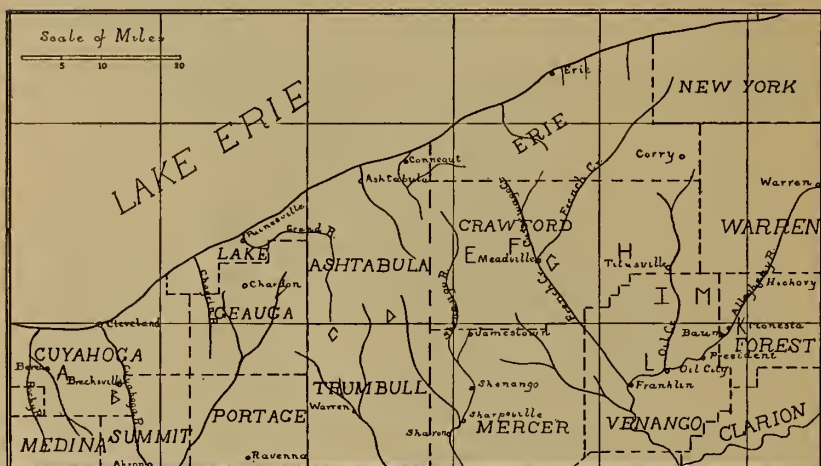


FIG. 2. Map of northeastern Ohio and northwestern Pennsylvania, showing the location of sections plotted in fig. 1.

the correlation of the Venango 1st oil sand with the Berea have largely been accepted. For example, in the Foxburg and Clarion quadrangles, which lie immediately south of the region discussed in the preceding pages, the Hundred-foot sand is considered equivalent to the Berea sandstone,† whereas the sandstone, which in the estimation of the author is the true Berea, is called the Sharpsville sandstone.‡

In the Sewiekey quadrangle Munn makes the same correlation, and places the base of the Pocono at the base of the Hundred-foot, thus giving it a thickness of approximately 800

\* Pa. 2d Geol. Survey, vol. i<sup>3</sup>, pp. 178 and 272.

† U. S. Geol. Survey, Folio No. 178, p. 4, 1911.

‡ U. S. Geol. Survey, Bull. No. 454, p. 18, 1911.

feet.\* The same is true of the Claysville,† and the Burgetts-town and Carnegie quadrangles.‡ In the Claysville quadrangle the author (M. J. Munn) evidently realizes that there is a discrepancy somewhere and tries to explain it in the following words: "The writer does not question the correlation by Butts for northern Pennsylvania, but, in tracing the Hundred-foot sand southward to Washington county from Clarion, there is evidence that the sand is broken by persistent shale beds into a group of sandstones embracing the Fifty-foot, the Gantz and the Murrysville or Butler Thirty-foot sands, and that the last sand is equivalent to the thin oil-bearing sand in southeastern Ohio, which is widely known as the Berea sand."§ Thus he clearly defines the position of the "Berea sand" of Ohio, but not the Berea sandstone of northern Ohio, for he includes in it all the rocks down to the base of the Venango 1st oil sand; and concludes: "If this is true, the Berea sand of southern Ohio is equivalent to only the upper portion of the Berea of northern Ohio." On the basis of the above correlation the Pocono is made to include all rocks between the top of the Burgoon and the base of the Hundred-foot.

This tendency to fix the lower limit of the Pocono at the base of the Berea or its equivalent is no doubt an excellent one. Although the evidence of a disconformity is perhaps not as striking or apparent as in the case of the other systems, yet it certainly occurs locally. Furthermore, the paleontologic evidence is sufficiently convincing to indicate a probable break. At any rate it is granted by some of our most eminent authorities|| that the base of the Berea certainly forms the most convenient place to draw the line between the Devonian and the Mississippian systems. Assuming that this is the case, it will immediately be patent to one familiar with the stratigraphy of western Pennsylvania that a great deal of obscurity and uncertainty in correlation will be eliminated. It is admitted by all who have worked in the oil fields, that the top of the Devonian is difficult to fix. It seems, therefore, that the proper correlation of the Berea sandstone should serve also to fix the base of the Pocono or the Mississippian. This, of course, is not a new idea. It simply became apparent that no sharp dividing line between the systems could be established by tracing the formations from the east, hence they were traced from the west.

\* U. S. Geol. Survey, Folio No. 176, 1911.

† *Ibid.*, No. 180, 1912.

‡ *Ibid.*, No. 177: also Bull. No. 456, 1911.

§ U. S. Geol. Survey, Bull. No. 456, p. 16, 1911. Also Folio No. 180.

|| Prosser, C. S., *The Huron and Cleveland Shales of Northern Ohio*, Jour. of Geol., vol. xxi, p. 362, 1913. Prosser, C. S., *Geol. Survey of Ohio*, Bull. 15, pp. 106 and 512. Girty, G. H., *Proc. Wash. Acad. Sci.*, vol. vii, p. 6, 1905. Also see "Geologic Age of the Bedford Shale of Ohio," *Ann. of N. Y. Acad. Sci.*, vol. xxii, p. 295, ff.

Thus L. H. Woolsey\* defines the Pocono as extending from the top of the Burgoon to the base of the Berea, which is correctly identified in this bulletin, and lies about 350 feet below the top of the Burgoon. No doubt other investigators had this in mind when they included the rocks down to the base of the Hundred-foot in the Pocono, since they considered it the equivalent of the Berea.

Summarizing briefly the above, we would then have the following correlation of oil sands in western Pennsylvania:

Pocono	{	Burgoon	= =	Big Injun (as explained above)
		Berea	= =	{ Murrysville or Butler Gas or 1st sand Butler Thirty-foot
Venango 1st	= =			{ Hundred-foot or Gantz & Fifty-foot Butler 2d.

The literature dealing with the stratigraphy to the north is not so voluminous. Perhaps the most important recent work published is that of the Warren quadrangle† and the section along the Allegheny River.‡ The latter was discussed somewhat in the preceding pages. It may be added that it appears probable that the interval between the 1st Venango oil sand (called "Berea") and the Shenango sandstone was named Cuyahoga simply because the Berea was used as the key formation and hence with a total disregard of other evidence. This interval corresponds to the Riceville in its lower part (from the top of the Venango oil sand (Berea) to the base of the Berea (middle Cuyahoga sandstone), and would be left without a name in Butts's classification. That part of the section between Butts's middle Cuyahoga sandstone and the base of the Shenango sandstone will then become the Cuyahoga formation and represent it *in toto*. The section along the Allegheny River, reconstructed in this manner, will then appear as in section K<sup>2</sup> of fig. 1.

The Berea can be traced with ease along the Allegheny from Venango county north toward Warren; and it will be found to disappear from the section about a mile south of Tidioute, being absent north of this point because of erosion. This fact will necessitate a revision of the geologic section in the Warren quadrangle. The succession in the quadrangle is given as follows:§

\* Econ. Geol. Beaver Quad., U. S. G. S., Bull. No. 286, 1906.

† Butts, Chas., U. S. Geol. Survey, Folio No. 172, 1910.

‡ Butts, Chas., Pre-Pennsylvanian Stratigraphy, Rept. Topog. & Geol. Surv. Comm. of Pennsylvania, 1906-1908.

§ U. S. Geol. Survey, Folio No. 172, p. 23, fig. 5, 1910.

Pennsylvanian	Pottsville	35 ft.—200 ft.
----- (unconformity)		
Mississippian	{ Cuyahoga	5 ft.—200 ft.
	{ Berea sandstone	2 ft.
Devon-Carbonif.	{ Knapp	80 ft.
	{ Conewango	510 ft.—560 ft.
Devonian	Chemung	1120 ft.

Regarding the Berea the author says: "It has not been seen exposed in place in the quadrangle, but loose pieces of sandstone crowded with its fossils have been found at many points in such position as to indicate that their parent bed immediately overlies the upper member of the Knapp formation, whether that be conglomerate or sandstone."\* In tracing the Knapp formation to the south, it strikes one immediately as not improbable that the Knapp is the northern representative of the Venango 1st oil sand. This equivalence is admirably substantiated by the fossils contained in them, both being characterized by a *Syringothyris* fauna.† It follows from this that we should look for the Berea sandstone at a higher stratigraphic level. This interval is approximately 150 feet at a point a few miles south of Tidioute. North of this point the shales underlying the Berea come up from beneath and present an eroded surface to the Pottsville. This erosion plane cuts across successively older portions of the Riceville shales as it is followed northward. The Berea is therefore absent in the Warren quadrangle. This conclusion automatically eliminates the Cuyahoga formation from the Warren section. The rocks which have been included under that heading are stratigraphically the equivalent of the Riceville of I. C. White; and, as far as we may be guided by our present knowledge, there seems no good reason to change this name.

Doubtless much work still needs to be done, before the exact equivalence of the Mississippian and Devonian rocks of the Appalachian and Ohio basins can be precisely established; however, it is hoped that the facts set forth in the above discussion may prove of some value in attaining this result.

The sections I, L, and M are considered most important of those platted in fig. 1 and are appended in greater detail for those readers who desire more precise data.

\* *Idem*, p. 36.

† N. Y. S. Mus. Bull. No. 69, p. 995, 1902.



## Section L, Oil City, Pa.

No.		Thick- ness Feet	Total Feet
4.	<i>Shenango shale.</i> Bluish-gray, argillaceous shale, interbedded with thin shaly sandstones. ....	12	216
3.	<i>Shenango sandstone.</i> Massive layers up to 5 feet in thickness, fairly coarse grain, whitish quartz sand weathering buff. About 9 feet from the bottom occur abundant micaceous layers. Many layers throughout the mass also show bands of white, opaque quartz pebbles. Iron is present in considerable proportion. It occurs largely as botryoidal filling of hematite in geodes, some is concretionary and some appears in thin bands .....	33	204
2.	<i>Meadville, Sharpsville and Orangeville.</i> This interval is largely covered, except the lower 50 feet or thereabouts, which consists of rather sandy shales, drab in color and micaceous, interbedded with thin sandstones .....	155	171
1.	<i>Corry.</i> Sandstone, medium-grained, compact, hard, buff in color; the layers are massive, some reaching a thickness of 3 feet; however they show great irregularity in this respect, the same layer often showing marked difference when traced horizontally. Also a more or less conchoidal mode of breaking up is much in evidence. Some shale occurs toward the top .....	16	16

This section was secured at Oil City, Pa. It begins in the old quarry of the Oil Well Supply Co. and follows down the adjacent ravine to the Pennsylvania Railroad tracks. Some excellent exposures of the Corry occur along the tracks and it may be easily traced to the north in the numerous rock cuts of the railroad.

## Section I, Miller Farm, Pa.

No.		Thick- ness Feet	Total Feet
10.	<i>Meadville and Sharpsville.</i> Sandstone, flaggy, bluish-gray and brownish due to weathering; some sandy shale is interbedded .....	45	205½
9.	<i>Orangeville.</i> Shale, soft, argillaceous, drab and blue; thin sandy layers occur at intervals; the surface of the whole is much stained by incrustations of iron compounds. Fossils may be found at various horizons and in considerable abundance .....	50	160½



No.		Thick- ness Feet	Total Feet
8.	Sandstones, mostly thin and bluish ; some of the lower layers are buff in color and rather hard ; interbedded are typical Orangeville shales ..	20	110 $\frac{1}{4}$
7.	<i>Corry</i> . Sandstone, mostly massive buff layers up to 2 $\frac{1}{2}$ feet in thickness, though some are thin and flaggy .....	28	90 $\frac{1}{4}$
6.	<i>Cussewago limestone</i> . Very typical, a blue siliceous lime-rock which also carries much iron. On weathering the carbonate of lime is dissolved, leaving behind a crust of deeply stained ferruginous sand. This separates in more or less conchoidal layers, thus leaving the unaltered rock with rounded edges .....	1 $\frac{3}{4}$	62 $\frac{1}{4}$
5.	<i>Cussewago shale</i> (and <i>Cussewago sandstone</i> ?). Sandstone and shale ; the sandstones resemble the Corry very much; some layers are quite massive (1 foot thick), buff in color and hard ; the other sandstones and the shales are bluish-gray .....	14	60 $\frac{1}{2}$
4.	Shale, bluish, some sandy layers .....	10	46 $\frac{1}{2}$
3.	Sandstone ; in this interval there are again some hard buff layers interbedded with blue sandstones and shales .....	6	36 $\frac{1}{2}$
2.	<i>Riceville</i> . Sandstone, rather limey with fossils	0 $\frac{1}{2}$	30 $\frac{1}{2}$
1.	Shale and thin sandstones to the level of the R.R. tracks ; bluish-gray and mostly arenaceous .....	30	30

Less than a quarter of a mile south of the station called Miller Farm on the Oil City branch of the Pennsylvania R.R. is a rather high rock cut. Here the above section was made. It is an excellent one to show the character of the Berea formation along Oil Creek. The Corry sandstone can be followed without much difficulty along the R.R. tracks from here south to Oil City, at which point it can be conveniently connected up with the Allegheny River section.

*Section M, Shamberg Well Record.*

No.	Driller's terms	Geological equivalent	Thick- ness Feet	Total Feet
15.	Bluff rock	Connoquenessing	60	992
14.	Slate and shale	Pottsville & Shenango shale	140	932
13.	Mountain sand (90 ft.)	Shenango sandstone	30	792
12.		Meadville upper sandstone	60	
11.	Slate and shale	Meadville, Sharpsv. & Orangeville	100	702

No.	Driller's terms	Geological equivalent	Thick- ness Feet	Total Feet
10.	Blue Monday (40-foot)	Corry sandstone	40	602
9.	Shale blue	Riceville	100	562
8.	Shale red		100	462
7.	First sand	Top of Venango oil group	50	362
6.	Slate and shale		100	312
5.	Salt sand	Venango 2d oil sand	30	212
4.	Slate and shells		90	182
3.	Gray sand	Stray 3d	12	92
2.	Slate and shells		40	80
1.	Third sand	Base of Venango group	40	40

This record was furnished by Mr. L. N. Stevenson, a well driller residing in Petroleum Center, Pa. It was drilled by him in July, 1915, for Mr. Robert Foggans on the Clarke farm near Shamberg (about 3 miles east of Miller Farm), Venango Co., Pa. The correlations indicated in the second column are based on a careful study of the rocks on the outcrop in the surrounding region. It was on this basis that the "mountain sand" was subdivided as indicated in Nos. 12 and 13.

*Section at President, Pa.*

No.		Thick- ness Feet	Total Feet
4.	<i>Berea sandstone.</i> Coarse sandstone, consisting of rather loosely-cemented white quartz grains which are, however, much discolored, giving the rock a spotty appearance. Pebbles averaging the size of a pea occur, more or less abundantly scattered through the mass -----	12	46
3.	Sandstone, more compact, fine-grained, massive, buff -----	15	34
2.	Shale, drab in color, arenaceous -----	1	19
1.	Sandstone, same as in No. 3 -----	18	18

This section was added because it shows the character of the Berea along the Allegheny River and some distance east of Oil City. It was found just south of the R.R. station of President on the north side of the river. The striking thing about it is the lithologic character of the upper part. Zones No. 1 and 3 are very typical. Unfortunately, the base is covered, so that the presence of the Cussewago limestone could not be determined. There is little doubt that it exists here, however, since it may be found typically developed a few miles north of this locality, where the dip of the rocks brings the base above the level of the R.R. tracks. Another section was made at Hunter (about 3 miles north). Here the upper coarse part of the Berea was found to have a thickness of 22 feet.

ART. VII.—*On Hydrozincite*; by W. E. FORD and W. A. BRADLEY.

HYDROZINCITE is a basic carbonate of zinc that has long been recognized as a distinct mineral species. It is a secondary mineral that commonly occurs as an incrustation on other zinc minerals. Its structure is usually massive to fibrous or often earthy to compact. Frequently it occurs as botryoidal crusts with a concentric formation. As far as is known, it has never been observed in crystals until its recent discovery at Good Springs, Lincoln County, Nevada. Since no determinations of the crystal or optical characters of the mineral have ever been made and since the varying results of the recorded chemical analyses have left its composition in doubt, it was thought worth while to undertake an investigation of this crystalline material.

The specimens from Good Springs are composed chiefly of a massive, earthy material of a light brown color which is apparently mostly smithsonite. Occasional small crystalline masses of calamine and calcite are to be observed. The hydrozincite is found lining the cracks and irregular openings in the massive material. It occurs as delicate incrustations of very small crystals grouped in radiating masses. Commonly underneath the crystals is found a thin layer of the same mineral in a mass of interlacing crystalline needles.

When the crystals are examined under the microscope it is seen that they are exceedingly thin with a tabular, lath-shaped form. They are usually sharply pointed at their free ends, but the terminations were too irregular to permit of the measurement of any angles. They show a pearly luster with frequently an iridescent play of color on their surfaces. With crossed nicols they always showed an extinction parallel to their elongation. This was found to be the direction of the slower ray while the direction across the crystals was that of the faster ray. With convergent light they proved to be biaxial in character and to have apparently their tabular development parallel to the optical axial plane. Obscure dark interference curves were shown which moved rapidly from the field when the sections were turned from the position of extinction. Their character was such as would be expected with sections that were parallel to an axial plane. These curves moved out of the field toward the vibration direction *a*. If the orientation of the sections was as suggested, this direction is, therefore, that of the acute bisectrix and the mineral is optically negative. The two extreme indices of refraction were deter-

mined by the immersion of the crystals in high refracting oils. The results were,  $a = 1.650$  and  $\gamma = 1.740$ ; both,  $+0.005$ . In spite of the high birefringence, which equals about .09, the interference colors shown are usually gray or yellow of the first order, although occasionally second order colors were seen. This is due of course to the extreme thinness of the crystal plates.

In studying the optical nature of minerals similar to hydrozincite it was found that there is an almost complete agreement between the characters given above with those of aurichalcite as determined by Buttgenbach.\* His observations, which have been confirmed by the present authors, were made on the fine material found recently at the Kelly mine, Magdalena, New Mexico. He describes this material as follows: "The aurichalcite is in small elongated plates with a pearly luster. Between crossed nicols the very thin plates give various colors which do not go higher than the yellow of the second order. The extinction is parallel to the elongation of the crystals with this direction coinciding with the  $c$  vibration direction. The plates, examined in converging light, are parallel to the plane of the optical axes. By the movement, however, of the dark curves which leave the center of the field when, after having formed the black cross, the table of the microscope is turned a little, it is easily determined that the direction of the acute bisectrix coincides with the direction  $a$ . This proves that the sign of the mineral is negative. The indices of refraction of aurichalcite are given by Lacroix† as approximately between 1.67 and 1.755."

From the above it is readily seen that as far as the crystal and optical characters are concerned the two minerals are practically identical. The refractive indices of aurichalcite are a little higher, but some variation here would have been expected because of the presence of copper in that mineral.

It would naturally be expected, therefore, that the formula of hydrozincite should be analogous to that of aurichalcite. The latter mineral was analyzed by Penfield‡ on excellent material and with results that left no doubt but that its formula should be  $2(\text{Zn,Cu})\text{CO}_3 \cdot 3(\text{Zn,Cu})(\text{OH})_2$ . Hydrozincite, therefore, if the agreement between the physical properties as given above is significant, should have the same formula, but without the presence, of copper, or  $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ . If that is true the theoretical composition of hydrozincite would be that given below.

\* Ann. Soc. geol. de Belgique, xl, B119, 1913.

† Min. de la France, iii, 739.

‡ This Journal (3), xli, 106, 1891.



Theory for  $2\text{ZnCO}_3, 3\text{Zn}(\text{OH})_2$ .

ZnO .....	74.14
CO <sub>2</sub> .....	16.03
H <sub>2</sub> O .....	9.83
	<hr/>
	100.00

About thirty analyses of hydrozincite have been published which have shown considerable variation, due largely doubtless to the unsatisfactory character of the material examined. Twenty-seven analyses were collected, more than half of which are given in the fifth and sixth editions of Dana's System of Mineralogy. These included the new analyses given below together with all published analyses except such as showed considerable amounts of unusual constituents. No other attempt was made to consider them critically. The average of these analyses is as follows:

Average of 27 hydrozincite analyses.

ZnO .....	73.47
CO <sub>2</sub> .....	15.19
H <sub>2</sub> O .....	11.24
	<hr/>
	99.95

This result does not agree very closely with our assumed composition, but considering all facts is probably close enough to lend support to that formula. In the great majority of cases the material analyzed was amorphous in its structure. Further, one of the constituents was unquestionably commonly determined by the method of difference. It will be noted that the average percentage of the most important and probably most accurately determined oxide, ZnO, is only about 0.70 per cent too low.

It was felt that new analyses of the mineral, particularly upon the crystallized material, would be of importance. Unfortunately the amount of material available was very limited, which necessitated making the analyses on small amounts, and the use of analytical methods which were not the most desirable. Two different analyses were made on the mineral from Good Springs, one on carefully selected material consisting only of crystal fragments and the other on the crystalline material that lay beneath the coating of crystals and which it was felt might not be quite as pure. No evidence was found, however, to show that there was any impurity present in the latter material and as a larger amount of it was available for analysis it is thought probable that its analysis is more nearly correct than that of the crystals. In order to experiment with



the analytical methods used, a third analysis was made on massive material in the Brush Mineral Collection from Malfidano, Sardinia.

The analytical method adopted was extremely simple. The water was determined directly by heating the mineral in a closed glass tube, collecting the water in the upper part of the tube and weighing it, making the proper corrections for the presence of  $\text{CO}_2$  in the tube. The zinc oxide was determined by igniting the mineral, driving off all the water and carbon dioxide and weighing the residue. This method was tested by dissolving the residue and redetermining the amount of the zinc oxide after the precipitation as sulphide from a formic acid solution. The two results agreed. Careful tests were made for the presence of other possible elements but with negative results. The carbon dioxide had to be determined by difference. The analyses by Bradley follow:

Good Springs, Nevada.

	Crystals	Crystalline material	Theory for $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$	Sardinia
ZnO .....	75.58	74.67*	74.14	73.72
$\text{CO}_2$ .....	[15.78]	[16.41]	16.03	[15.47]
$\text{H}_2\text{O}$ .....	8.64	8.92	9.83	10.81
	100.00	100.00	100.00	100.00

\* Average of two closely agreeing determinations.

These results do not agree as closely with the assumed formula as could be desired. It is to be regretted that more material was not available in order that the portions used could have been larger and direct determinations made of all constituents. Still, no other formula could be proposed which would agree more closely with the analytical results except one that would be very complicated and improbable. Considering, therefore, the unfavorable conditions of the analysis and the very strong argument provided by the close physical resemblance between aurichalcite and hydrozincite, it is felt that the formula given must be correct.

The conclusion of the investigation, therefore, is that aurichalcite and hydrozincite are practically one species, only distinguished from each other by the introduction into the former of some copper oxide which replaces an equivalent amount of zinc oxide.

Mineralogical Laboratory of the Sheffield  
Scientific School of Yale University,  
New Haven, Conn., March 22, 1916.

## ART. VIII.—Rotation of Interference Fringes in Case of Non-reversed and of Reversed Spectra; by C. BARUS.\*

1. *Non-reversed spectra.*—When the slit is oblique, it effectively reproduces the wide slit, locally, and therefore does not destroy the colored fringes. At every elevation in the field the slit is necessarily linear though not vertical. In figure 1 let the heavy lines,  $H$ , denote the colored fringes for a fine vertical slit and white light, showing nearly the same distance apart, throughout. Let the light lines,  $L$ , denote the fringes for a wide vertical slit and homogeneous light,  $\lambda$ . These fringes are due to the successively increased or decreased obliquity of the rays, in the horizontal plane. Now let  $acb$  be the image of the oblique slit in homogeneous light. It is thus merely an oblique strip, cut from the area of light lines or striations, as it were, and consists of an alternation of black and bright dot-like vertical elements, in correspondence with the original striated field. We may suppose  $ab$  to have rotated around  $c$ , so that the vertical through  $c$  is its position on the colored field (white light and fine vertical slit).

A color,  $\lambda'$  (near the one  $\lambda$ ), corresponding to the field of the lines,  $L$ , in case of a wide slit and homogeneous light,  $\lambda'$ , will supply nearly the same grid, so far as the distance apart of fringes is concerned. But the grid is displaced laterally, in consequence of the different angle of diffraction,  $\theta$ . This is shown by the dotted lines  $D$ , in figure 1, the effect being as if the slit had been displaced laterally. If the wide slit for homogeneous light  $\lambda'$  is now narrowed and inclined as before, an alternation of bright and dark elements will appear in the image of the slit,  $ed$ , corresponding to  $\lambda'$ . If we suppose that for white light and the fine vertical slit, the position of the fringe ( $\lambda'$ ) was at  $c'$ , we may again regard  $c'$  as an axis of rotation. To find the fringes such as  $ff$ , it is then only necessary to connect corresponding black elements on  $ab$  and  $ed$ . Their inclination is thus opposite to  $ab$  and  $ed$ , or they have rotated in a direction opposite to that of the slit. If, for, instance, the slit image  $ab$  or  $ed$  is gradually moved back to the vertical, the points  $g$  and  $h$  will move with great rapidity and in both directions toward infinity and the fringes  $ff$  and  $f'f'$  become vertical lines through  $c$  and  $c'$ , respectively.

\* Work done on a grant from the Carnegie Institution of Washington, D. C. See earlier papers in this Journal, xl, pp. 486-498, 1915; xli, pp. 414-434, 1916. The phenomena of §1 are most easily produced with two transmitting gratings, parallel and having their ruled faces towards each other. Science, xlii, p. 841, 1915.

It is interesting to inquire into the frequency of fringes,  $n$ , when the angle of diffraction,  $\theta$ , is changed. From the original equation  $e = n\lambda/(1 - \cos \theta)$ , since  $d\lambda/d\theta = D \cos \theta$ , the rate of change

$$\frac{dn}{d\theta} = \frac{e}{D} \frac{1}{1 + \cos \theta} = \frac{e}{D + \sqrt{D^2 - \lambda^2}},$$

where  $e$  is the distance apart of the rulings and  $D$  the grating space. Since  $\cos \theta$  varies but slowly with  $\theta$  and is additionally

FIG. 1.

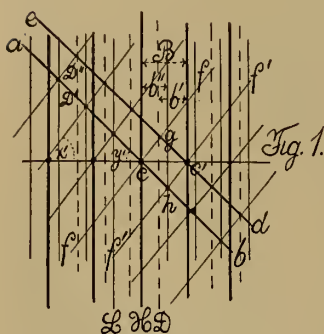
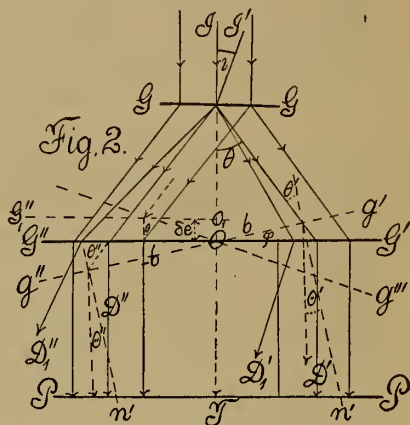


FIG. 2.



augmented by 1,  $dn/d\theta$  is nearly constant and about equal to  $e/2D$ .

The fringes and slit images are thus given by the two sides of the parallelogram  $cgc'h$ , for the two colors  $\lambda$  and  $\lambda'$ . The diagonal  $cc'$  represents  $d\theta$ ; the diagonal  $gh$  has no signification. On the other hand the normal distance apart  $D'$  and  $D''$  of  $ff'$  and  $f''f'''$  and  $ab$  and  $ed$  are both important.

The equations useful elsewhere\* have very little immediate value here, because the experimental variables, figure 1, are  $B$ , the distance between two consecutive colored fringes, and  $b''$  and  $b'$ , the corresponding distance between the fringes in case of homogeneous light in each case  $\lambda, \lambda'$  and the angle  $\gamma'$ , which indicates the inclination of the slit. Thus  $Bb'b''$  are given by computation and  $\gamma'$  is specified at pleasure. Ob-

\* This Journal, xli, p. 428, 1916.

viously, if parallelograms are to be obtained in figure 1,  $b' = b''$ , appreciably. This is the case in experiment. Hence if we evaluate the height in the triangle  $cgc'$  for each angle, it follows that

$$\sin x' = \frac{\tan y'}{\sqrt{(B/b' - 1) + \tan^2 y'}}$$

If  $B = b'$ ,  $x = 90^\circ$  for all values of  $y'$ ; i. e., the fringes remain vertical. If  $B$  is equal to  $2b'$ ,  $x' = y'$ , the fringes and slit are symmetrically equiangular with the longitudinal axis of the spectrum. This is nearly the case in figure 1 and frequently occurs in experiment. If  $b'$  differs from  $b''$ , the fringes would not be straight. This also occurs, particularly when the thickness  $e$  of the air film is very small.

2. *Treatment of reversed spectra.*—To obtain an insight into the cause of the interferometer fringes as obtained with reversed spectra and two gratings, it is convenient to represent both gratings, figure 2,  $GG$  and  $G''G'$  as transmitting, and suppose both diffracted beams,  $ID'$  and  $ID''$ , subsequently combined in view of the principal plane,  $PP$ , of an objective or a lens. It is clear that this simplified device can apply only for homogeneous light. In the case of white light, the opaque mirrors,  $M$  and  $N$ , of the interferometer (l. c.) return a divergent colored beam or spectrum, so that only for a single color can the second incidence be the same as the first. Again, if the constants of the two gratings are different, it is the function of these mirrors to change the incidence at the second grating, correspondingly, so that for homogeneous light the rays issue in parallel. Finally, no reference to the lateral displacements,  $OG''$  and  $OG'$ , of rays need be made because (as shown in the next paragraph) this is eliminated by the theory of diffraction.

The motion of the opaque mirrors  $M$  and  $N$  (above), on a micrometer merely shortens the air path  $GG'$  or  $GG''$  in its own direction and consequently the same fringe reappears for a displacement of half a wave length, as in all interferometers.

The case of a single grating, moreover, is given if the planes of the grating  $GG$  and  $G'G''$  and their lines are rigorously parallel, the planes  $OG'$  and  $G''O$  being coplanar. To represent the interferences of the two independent gratings and with homogeneous light for the case of oblique incidence, it is necessary to suppose the grating  $G'G''$  cut in two halves at  $O$ , parallel to the rulings, and to displace the parts  $OG'$  or  $OG''$  separately, normally to themselves as at  $O, G_1''$ . The figure

shows that for normal incidence,  $i = 0$ , the displacement per fringe  $\delta e$  would be

$$\delta e = \frac{\lambda}{1 - \cos \theta},$$

or the fringes are similar to the coarse set described elsewhere.\*

If the rays impinge at an angle  $i$ , figure 2, they will be parallel after the two diffractions are completed; for it is obvious that the corresponding angles of incidence and diffraction are merely exchanged at the two gratings. Hence the homogeneous rays  $I'$ , impinging at an angle  $i$ , leave the grating at  $D_1'$  and  $D_1''$  in parallel, at an angle of diffraction  $i$ , and the rays unite into a bright image of the slit. If however  $OG'$  be displaced a distance,  $e$ , to  $O_1G_1''$ , parallel to itself, as in figure 2, the paths intercepted are

$$\frac{e}{\cos i} \quad \text{and} \quad \frac{e}{\cos i} \cos(\theta - i)$$

and the path difference per fringe therefore

$$\delta e = \frac{\lambda \cos i}{1 - \cos(\theta - i)},$$

which reduces to the preceding equation if  $i = 0$ . Hence a series of interference fringes of the color  $\lambda$  must appear in the principal focus of the telescope or lens on either side of  $i = 0$ . The theory of diffraction again annuls the apparent path difference between  $GG$  and  $G'G''$ .

As to the number of fringes,  $n$ , between any two angles of incidence  $i$  and  $i'$ , it appears that  $n$  vanishes with  $e$ , or the fringes become infinitely large.

If the grating  $G'$  is rotated over an angle  $\phi$ , fig. 2, and  $e = b\phi$ , where  $b$  is half the virtual distance apart at the grating  $G'$  of the rays impinging upon it, the rotation per fringe is

$$\delta\phi = \frac{\lambda}{b} \frac{\cos i}{1 - \cos(\theta - i)}.$$

Again,  $n$  (above) passes through zero as  $\phi$  or  $b$  decreases from positive to negative values. Variable  $b$  implies a wedge effect superposed on the interferences.

It is this passage of  $n$  through zero that is accompanied by the rotation of the fringes, as observed.

In case of two independent gratings  $GG$  and  $G'G''$  ( $G'G''$  to be treated as consisting of two identical halves  $OG'$  and  $G''O$ ), nearly in parallel, fringes may be modified by rotating  $G'G''$  around the three cardinal axes passing through the point of symmetry  $O$ . The rotations of  $G'G''$  around an axis  $O$  normal

\* Phys. Review, vii, pp. 79-86, 1916.



to the diagram is equivalent to the *fore and aft* motion of  $G'G''$  when mirrors are used.\* The rotation around  $OT$  in the diagram and normal to the face of the grating, requires adjustment at the mirrors around a horizontal axis, to bring the spectra again into coincidence. This is equivalent to rotation around  $G''OG'$ . Both produce enlargement and rotation of fringes as already explained.

Let the grating  $G'G''$  be rotated over an angle  $\phi$  into the position  $g'g''$ . Then it may be shown that only so long as  $\phi$  is very small are the rays appreciably parallel on emerging; but this is usually the case, as  $\phi = 0$  is aimed at, and fringes are thus seen in the principal focus.

The next question at issue is the rotation of fringes with fore and aft motion, or rotation around  $O$  normal to the diagram. When  $e$ , the virtual distance apart, is zero, since  $n \propto e/\lambda$ , the fringes are infinitely large horizontally. The collimator, however, furnishes a pencil of rays which are parallel in a horizontal plane, only. They are not collimated or parallel in the vertical plane (parallel to the length of the slit). Hence when the fringes are reduced to a single one of infinite size horizontally, this is not the case vertically, i. e. from top to bottom of the spectrum the path difference still regularly varies. The adjustment around an axis through  $O$ ,  $G'OG''$ , normal to the rulings, is still outstanding.

Finally, the rotation around an axis parallel to  $IT$  in figure 2 is to be considered. This has already been given in terms of colored fringes (white light), but it occurs here for homogeneous light, in which case the above explanation is not applicable. Seen in the principal focal plane with telescope and wide slit, the *non-reversed* spectra require careful adjustment of longitudinal and transverse axes; otherwise they vanish. Nothing will rotate them.

Figure 2 shows that if  $G'G''$  is rotated about  $IT$ , the effect is merely to destroy the fringes, since the coincidence of the longitudinal axes of the spectra is here destroyed. No effect is produced so far as path difference is concerned. To restore the fringes therefore, either of the opaque mirrors,  $M$  or  $N$  of the apparatus, must be rotated on a horizontal axis, until the two spectra are again longitudinally superposed. It is this motion that modifies the path difference of rays in a vertical plane. In other words, when the fringes corresponding to any virtual distance apart,  $e = b\phi$  of the two halves of the grating  $G'G''$ , have been installed, the rays *as a whole* may still be rotated at pleasure, around a horizontal axis. In this way a change in the number of fringes intersected by a vertical line through the spectrum, is produced. The number of inter-

\* This Journal, xli, p. 419, 1916. See fig. 12.

sections will depend on the obliquity of the rays (axes of vertical pencils), and will be a minimum when the center of the field of view corresponds to an axis of rays, normal to the grating  $G'G''$ . In other words, the vertical maximum occurs under conditions of complete symmetry of rays in the vertical plane. If therefore  $e$ , or the virtual distance apart of the half gratings,  $G''O$  and  $OG'$ , is also zero, the field will show the same illumination throughout.

Therefore, to completely represent the behavior of fringes, it will be sufficient and necessary to consider that either grating,  $G'G''$  for instance, is capable of rotation, not only around a vertical axis through  $O$ , but also through a horizontal axis through  $O$  parallel to the grating. The last case has been directly tested. But a rotation around these two axes is equivalent to a rotation around a single oblique axis and the fringes will therefore in general be arranged obliquely and parallel to the oblique axis.

Thus if  $\phi_v$  and  $\phi_h$  is the angle of rotation of the grating (always to be small) around a vertical and a horizontal axis respectively, and if  $x'$  is the angle of the interference fringes with the horizontal edge or axis of the spectrum,

$$\tan x' = \frac{\phi_v}{\phi_h}$$

so that if  $\phi_v = 0$ ,  $x' = 0$ ; if  $\phi_h = 0$ ,  $x' = 90^\circ$ . In other words, for a rotation of grating around a vertical axis (parallel to slit) the fringes of maximum size will be horizontal, because the adjustment around the horizontal axis remains outstanding and the residual fringes (large or small) are therefore parallel to it. For a rotation of grating around a horizontal axis, the fringes of maximum size will be vertical, for the vertical adjustment is left incomplete. When both adjustments are made a single fringe fills the whole infinite field, and this result follows automatically if but a single grating is used to produce the fringes, as in the original method (l. c.).

3. *Case of Reflecting Gratings. Homogeneous Light.*—The results exhibited in figure 2 for transmitting gratings are shown in figures 3 and 4 for the combination of one transmitting grating  $G$  and one reflecting grating  $G'$ , the adjustment used in the preceding paper (l. c.) and for which the path lengths of rays were computed without allowances. (Cf. figures 10, 11, §8). The path differences obtained were inadmissible. It is now necessary to completely modify the demonstration.

In figure 3 the rays are shown for the case of symmetry of all parts, gratings at  $G$  and  $G'$  vertical and parallel, opaque mirrors at  $M_1$  and  $N_1$ , telescope or lens at  $T$ . The incident ray  $I$  at normal incidence is diffracted and reflected into

$Y, X, T,$  and  $Y', X', T,$  respectively; the incident ray  $I$  at an angle of incidence  $di$ , into  $Y_1, X_1,$  etc., and  $Y'_1, X'_1,$  etc., respectively; both at a mean angle of diffraction  $d\theta$  (nearly) to the right, corresponding to  $di$ .

The angles of diffraction ( $di = 0$ ) are  $\theta_1,$  and  $\theta_2,$  the double angles of reflection therefore  $\delta = \theta_2 - \theta_1,$  on both sides, the

FIG. 3.

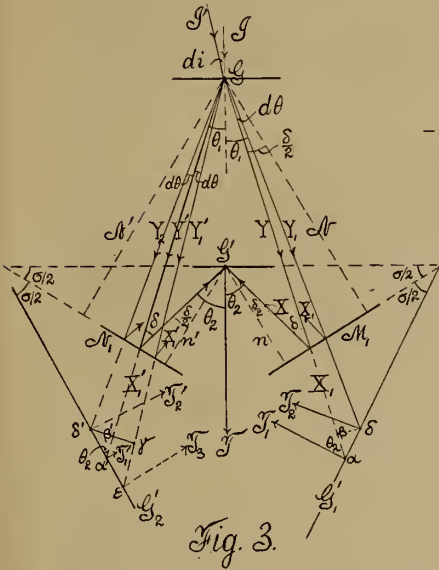
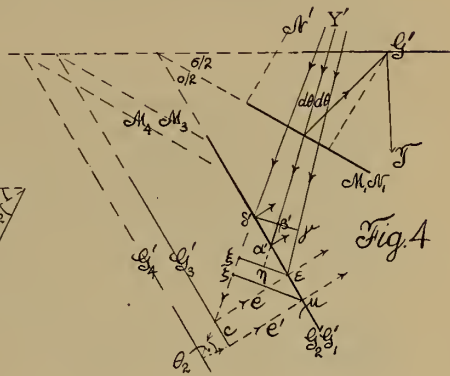


FIG. 4.



double angles of the grating  $G'$  with the mirrors  $M_1$  and  $N_1$  symmetrically,  $\sigma = \theta_1 + \theta_2.$

The normal from the point of incidence at  $G,$  and at  $G', N$  and  $n,$  makes angles  $\delta/2$  with  $Y$  and  $X,$  respectively, on both sides.

The method of treatment will consist in reflecting  $G'$  in  $M_1$  and  $N_1,$  producing the planes  $G'_1$  and  $G'_2$  (virtual images), and then rotating  $M_1$  and  $G'_1$   $180^\circ$  around  $IT$  (axis of symmetry) into coincidence with  $N_1$  and  $G'_2$  (interferences). Thus the rays prolonged into  $a$  and  $\beta$  coincide with the rays prolonged into  $a'$  and  $\delta'$  and the (virtual) diffracted rays  $T_1, T_2,$  become  $T'_1$  and  $T'_2.$  The ray on the left prolonged into  $\epsilon,$  is diffracted into  $T_3.$  Then the interferences will all be given by discussing the left half of this diagram, which is amplified in figure 4.

Since the distance  $GG',$  figure 3, is very large, the rays are nearly parallel, and hence the arc  $\delta\gamma$  with its center at  $G,$

is practically a plane wavefront, perpendicular to the rays in  $\delta'$ ,  $\beta'$ ,  $\gamma$ , and the diffracted rays  $T_1'$ ,  $T_2'$ ,  $T_3'$ , are also practically parallel. Hence in case of symmetry and coincidence of  $M_1, N_1$ , the points  $\delta'$ ,  $\beta'\gamma$ ,  $\delta', a'\epsilon$ , are in the same phase (diffraction). In other words, there is no path difference between  $Y + X$  and  $Y' + X'$ , whether the angle of incidence is zero or not ( $Y_1 + X_1$  and  $Y_1' + X_1'$ ). The whole field in the telescope must therefore show the same illumination (homogeneous light, wide slit) between the maximum brightness and complete darkness. Interference fringes can only occur when the opaque mirror  $M_1$  is displaced parallel to itself, out of the symmetrical position. If  $M_1$  and  $N_1$  are symmetrical, as in figure 3, the displacement of  $G'$ , fore and aft, parallel to itself, is without influence.

This reduces the whole discussion to the normal displacements of the system  $G', M_1, N_1$ , given in figure 4. Let the mirror  $M_1$  be displaced over a normal distance,  $e_m$ , to the position  $M_2, N_1$  remaining in place. Then the image of  $G'$  will be at  $G_3'$ , at a perpendicular distance  $e$  from its original position  $G_1'$ . The path difference so introduced, since  $\delta'$ ,  $\beta'$ ,  $\gamma$ , then  $\delta'$ ,  $a'$ ,  $\epsilon'$ , finally  $\epsilon'$ ,  $\eta$ ,  $\xi$ , are in the same phase, is

$$2e_m \cos \delta/2$$

$\delta$  being the double angle of reflection, and the displacement per fringe will be

$$\delta e = \frac{\lambda}{2 \cos \delta/2}$$

which is very nearly equal to  $\lambda/2$ , as in most interferometers, remembering that  $e$  and  $\delta e$  refer to the displacement of the virtual image of the grating  $G'$  and  $e_m$  to  $M_1$ . Two interfering rays will be coincident.

If the mirror  $M_1$  is further displaced normally to  $M_2$ , the image of  $G'$  will be at  $G_4'$  (the total displacement being  $e'$ ), and the rays in  $\epsilon$  and  $\mu$  (at a distance  $e$  apart on the grating  $G_1'$ ) will correspond with the path differences

$$2e_m' \cos \delta/2$$

while per fringe  $\delta e = \delta e'$ .

In the next place,  $e$  and  $\delta e$  may be reduced to the corresponding displacements  $e_m$  and  $\delta e_m$  of the mirror  $M_1$ . From figure 3

$$e_m = e \frac{\sin \sigma/2}{\sin \sigma} = \frac{1}{2} e \sec \sigma/2.$$

If  $G'$  is displaced parallel to itself,  $\delta e$  will not be modified, since each virtual image  $G_1'$ ,  $G_3'$  moves in parallel in the same

direction, by the same amount. If then the grating  $G_1'$  is rotated around an axis at  $G'$ , perpendicular to the diagram, fig. 3, over a small angle,  $\phi$ , the result (apart from the superposed rotational effect) is equivalent to a displacement of the mirrors  $M_1$  and  $N_1$  in opposite directions, producing a virtual distance apart  $e$  and the corresponding interference fringes. In other words, the rotational effects may be explained here in the same way, as in the preceding paragraph.

The angle  $2d\theta$  within which the interference rays lie, per fringe, is subtended by  $\delta e$  and is very small, scarcely  $\frac{1}{10000}$  of the  $D_1D_2$  distance of sodium light. Hence all pencils consist of practically parallel rays.

Another result is the angular size of fringes: i. e., if  $e_m$  and  $\lambda$  are given

$$-\frac{d\theta_2}{dn} = \frac{\lambda}{e \sin \delta/2}$$

Thus they become infinitely large when  $e$  passes through zero. The angular size is independent of the distance between the gratings. It ought, therefore, to be easy to obtain large interference fringes, which is not the case. The reason lies in this, that the two opaque mirrors are not quite symmetrical, so that in fig. 3, on rotation of  $M_1$   $180^\circ$  on  $GG'$ , the trace of  $M_1$  crosses  $N_1$  at an angle (wedge effect). If  $d\theta/dn = 3.7 \times 10^{-4}$ , the distance apart of the sodium lines, and  $D_2 = 173 \times 10^{-6}$  cm.,  $e = 1.8$  cm., i. e., path lengths on the two sides would differ by about 2 centimeters.

4. *Nonsymmetrical positions. Fore and aft motion.*—It remains to account for the marked effect produced on displacing the grating  $G'$ , in a direction nearly normal to itself. If the displacement is symmetrical, or even if the grating and mirrors are reciprocally non-symmetrical, the former at an angle  $\phi$  to the transverse line of symmetry  $gg'$ , figure 5, no effect results from the displacement of  $G'$ . The virtual images  $G_m$  and  $G_n$  are parallel and the different rays therefore also parallel.

If, however, this compensation does not occur, if the grating  $G'$ , the mirrors  $N_1$  and  $M_1$  make angles  $\phi$ ,  $\sigma/2$ ,  $\tau/2$ , respectively, with the transverse line of symmetry  $gg'$ , the fore and aft motion of  $G'$  is more effective as  $\alpha - \phi$  ( $\alpha$  angle between the mirrors) is greater. The diffracted rays are then no longer parallel, but make angles of incidence at the second grating,  $\theta_2'$  for the  $N_1$  side and  $\theta_2$  for the  $M_1$  side, and of diffraction  $i$  and  $i'$ , respectively, as shown in figure at  $T_n$  and  $T_m$ . The following relations between the angles are apparent

$$\sigma = \theta_1' + \theta_2' - \phi \qquad \tau = \theta_1 + \theta_2 + \phi$$



If at the first grating  $\theta_1 = \theta'_1$ ,

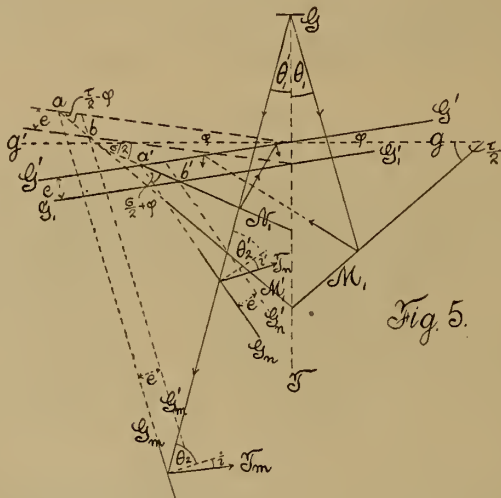
$$2a = \tau - \sigma = \theta_2 - \theta'_2 + 2\phi.$$

The images are at an angle  $\beta$ , where

$$\beta = 2(a - \phi) = \theta_2 - \theta'_2.$$

If  $G'G'$  is displaced to  $G''G''$  over a normal distance  $e$  or  $e/\cos \phi$  along the line of symmetry  $GT$ , the virtual images

FIG. 5.



$G_{m_2}$  and  $G_n$  will be displaced to  $G'_{m_2}$  and  $G'_n$  over the same normal distance  $e$ . This is obvious, since the quadrilaterals  $ab$  and  $a'b'$  are rhombuses by the law of reflection, and have the perpendicular distance  $e$  between the (equal) sides all identical.

If  $D_2$  is the grating space of  $G'$ ,

$$\begin{aligned} \sin \theta_2 + \sin i &= \lambda/D_2 \\ \sin \theta'_2 + \sin i' &= \lambda/D_2 \end{aligned} \tag{1}$$

or if  $i$  and  $i'$  are very nearly equal and both small, as in the experiment,

$$\cos \theta_2 d\theta = -\cos i di. \tag{2}$$

Again in case of a displacement  $e$  of  $G'$ , the paths are shortened at  $G_m$  by

$$\frac{e}{\cos \theta_2}$$

at  $G_n$  by (3)

$$\frac{e}{\cos\theta_2'}$$

resulting in the path difference  $\Delta P$ , the difference between these expressions.

Since  $\theta_2$  and  $\theta_2'$  are nearly the same,  $\Delta P$  may be simplified. One may notice in passing that in equation (1) and (3) the negative sign of  $di/d\theta$  and the positive sign in  $\cos(\theta + i)$  belong together.

Differentiating the functions (3) with respect to  $\theta$ , putting  $d\theta = \theta_2 - \theta_2' = 2(a - \phi)$ , and reducing the displacement  $\delta e$  per fringe, apart from sign, is

$$\delta e = \frac{\lambda \cos^2\theta}{2(a - \phi) \sin\theta} \quad (4)$$

Thus if

$$\lambda = 6 \times 10^{-5} \text{ cm.}, \quad a - \phi = 1^\circ = .0175, \quad \theta = 20^\circ \\ \delta e = .0044 \text{ cm.}$$

The effectiveness of the fore and aft motion, according to this equation, is evidence of a considerable angle of non-symmetry,  $a - \phi$ . This is not improbable, as my apparatus was an improvised construction, lacking mechanical refinement. Further the wedge effect due to  $a$  would be superimposed on the interferences and hence these could not be increased in size above a certain maximum. This is also quite in accord with observation.

If  $a = \phi$ ,  $\beta = 0$ ,  $\theta_2 = \theta_2'$ ; i. e., the virtual images  $G_m$  and  $G_n$  and the diffracted rays are parallel and  $\delta e = \infty$ . In other words, the fore and aft motion has no effect. If  $a = 0$ ,  $\beta = 2\phi$ ; or if  $\phi = 0$ ,  $\beta = 2a$ . In either cases  $\delta e$  is finite, and fore and aft motion is effective. If the mirrors and grating were rotated in counter direction so that  $\phi$  is negative,  $\delta e$  will depend on  $a + \phi$ , and the fore and aft effect be correspondingly marked. In general, moreover, the interference will not appear in the principal focus, but as a rule sufficiently near it for adjustment.

If  $\delta e_g$  is the actual displacement of the grating  $G'$  in the line of symmetry,  $\delta e_g = \delta e / \cos\phi$ , so that the angle  $\phi$  enters equation (4) again, but only to a small extent.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *The Qualitative Separation of Tin, Arsenic and Antimony.*—J. M. WELCH and H. C. P. WEBER have observed that the method of Noyes and Bray which consists in treating the three higher sulphides with concentrated hydrochloric acid on the steam bath, thus leaving the sulphide of arsenic undissolved, then diluting the liquid with about four volumes of water and precipitating sulphide of antimony in hot solution with hydrogen sulphide, and finally precipitating sulphide of tin after further dilution, does not give satisfactory results in many cases in the hands of inexperienced operators on account of failure to adhere to the exact conditions. They observed that when antimonious and stannic sulphides happen to precipitate together they frequently show a brown color which is not intermediate between the usual colors of the two sulphides, but much darker. The authors consider this dark precipitate as a characteristic test for both tin and antimony, and they prefer to allow the hydrochloric acid solution to cool while hydrogen sulphide is being led in, so as to obtain this test if possible. To finish the analysis they dissolve the sulphides by evaporating or using an oxidizing agent, then add oxalic acid (F. W. Clarke's method), precipitate antimony with hydrogen sulphide, boil the filtrate with granulated lead and test for tin with mercuric chloride.—*Jour. Amer. Chem. Soc.*, xxxviii, 1011.

H. L. W.

2. *A New Method for Estimating Ammonia.*—For determining ammonia in dilute waste liquors, G. E. FOXWELL takes 5<sup>cc</sup> of the liquid, makes it up to 300<sup>cc</sup> with water, puts 5<sup>cc</sup> of the diluted solution into a test-tube, and then adds 1<sup>cc</sup> of 4 per cent phenol solution and 1<sup>cc</sup> of a dilute sodium hypochlorite solution and heats by placing the test-tube in boiling water for at least 1½ minutes. A blue color is developed which is compared with a series of 13 test-tubes containing from 0.1 to 3<sup>cc</sup> of a solution of ammonium chloride containing 0.063 g. of the salt in 1000<sup>cc</sup>, all of which are diluted to 5<sup>cc</sup> and treated in exactly the same way as the other liquid. Free acid vitiates the test, while CaO has no influence. The method is not recommended for larger amounts of ammonia, and it is not as accurate as the distillation method for the smaller amounts. It serves well, however, for control purposes, as a test can be made in 3 or 4 minutes. As a qualitative test the method gives a distinct coloration with less than 0.0001 mg. of NH<sub>3</sub>.—*Gas World*, liv, No. 1654.

H. L. W.

3. *Analytical Chemistry*; by F. P. TREADWELL, translated and revised by W. T. HALL. Volume I, *Qualitative Analysis*. 8vo, pp. 538. New York, 1916 (John Wiley & Sons, Inc.).—This is the fourth edition in English, which is based upon the eighth German edition. The translator has not strictly followed the

German text, but has made many changes and additions, particularly in laying greater stress upon the theoretical side of the subject in connection with the applications of the principles of mass action, the ionization theory, and the theory of oxidation and reduction. The first part of the book comprising 76 pages is devoted to general principles and presents in an excellent manner the important theories bearing upon the subject. It is to be hoped that the student is not expected to learn this part thoroughly before beginning the study of qualitative analysis, for without a basis of many facts much of the theory would be very difficult to understand. The second part of over 200 pages deals with the metals, while the remaining parts deal with the acid constituents, systematic analyses, and the reactions of some of the rare elements. The descriptive parts are very comprehensive and equations of reactions are liberally supplied. Many equations are given in the ionic form, but this feature is not carried far enough to be particularly objectionable. The analyses are given in tabular form, but each of the tables is accompanied by a full description of the procedure, to which convenient reference is made by numbers in the tables. It is a very excellent text-book, containing a vast number of facts, and giving very satisfactory methods of qualitative analysis. Its use in this country has been very extensive, and the new and improved edition will undoubtedly add to its popularity.

H. L. W.

4. *A System of Physical Chemistry*; by WILLIAM C. McC. LEWIS. 12mo, 2 vols. Pp. 523 and 552. London, 1916 (Longmans, Green and Co. Price \$2.50 per vol. Sold separately).

This book is of quite different character from most treatises on physical chemistry. As the two volumes indicate, the treatment is far more elaborate than in many text books, while it is not in any sense a reference book like Ostwald's lehrbuch. It might perhaps be classed as a treatise on chemical physics than on physical chemistry. The arrangement of the book is interesting. It "consists in regarding all physico-chemical phenomena as being capable of separation into two classes: first, phenomena exhibited by material systems when *in* a state of equilibrium; and, secondly, phenomena exhibited by material systems which have *not* reached equilibrium." In the first volume, the two classes of phenomena are treated from the standpoint of the kinetic theory while the second volume is devoted to considerations based on thermodynamics. As an illustration, equilibrium from the standpoint of the law of mass-action is considered in the first volume, while the application of the phase rule to equilibrium is in the second. In fact, equilibrium is the main subject in both volumes, but treated in each from an entirely different standpoint.

The newer developments of physical chemistry are given full consideration. Thus, some forty pages are devoted to Nernst's heat theorem, which formed the basis of his Silliman lectures at Yale a few years ago.

The book should prove of great interest and value to advanced students.

H. W. F.

5. *Practical Physiological Chemistry*; by PHILIP B. HAWK. Fifth Edition. Pp. xiv, 638. Philadelphia 1916 (P. Blakiston's Son & Co.; price, \$2.50).—The latest edition of this widely used manual has experienced very substantial enlargement by the addition of descriptions of new chemical methods applicable to biochemical analysis. Chapters on Nucleic Acids, Intestinal Digestion, Blood Analysis and Metabolism have been added. The directions for conducting metabolism experiments under laboratory conditions represent a somewhat novel and useful addition to a book of this character. The descriptions of procedures continue, as in the earlier editions, to be presented with accuracy and sufficient detail to serve as a useful basis for practical work. Even cursory examination of the analytical technic or demonstration procedures selected shows that the volume is an up-to-date product.

L. B. M.

6. *The Ionization and Dissociation of Hydrogen*.—It has been shown by J. J. Thomson that in a discharge tube containing hydrogen there are present charged atoms, charged molecules, and sometimes a constituent having a mass three times that of the hydrogen atom. The pressure used was about  $0.003^{\text{mm}}$  of mercury and the necessary potential difference was of the order of 20,000 volts. A different experimental method of obtaining positive rays has been recently devised and successfully employed by A. J. DEMPSTER. The electrons leaving a Wehnelt cathode were accelerated by the field between this electrode and the anode. The electrons ionized the gas between the electrodes and thus produced positive particles which acquired a sufficiently great velocity to carry them past the edge of the cathode ( $2^{\text{mm}}$  wide) and thence through a hole of small diameter which had been made in a screen. This screen was roughly normal to the electric field and parallel to the axis of a magnetic field which could be established at will between the poles of an electromagnet placed opposite to the emergence end of the hole. The north and south pole pieces also served respectively as the negative and positive ends of an electrostatic field. After passing through these two superposed deviating fields the positive particles fell upon another screen in which a suitably-disposed parabolic slit had been cut. By properly adjusting the deviating fields the parabolas corresponding to each constituent of the beam of positive particles could be brought successively into coincidence with the slit. After passing through the curved slit the particles entered a Faraday chamber and recorded their charges in the usual way. The advantages afforded by the Wehnelt cathode are that low potentials may be used, and that the pressure of the gas may be made as small as desired and may also be varied without changing the potential.

Three diagrams are shown in the paper, each having the strength of the deflecting magnetic field plotted along the axis of abscissas with the charge on the Faraday chamber as ordinates. The first curve corresponds to 800-volt rays produced in hydrogen at a



pressure of about  $0.01^{\text{mm}}$ . It has three pronounced peaks or maxima which pertain to  $H_1$ ,  $H_2$  and  $H_3$ . The maximum for  $H_1$  is nearest to the axis of ordinates while the peak for  $H_2$  is reached at a more intense magnetic field than is required for either  $H_1$  or  $H_3$ . The value of the charge at the maximum for  $H_2$  is slightly greater than for  $H_1$ , whereas the greatest ordinate for  $H_3$  is decidedly higher than for  $H_2$ . It thus appears that the particles of molecular weight 3 were present in relatively large numbers. The second curve was obtained with a gas pressure of  $0.0017^{\text{mm}}$ . It too presents three peaks, but now the  $H_2$  maximum is about two and one-half times as high as either one of the remaining peaks. The third curve indicates the relative proportions of  $H_1$ ,  $H_2$  and  $H_3$  when a pressure less than  $0.0005^{\text{mm}}$  was used. Under these circumstances the  $H_1$  and  $H_3$  peaks have nearly disappeared while the  $H_2$  maximum has retained its former value. That this change was caused by decreasing the pressure, and not by the removal of some constituent of the gas by the charcoal was shown by the fact that when hydrogen was admitted, while the charcoal and liquid air were kept in action,  $H_1$  and  $H_3$  regained their original relative intensities.

The writer of the paper accounts for the phenomena in the following way. Since in the high vacuum the free-path of the molecules is very great, the positive ions which are still formed by the dense stream of electrons coming from the Wehnelt cathode make very few collisions with the hydrogen molecules. Hence these positively charged diatomic molecules are analyzed in the condition in which they were at the instant of their formation. We must conclude, then, that electrons ionize only by detaching a single electron from a molecule, and are not able to dissociate a molecule into atoms. When the pressure is greater, some of the positive ions collide with the neutral molecules of the gas before the cathode and dissociate them. A positively charged atom thus formed may attach itself to a neutral molecule and give rise to  $H_3$ . The author also concludes that  $H_3$  cannot be regarded as a stable gas since it is not present when there is no dissociation of the hydrogen molecules.—*Phil. Mag.*, xxxi, p. 438, May, 1916.

H. S. U.

7. *The Structure of Broadened Spectrum Lines.*—In the preceding number of this Journal the results obtained by Nicholson and Merton were given, but details of the experimental method were lacking in the original paper. Consequently it may not be superfluous to give a brief description of the essential feature of this method as explained in another article by T. R. MERTON. A neutral-tinted wedge (of the type used for recording the sensibility curves of photographic plates) of density graded from 0.2 to 4.2 was mounted on the slit of a single-prism spectograph with its refracting edge at right-angles to the axis of the slit. Before the wedge was placed in position care was taken to have the slit uniformly illuminated over its entire effective length. Under these conditions each line of the spectrum appears brightest at

the points corresponding to the thin end of the wedge and gradually fades off toward the thick region of the absorbing screen. It is evident that the relative intensities of two lines can be calculated from the lengths of their images, provided the lines are so close together that errors due to the variation of the sensibility of the plate to different wave-lengths are negligible. A broadened line gives a wedge-shaped impression on the plate, the apex corresponding to the maximum of intensity in the radiation, and, from the shape of these wedges, the intensities at different distances from the maximum can be deduced. It is thus clear that the method consists in picking out points of equal density at different wave-lengths and determining the thicknesses of the wedge to which they correspond. Points of equal photographic density must indicate equal illumination since they are exposed for the same time and subjected to the same chemical treatment. The neutral-tinted wedge, of course, does not vary in absorbing power for neighboring wave-lengths. Accordingly the method is unaffected by the eccentricities of the photographic emulsion, and it is only necessary to assume that there is one particular density which can be recognized at different points.

Enlargements of spectrograms of the first three series lines produced by the passage of condensed sparks through hydrogen at atmospheric pressure are reproduced in the paper.  $H\alpha$  consists of a strong maximum falling off rather rapidly and apparently regularly. The intensity decreases much less rapidly for  $H\beta$  and there is a distinct minimum at the center of the line, which appears to be a close doublet.  $H\gamma$  has a bright axis with very wide, nebulous wings. The distribution of intensity in each of these lines is in complete accord with that deduced from Stark's data on the electric resolution and polarization of the lines.—*Proc. Roy. Soc.*, vol. xcii (A), p. 322.

H. S. U.

8. *The Single-Line Radiation of Magnesium.*—The earlier work of McLennan and Henderson showed that the vapors of each of the elements cadmium, mercury, and zinc, can be caused to emit a single spectral line by bombarding the particles with electrons possessing a certain amount of kinetic energy. For cadmium and zinc the range of kinetic energy corresponds to potential differences lying between 4 volts and 13.6 volts. This investigation has been recently extended by McLennan to magnesium. The vapor of this metal was found to emit the line of wave-length 2852.22 Å, and no other line, when the kinetic energy was included within definite limits. The numerical values of the limits have not yet been determined, but the range agrees, in part at least, with the interval for cadmium and zinc. Absorption lines homologous to those already observed for cadmium, mercury, and zinc were photographed in the case of magnesium. The wave-lengths of the two absorption lines are recorded as 2852.22 Å and 2073.36 Å. When sufficiently magnified the less refrangible band is seen to consist of two very close narrow bands similar to the mercury doublet at  $\lambda$ 2536.72. On the

other hand, the corresponding bands for cadmium and zinc have not yet been resolved into two components. The absorption lines of all four metals are the first members of the combination series symbolized (on Paschen's notation) as  $\nu = 2, p, -m, S$ , and  $\nu = 1.5, S - m, P$ . Finally, the author computes the ionizing potentials of cadmium, magnesium, mercury and zinc to be 8.85, 9.13, 10.27 and 9.24 volts, respectively.—*Proc. Roy. Soc.*, vol. xcii (A), p. 305. H. S. U.

9. *A Treatise on Electricity*; by F. B. PIDDUCK. Pp. xiv, 646, with 369 figures. Cambridge, 1916 (University Press. Also G. P. Putnam's Sons).—This book is not intended for beginners but is designed for those readers who require an advanced text covering both the theoretical and practical sides of the subject. The first eight chapters have been kept fairly simple and contain all the mathematical and physical principles necessary for a right appreciation of the subject, while the remaining six chapters form introductory accounts of special fields, which may be consulted by students before starting on treatises devoted to them exclusively.

Thus the ninth chapter, entitled "Applied Electricity," deals with shunt, series, and compound wound dynamos, with direct and alternating current motors, with induction motors, with electric lighting, etc. Chapter X, on electrolysis, is followed by a longer and very interesting chapter on electric oscillations. Among other things this chapter contains accounts of the experiments of Tesla, Hertz, Bjerknes, and of Sarasin and de la Rive. Coupled oscillation circuits, the singing arc, the electromagnetic theory of light, and wireless telegraphy also receive due attention. Chapter XII is devoted to the conduction of electricity through gases. It is fully up to date and includes, for example, the theory of the sparking potential, the phenomena of the photoelectric effect, and the theory of the diffraction of Röntgen rays. The next two chapters pertain respectively to radioactivity and the theory of electrons. This last chapter involves the electron theory of metallic conduction, Lorentz's equations, the theory of the normal Zeeman effect, the Lorentz-Einstein transformation, the theory of quanta, etc. The text has been written carefully and accurately, the selection of material is excellent, and the number of typographical errors is very small so that the volume should be found very useful by first-year graduate students in particular, and by others who need an introduction to the highly specialized, advanced treatises. H. S. U.

10. *The Physical Properties of Colloidal Solutions*; by E. F. BURTON. Pp. vii, 200. London, 1916 (Longmans, Green and Co.).—"The present attempt to give an outline of the study of colloidal solutions has to do particularly with its interest to the student of Physics." The second chapter deals with the preparation and classification of colloidal solutions. It contains systematic tables of various classes of colloids having something in common, and quotations of types of methods of preparation which will enable the reader to find out where to look for detailed

information. In the very nature of the case, this chapter is rather dry, while the next five chapters, which deal with the pure physics of colloidal phenomena, are very interesting both on account of the subject matter itself and also because of the clearness of presentation. More specifically, these chapters deal with the ultramicroscope, the phenomena and theory of Brownian motion, the optical properties of colloidal solutions, the determination of the size of ultramicroscopic particles, and the motion of colloidal particles in the electric field. The titles of the eighth, ninth and tenth chapters are respectively: "The Coagulation of Colloids," "Theory of the Stability of Colloids," and "Practical Applications of the Study of Colloidal Solutions." This last chapter is also very useful since it deals with various manufacturing processes, dyeing, purification of effluent waters, agriculture, and physiological applications.

The value of the monograph is increased by the presence at the end of each chapter of a long list of bibliographical references. Since the important subject of colloidal solutions is often neglected this compact and excellent text should be welcomed by advanced students and teachers of physics.

H. S. U.

## II. GEOLOGY AND NATURAL HISTORY.

1. *Stratigraphy and fauna of the Tejon Eocene of California*; by ROY E. DICKERSON. Univ. California Pub., Bull. Dept. Geology, vol. ix, No. 17, 1916, pp. 363-524, pls. 36-46, text figs. 1-14.—This valuable work has far-reaching import in that it stratigraphically and faunally establishes the Tejon formation in its variable development throughout California. The Tejon, although a thick formation, is a faunal unit, and unconformably overlies the basal Eocene, the Martinez; it in turn is usually unconformably overlain by the Oligocene. The fauna consists of about 300 species and many range throughout the series. Not more than four forms pass into the Oligocene and but 25 are derived from the Martinez. The Tejon is divided into four faunal zones and their distribution is shown on paleogeographic maps; the youngest zone has widest distribution when the Pacific Ocean lapped the base of the Sierra Nevadas, depositing here the Ione formation and its equivalent, the auriferous stream and bench gravels of the Sierra Nevadas. The Eocene closed with extensive deposits of rhyolitic ash and mud flows, followed by andesitic tuffs, lavas, and mud flows.

The Tejon fauna is partly a descendant of the earlier Martinez, to which were added many migrants from the Gulf of Mexico by way of the Panama or Tehuantepec portals, though less than 20 species, or about 7 per cent, are common to the two realms. The relationship of the Tejon is with the Midway, Wilcox, and Claiborne of the Gulf of Mexico area, but more decidedly with the last, while the Martinez appears to be older than anything in the Tertiary of the Atlantic area.

C. S.



2. *New fossil Coleoptera from the Florissant beds*; by H. F. WICKHAM. Bull. State Univ. Iowa, vol. vii, No. 3, 1916, pp. 3-19, pls. 1-4.—The author describes four new genera and 21 new species; the Miocene of Lake Florissant is now known to have no less than 515 different forms of beetles, the majority of which are inconspicuous. The climate was then mild and moist. "The insects of the Florissant Miocene stand in direct ancestral relationship to our present fauna." c. s.

3. *I. Eocene of the Lower Cowlitz River valley, Washington*; *II. The post-Eocene formations of western Washington*; *III. The Oligocene of Kitsap County, Washington*; by CHARLES E. WEAVER. Proc. Calif. Acad. Sci., 4th ser., vol. vi, Nos. 1-3, 1916, pp. 1-52, pl. 1, fig. 1.

*Tertiary faunal horizons of western Washington*; by CHARLES E. WEAVER. Univ. Washington Pub. in Geology, vol. i, No. 1, 1916, pp. 1-67, pls. 1-5.—The last-named paper is a record of 305 Tertiary localities in Washington, together with descriptions of 41 new species, mainly from the Oligocene, and lists of the Eocene (130 species), Oligocene and Lower Miocene (155), and Upper Miocene (81) molluscs found in the state. The maximum thickness of these deposits is 34,000 feet; the time of most marked deformation was in the Middle Miocene, with marked volcanic activity toward the close of the Eocene. c. s.

4. *The Upper Cretaceous floras of the world*; by E. W. BERRY. Maryland Geol. Surv., Special publication from Upper Cretaceous Report, 1916, pp. 183-313.—The author presents here lists of the Cretaceous floras of the world and comments more or less on their age relations. He accepts as the base of the Cretaceous the Albian of the European standard. Accordingly the Raritan is of Cretaceous age but older than the Dakota, and he correlates it with the Washita, and both with the European Cenomanian. This is a striking and far-reaching conclusion. As the Washita is a part of the Comanchian and is of Upper Cretaceous age, he further concludes that this term is invalidated as a substitute for Lower Cretaceous. This is a great and unadjusted question in American stratigraphy and can not be so easily fixed. In the first instance it is accepted that the Trinity, Fredericksburg and Washita divisions of the Comanchian represent an unbroken series of deposits that together make up the Comanchian. On the principle that diastrophism is periodic and more or less simultaneous throughout the world, we should then have to refer not only the Washita but all of the Comanchian to the Cretaceous. The reviewer does not intend to go into this correlation, but wishes to ask, Are the Lower and Upper Cretaceous divisions of the European standard representative of but one period, or of two (Lower and Upper Cretaceous), or of three (Lower, Middle and Upper Cretaceous) periods? Further, between what series do the important diastrophic movements of the sea occur? Certainly the break between the Comanchian and the American Cretaceous is clearly marked and universal in the



United States, and appears to be of the order that distinguishes periods.

The author leans to the hypothesis that the dicotyledon floras originated "in high latitudes, from which region they spread southward over the continents of the northern hemisphere in successive waves of migration." The Cretaceous climate was more uniform than at present and the floras are of a "warm temperate rain-forest type, less tropical than succeeding Eocene and Oligocene floras." Hardly any of the Cretaceous species "survive into the Eocene" and "many of the genera, particularly among the conifers, die out before the close of the period." c. s.

5. *Geology and underground water of Luna County, New Mexico*; by N. H. DARTON. Bull. 618, U. S. Geol. Surv., 1916, 188 pp., 13 pls., 15 text figs.—This welcome report on an area almost unknown geologically presents a discussion of the geology and mineral and water resources of southern New Mexico to the west of El Paso, Texas. The marine geologic record is of Upper Cambrian, Beekmantown, Richmond, Silurian, ?Devonian, Lower Mississippian, Pennsylvanian, Comanchian, and Benton times. There is also non-marine Tertiary present. c. s.

6. *Contributions from Walker Museum*, Vol. I, No. 9, (1) *The Osteology of some American Permian vertebrates*; (2) *Synopsis of the American Permo-Carboniferous Tetrapoda*. Vol. I, No. 10, (1) *Atactocrinus, a new crinoid genus from the Richmond of Illinois*; (2) *Description of a Ste. Genevieve limestone fauna from Monroe County, Illinois*. 1916.—A new scientific publication has been started by the University of Chicago under the title of "Contributions from Walker Museum." So far ten numbers have appeared. In No. 9 of Volume I, Professor WILLISTON describes the Permian cotylosaurian *Pantylus*, the oldest armored reptile; *Isodectes*; *Therapsleura*, as represented by a wonderfully good specimen which proves that the sternum of vertebrates evolved out of the anterior ventral ribs, the parasternum of Gegenbaur; and *Puercosaurus*, a new reptilian genus from New Mexico. The second paper in No. 9 presents a new synoptic review of the genera, families, and orders of the earliest Amphibia and Reptilia, furnishing very valuable material for further attempts toward unravelling the true genetic relations of these old animals. No. 10, by Professor WELLER, describes a new Ordovician genus of crinoids, and an interesting Upper Mississippian fauna of fifty-six species which lived in an oolite environment. c. s.

7. *Virginia Geological Survey, University of Virginia*; THOMAS LEONARD WATSON, Director.

Administrative Report of the State Geologist for the Biennial Period 1914-1915. Pp. 45, 2 pls., 1916.—A summary is given here of the work done by the Virginia Survey in 1914 and 1915. The coöperation of the United States Geological Survey, both as to topography and geology, has enabled the state organization to accomplish much more than would otherwise have been possible.

The work done is largely economic in character, and maps of the coal fields in the southwestern part of the state show the progress which has been made, and what areas still remain to be covered.

Bulletin No. X. Surface Water Supply of Virginia; by G. C. STEVENS. Pp. 245; 5 pls.—This bulletin, prepared in coöperation with the United States Geological Survey, presents the records accumulated in regard to the prominent river basins of the state.

8. *The Physical Geography of Wisconsin*; by LAWRENCE MARTIN. Pp. xxii, 549; 41 pls., 206 figs. Wisconsin Geological and Natural History Survey. E. A. BIRGE, Director. Bulletin No. XXXVI. Educational Series No. 4. Madison, 1916.—The surface features of Wisconsin are so varied in character that the systematic presentation of them in the present volume results in a reference book on physical geography, both complete and comprehensive. The text is prepared with a view to being made as intelligible as possible to the general public, and the illustrations are liberal in number and excellent in character.

9. *Publications of the U. S. Bureau of Mines*; VAN. H. MANNING, Director.—Recent Bulletins from the Bureau of Mines are noted in the following list (see Jan. 1916, p. 149). Numerous Technical Papers have also been issued.

No. 74. Gasoline mine locomotives in relation to safety and health; by O. P. HOOD and R. H. KUDLICH. With a chapter on methods of analyzing exhaust gases; by G. A. BURRELL. Pp. 83; 3 pls., 27 figs.

No. 86. Some engineering problems of the Panama Canal in their relation to geology and topography; by D. F. MACDONALD. Pp. 86; 29 pls., 9 figs.

No. 89. Economic methods of utilizing Western lignites; by E. J. BABCOCK. Pp. 74; 5 pls., 5 figs.

No. 91. Instruments for recording carbon dioxide in flue gases; by J. F. BARKLEY and S. B. FLAGG. Pp. 60; 1 pl., 25 figs.

No. 92. The feldspars of the New England and North Appalachian States, by A. S. WATTS. Pp. 181; 8 pls., 22 figs.

No. 93. Miners' nystagmus; by F. L. HOFFMAN. Pp. 67.

No. 96. The analysis of permissible explosives; by C. G. STORM. Pp. 88; 3 pls., 7 figs.

No. 97. Sampling and analyzing flue gases; by H. KREISINGER and F. K. OVITZ. Pp. 67; 1 pl., 34 figs.

No. 99. Mine ventilation stoppings, with especial reference to coal mines in Illinois; by R. Y. WILLIAMS. Pp. 30; 5 pls., 4 figs.

No. 100. Manufacture and uses of alloy steels; by H. D. HIBBARD. Pp. 77.

No. 102. The inflammability of Illinois coal dusts; by J. K. CLEMENT and L. A. SCHOLL, JR. Pp. 74; 5 pls., 2 figs.

No. 104. Extraction and recovery of radium, uranium, and vanadium from carnotite; by C. L. PARSONS, R. B. MOORE, S. C.

LIND, and O. C. SCHAEFER. Pp. 124; 14 pls., 9 figs. See notice on p. 214, vol. xli.

Nos. 113, 118. Abstracts of current decisions on mines and mining reported from May to September, 1915; by J. W. THOMPSON. Pp. 123. No. 118, October to December, 1915. Pp. 74.

No. 114. The manufacture of gasoline and benzene-toluene from petroleum and other hydrocarbons. Pp. 268; 9 pls., 45 figs.

No. 115. Coal-Mine fatalities in the United States 1870-1914, with statistics of coal production, labor, and mining methods, by states and calendar years; compiled by ALBERT H. FAY. Pp. 370; 3 pls., 13 figs.

10. *Canada, Department of Mines.*—The following are important recent publications (see vol. xli, pp. 467-469):

(1) *Geological Survey Branch.* R. W. BROCK, Director.

Summary Report of the Geological Survey for the calendar year 1915. Pp. viii, 307; 8 maps, 3 figs. Ottawa, 1916.

MEMOIRS.—No. 55. Geology of Field Map-area, B.C. and Alberta; by JOHN A. ALLAN. Pp. vii, 312, vi; 21 pls., 5 figs.

No. 77. Geology and Ore Deposits of Rossland, British Columbia; by CHARLES W. DRYSDALE. Pp. ix, 317, vii; 25 pls., 26 figs.

No. 79. Ore Deposits of the Beaverdell Map-area; by LEOPOLD REINECKE. Pp. v, 178, vii; one map, 13 pls., 9 figs.

(2) *Mines Branch.* EUGENE HAANEL, Director.

Annual Report on the Mineral Production of Canada during the calendar year 1914; JOHN MCLEISH, Chief of the Division of Mineral Resources and Statistics. Pp. 362.

11. *Oil and Gas Map of Southwestern Pennsylvania, 1915.* Pp. 22 with map on scale of 1:250,000. Topographic and Geologic Survey of Pennsylvania; RICHARD H. HICE, State Geologist. Harrisburg, 1916.—It is stated in the pamphlet accompanying the large and detailed map now issued, that the value of the petroleum produced in Pennsylvania in 1900 was \$18,000,000 and nearly \$20,000,000 in 1913. Between these two dates the value fluctuated, falling as low as \$11,000,000 in 1911. On the other hand, the value of the natural gas has risen somewhat regularly from \$10,200,000 in 1900 to \$21,700,000 in 1913.

12. *Bulletin of the Imperial Earthquake Investigation Committee.* Vol. VIII, No. 2. *The Sakura-Jima Eruptions and Earthquakes.* II.; by F. OMORI. Pp. 35-179; pls. VIII-XXXII, Tokyo, April, 1916.—This Bulletin of the Japanese Earthquake Commission is devoted to a discussion of the recent violent volcanic eruption of Sakura-Jima. An introductory chapter gives notes in tabular form on the time distribution of Japanese eruptions dating back to the seventh century. The earliest recorded eruption of Sakura-Jima was in 1468 and the twenty-six eruptions noted, down to 1914, with their individual dates, are given with their special characters. The special topics discussed in regard to the eruption of January 12, 1914, are as follows: the meteor-

logical conditions ; the propagation of sound waves ; the accumulation and transportation of ashes ; the abnormal changes in the height of water at Kagoshima Bay ; also the changes of level and horizontal displacements in the ground. A series of excellent charts illustrate the entire subject, and help to make the volume a notable addition to vulcanology.

13. *Mineralogic Notes, Series 3* ; by W. T. SCHALLER, U. S. Geol. Surv., Bull. 610, 1916 ; pp. 164, 5 pls., 99 figs.—In this report Dr. Schaller gives the results of the various smaller pieces of mineralogical investigations carried on by him in the chemical laboratory of the Geological Survey, between July, 1911, and January, 1914. It includes some twenty-five different communications, the majority of which have not been completely published elsewhere. Among these are the descriptions of five new species, namely, koechlinite, inyoite, meyerhofferite, lucinite and velardeñite. Important contributions concerning variscite, schneebergite, romeite and the melilite group are included. Through the courtesy of Dr. Schaller it was possible to publish in the Third Appendix to Dana's System of Mineralogy, issued last year, brief summaries of the descriptions of the new species together with the other more important results which are given in this Bulletin.

W. E. F.

14. *The Emerald Deposits of Muzo, Colombia* ; by J. E. POGUE. Reprint from the Trans. Amer. Inst. Min. Eng., 1916.—This paper gives a brief and interesting account of the history, geology and mineralogy of the famous emerald deposits of Colombia. The emeralds are found almost entirely in calcite veins that traverse a black, carbonaceous, intensely folded formation consisting of thin-bedded shale and limestone. This formation lies discordantly upon steeply dipping strata composed of heavier beds of carbonaceous limestone intercalated with black shale. Between the two formations are thin layers of three other rocks consisting of (1) chiefly albite, (2) a granular aggregate of calcite, dolomite, quartz and pyrite, (3) aggregates of large calcite rhombs in a fine-grained matrix. Small amounts of pegmatite have been observed. The presence and association of emerald, parisite, fluorite, apatite, albite and barite in a sedimentary formation indicates the action of strong mineralizing solutions which introduced them. Structural conditions indicate that the emerald formation was overthrust to its present position upon the underlying series, and that this movement was followed by a period of mineralization which attained its most conspicuous results along the fault plane and its economic results above that plane.

W. E. F.

15. *Microscopical Determination of the Opaque Minerals: An Aid to the Study of Ores* ; by JOSEPH MURDOCH. New York, 1916, pp. vi, 163 (John Wiley and Sons).—Since the publication in 1906 of a paper by W. Campbell on "The Microscopical examination of opaque minerals," the use of this new and important means of identification of these minerals has been steadily grow-



ing. The study of the Secondary Enrichment Investigation concerning the occurrence and alteration of ore minerals necessitated the use and elaboration of these methods. The present book must be considered as one of the important results of this investigation.

The methods used involve the observation under the microscope by reflected light of polished sections of the opaque minerals. The means of identification include, first, the color of the polished mineral, which is more accurately judged by comparison with definite mineral standards; secondly, the hardness; and thirdly, microchemical reactions through the use of various reagents. By means of these tests and the use of the determinative tables given in the book, it is possible to accurately determine the character of a given mineral.

An important result of this new method of investigation has been to show that opaque minerals are very liable to contain impurities in greater or less amount which would entirely escape detection by any ordinary methods of observation. It will be necessary in the future to make such an examination of an opaque mineral before analysis in order to be certain of the purity of the material analyzed. A considerable number of species that have been described as definite compounds have already been shown to be mixtures of two or more different materials.

It is proposed to call this new branch of mineralogical study by the name "Mineralography."

W. E. F.

16. *The Collection of Osteological Material from Machu Picchu*; by GEORGE F. EATON. Quarto, pp. 96; 39 pls., 50 figs., 2 tables, one map. *Memoirs of the Connecticut Academy of Arts and Sciences*, New Haven. Volume V, May, 1916.—This valuable report on the osteological collections made in connection with the Peruvian Expedition of 1912 has been recently issued. A notice will appear in a later number.

17. *The Birds of North and Middle America*; by ROBERT RIDGWAY, Curator, Division of Birds. Part VII. Pp. xiii, 543, 24 pls. *Bulletin of the U. S. National Museum*. No. 50.—This extensive work on American birds was begun in 1901. The seven volumes thus far published include 564 genera and 2,319 species and sub-species, with a considerable number of extralimital genera and species, whose characters are given in the "Keys." The present volume contains the cuckoo-like birds, parrots, and pigeons. Part VIII, in preparation, will include the gulls and auks with their near allies.

18. *R. Comitato Talassografico Italiana*.—Notwithstanding the far from quiet condition of the seas which surround Italy during the past two years, the work of the Italian commission, begun in 1910, still goes on uninterruptedly. Fifty-two memoirs are now included in the list of publications. Recent sendings include the bi-monthly bulletin for 1915 and memoirs 44-52. The last-named are all on subjects in natural history except No. 50, which discusses the solubility of gypsum in sea water.



19. *British Museum Catalogues*.—The following have been recently received :

Catalogue of the Ungulate Mammals in the British Museum (Natural History). Volume V. Perissodactyla, Hyracoidea, Proboscidea ; with addenda to the earlier volumes ; by the late RICHARD LYDEKKER. Pp. xlv, 207 ; 31 figs.—This concluding volume opens with an excellent portrait of Mr. Lydekker, the author of the work, whose death occurred in April, 1915 (see vol. xl, p. 668). Fortunately it was found that his preparations for the present volume had progressed so far that it has been possible to bring it out as he left it. The families here included are the horses, tapirs, rhinoceroses, hyraxes and elephants.

Report on Cetacea stranded on the British Coasts during 1915 (with one map), by S. F. HARMER. Pp. 12.—War conditions have not been favorable for observations such as those included in the present paper, hence, only 28 specimens are recorded for 1915, compared with 76 in 1913 and 57 in 1914. This year, however, includes a record of a specimen of Cuvier's whale, and a new record of Sowerby's whale, both very rare on the British coast.

20. *The Museum of the Brooklyn Institute of Arts and Sciences*.—Science Bulletin, vol. 3, No 1, on the Long Island Fauna (IV), has recently appeared. The subject is "The Sharks," by JOHN T. NICHOLS and ROBERT C. MURPHY. Pp. 34 ; 3 pls., 19 figs.

21. *The Involuntary Nervous System* ; by W. H. GASKELL. Pp. ix, 178, with several diagrams in colors. London, 1916 (Longmans, Green and Co.).—This is the first volume of a series of monographs on physiology, to be written by English physiologists who have authority in their special fields of research. The book is essentially an epitome of the author's yearly lectures on the subject, and was completed during the last two months of his life. It consists of a general account of our present knowledge of the distribution and functions of the sympathetic and allied nervous systems of vertebrates.

W. R. C.

22. *Laboratory Manual in General Microbiology* ; by WARD GILTNER and Associates in the Laboratory of Bacteriology, Hygiene, and Pathology, Michigan Agricultural College. Pp. xvi, 418. New York, 1916 (John Wiley and Sons).—This laboratory guide contains complete directions for the isolation, cultivation, and study of bacteria, yeasts, and molds. The book is designed to furnish the student with sufficient information to enable him to carry on his laboratory experiments with the minimum assistance from the instructor. There are explicit directions for preparing culture media, stains, and other reagents, with typical experiments to illustrate the physiology of microorganisms. There are also special exercises on the microbiology of air, water, sewage, soil, dairy, and plants, and on animal diseases and immunity.

W. R. C.

## III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Carnegie Foundation for the Advancement of Teaching. Tenth Annual Report of the President, HENRY S. PRITCHETT and of the Treasurer, ROBERT A. FRANKS.* Pp. vi; 141. New York City, October, 1915.—In the regular work of the Carnegie Foundation, the total number of retiring allowances and pensions for the past year was 445 (in 1914, 432), of which 118 were widows' pensions; 43 new names were added to the list. The Foundation since the beginning has paid out the large sum of \$4,225,000 to 639 individuals. The expenditure in the past year for allowances and pensions was \$674,000 (\$635,000 in 1914), while \$55,000 was devoted to the department of educational inquiry and \$37,000 to administration.

The annual volume, in addition to the routine matter, discusses a number of problems of great importance from the educational standpoint. The subject of legal education in this country, presented in Bulletin No. 8, by Professor Redlich of the University of Vienna (see vol. xxxix, p. 611), has been further investigated with striking results. It seems that there are 147 resident schools, of which all but ten confer degrees, and 17 correspondence schools, a total of 164. It is worthy of note that of the degree-conferring schools, Connecticut has 1, Massachusetts 4, Pennsylvania 5, New York 9; while the District of Columbia has 8, California 10, and Illinois 12 with 8 correspondence schools in addition.

Other subjects now undertaken for study, but not reported upon at length, are those of Engineering Education and the Training of Teachers in Missouri. The legislative results following the publication of the Foundation's study of education in Vermont (Bulletin No. 7; see vol. xxxvii, p. 564) give a gratifying evidence of what the Foundation is able to accomplish. A discussion of the charges for tuition in one hundred representative institutions for the past ten years is given in another chapter, with interesting remarks showing the uniform tendency to advance the fees. Finally, to the study which comes closest to the definite work of the Foundation, and for which it has done most, that of systems of pensions, fifty pages are devoted, with a tabular summary of 65 pension systems for teachers and 58 industrial and institutional systems. All of these are regarded as unsound. The special Bulletin, now in press, describing the ten years' experience of the Foundation with its own system, and plans for its future development, will be looked forward to with great interest.

2. *Public Education in Maryland: A Report to the Maryland Educational Survey Commission;* by ABRAHAM FLEXNER and FRANK P. BACHMAN. Pp. xviii, 176, with illustrations. New York, 1916 (The General Education Board).—The Commission, charged with the investigation of the education in Maryland, was appointed by the legislature in 1914, and at its request

the General Education Board undertook the survey. The field covered embraces the elementary and secondary schools of the counties, but not the schools of Baltimore. The general decision reached is that the public education of Maryland is on the whole soundly organized and that the State deals with it generously, although some of the counties do less than their share. Practically, however, while a few counties have good schools, many of the schools are inferior, the inspection ineffective, the children irregular in attendance, and the buildings very unsatisfactory; for much of this the influence of politics is unfortunately responsible. The report discusses in detail the individual schools themselves and offers suggestions as to legislation calculated to improve the situation. These results are highly important, not for Maryland alone but for other States also, particularly those like it having a large negro population.

3. *The General Education Board*, FREDERICK T. GATES, Chairman. *Report of the Secretary*, WALLACE BUTTRICK, 1914-1915. Pp. xi, 82. New York, 1916 (61 Broadway).—The Rockefeller fund in the hands of the General Education Board amounts to some \$34,000,000, from the income of which appropriations amounting to \$1,577,000 were made in the year ending June 30, 1915. Eight colleges and universities are mentioned in the list as having received the greater part of this sum, namely, \$1,275,000, these appropriations being towards the maximum sum of \$5,200,000, to be raised by them. Other important measures discussed, towards which the funds of the Board are being used, include clinical instruction on the "full time plan," the education in the southern states, public education in Maryland (see above), etc.

4. *Napier Tercentenary Memorial Volume*. Edited by CAR-GILL GILSTON KNOTT. Pp. xi, 441, with illustrations, including 15 plates. London, 1915 (Published for the Royal Society of Edinburgh by Longmans, Green and Company).—The three hundredth anniversary of the invention of logarithms was celebrated in Edinburgh, July 24-27, 1914. Delegates were present from universities, observatories and learned societies in all parts of the world. Addresses were given and papers were read dealing with the life and work of John Napier, with the influence of his great discovery upon the progress of science, and with the history of the theory and art of calculation as it developed in the years which followed the publication of his *Mirifici Logarithmorum Canonis Descriptio*. There was also a most interesting exhibition of rare mathematical books and of calculating machines both ancient and modern—from abaci and sets of "Napier's Bones" to the most recent devices for mechanical computation, some of them of surprising complexity and ingenuity. In addition to the scientific attractions of the Congress, a number of social gatherings added much to the pleasure and interest of the occasion; among these was an evening reception by the Lord Provost and Magistrates of Edinburgh, and a garden party at Merchiston

Castle, the birthplace and home of Napier, now occupied by a boys' school.

In the present handsome volume, Dr. Knott has collected the addresses, lectures and papers given at the Congress together with an account of the celebration, copies of the congratulatory addresses to the Royal Society of Edinburgh, lists of the institutions which participated and of their representatives. It is illustrated by portraits of Napier, facsimile pages from his works and from other important early books, and by engravings of Merchiston Castle at different times.

The papers which deal with the historical development of the subject, especially the memorial address by Lord Moulton, can scarcely fail to excite the eager interest of anyone who has a taste for mathematics. The methods by which Napier reached his great discovery and the course of subsequent progress are at once fascinating and surprising. As one comes to realize, however, what the state of mathematical knowledge was three hundred years ago, the wonder is that such a discovery could have been made at that time and in a place so remote from the centers of intellectual life as Scotland then was. It was an achievement of genius and well worthy of being celebrated, as it was, by the last International Congress before the beginning of the Great War.

H. A. B.

5. *The Mining World Index of Current Literature*. Vol. VIII. Last Half Year, 1915; by GEO. E. SISLEY. Pp. xi, 228. xxv. Chicago, 1915 (Mining World Company).—The Index published by the Mining and Engineering World, which covers the world's current literature in this field, has now been completed for the last half year of 1915; it forms volume VIII of the Series (see earlier notices).

#### OBITUARY.

PROFESSOR SYLVANUS P. THOMPSON, the noted physicist and electrical engineer, died in London, June 13, in his sixty-sixth year. He was the author of several volumes on electricity and optics, etc., and made important contributions particularly in electrical machinery.

PROFESSOR OCTAVE LIGNIER, the able French paleobotanist of the university of Caen, died on March 19 at the age of sixty-one years.

PROFESSOR EMILE JUNGFLISCH, of the Collège de France, distinguished particularly for his work in organic chemistry, died on April 24 at the age of seventy-seven years.



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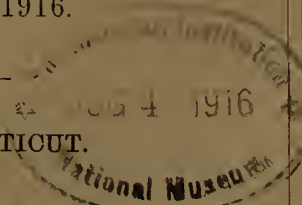
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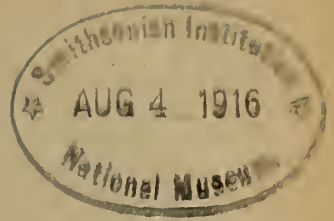
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# AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. IX.—*The Problem of Continental Fracturing and Diastrophism in Oceanica*;\* by CHARLES SCHUCHERT.

*Latitudinal arrangement of ancient lands.*—Paleogeographic studies during the past thirty years have been developing the hypothesis that the ancient continental platforms were arranged latitudinally rather than longitudinally as they are now, and further, that their areal extent, including their emerged and submerged portions, was greater than at present. It appears that vast landmasses have been fractured, broken up, and more or less permanently taken possession of by the oceans, a history which none exhibits better than the Australia-New Zealand region.

*Time when oceans became deep.*—We have learned from the several deep-sea expeditions something of the rare and strange life of the oceanic abysses. An analysis of these organisms shows that no Paleozoic forms occur among them and, indeed, very little of the life is ancestrally traceable even to the stocks of Triassic times. It is with the Jurassic and later life that the organisms of the abysses have their affinities. This seems to indicate that the oceans have been progressively deepened only since the Triassic. As one of the most marked crustal deformations, however, began in the Coal Measures of the Paleozoic and continued, though with pauses, well into the Triassic, it therefore appears that the oceans have been periodically enlarged and deepened ever since Permian time. This is in keeping with the theory that the earth's radius has been gradually diminishing, and that the periodic compensation

\* Read before the National Academy at Washington, April 17, 1916.

therefor has been greatest in the oceanic basins, the areas of greatest rock densities.

*Increase of water with time.*—If the oceans have progressively enlarged and deepened, it is natural to ask, Has the quantity of water increased with time, and if so, what was the source of supply? Some geologists, and more especially some petrologists, have concluded that every active volcano and most of the thermal springs are adding much new water—the so-called “juvenile” water, of magmatic origin—to the old accumulations of the hydrosphere. As yet we have but little in the way of estimates based on field or laboratory experiments to give us any adequate idea how much water an active volcano liberates. Some years ago the writer hazarded the guess that the increase of water since the beginning of Paleozoic time may have been as much as 25 per cent.

*Decrease of water during glacial periods.*—That the strand-lines of the oceans are decidedly mobile is well known and these oscillations are generally ascribed to the rising and sinking of the continents. This conclusion is undoubtedly in large measure true, but that the ocean bottoms also rise locally and so displace water, resulting in rising strand-lines, is readily deducible from the mere presence of oceanic islands and submerged ridges, because these masses have risen above the mean of the oceanic bottoms. On the other hand, it is known that periodically the ocean bottoms subside, but apparently no more than a few hundred feet at a time, and as a result of these subsidences the strand-lines the world over are markedly lowered when the overlapping marine waters are withdrawn and the continents are most emergent as they are at present. The mobility of the strand-lines is every now and then further augmented during the glacial periods when the volume of water in the oceans is decreased and the extracted quantity is piled up on the land as ice. During the Pleistocene, Daly<sup>1</sup> states that the strand-line was thus repeatedly lowered in the tropical areas, and estimates that the maximum was from 200 to 230 feet, during the times of greatest cold. At the same time reef-corals were then almost non-existent, permitting the ever active marine waves to cut down the protruding oceanic islands within the tropics to a little below sea-level. These truncations are now the submerged platforms that lie as a rule between 180 and 300 feet beneath the present sea-level, and on which the reefs have since grown, keeping pace with the

<sup>1</sup> R. A. Daly, The glacial-control theory of coral reefs, Proc. Amer. Acad. Arts Sci., li, 157-251, 1915.



rising strand-lines resulting from the melting of the ice. On the other hand, the Pleistocene strand-lines remained neutral at about  $35^{\circ}$  north and south latitudes; further poleward they were positive, due to the gravitative power of the great masses of polar ice.

*Permanency of continents and oceans.*—It is now more than fifty years since James D. Dana began to teach that the rising continents and the sinking oceanic basins have been, in the main, permanent features of the earth's surface. He did not mean, however, that the continents have always had essentially the same shape, elevation, and areal extent that they have to-day. Still, Dana did not fully appreciate the amount of continental fragmenting that has taken place in the course of geologic time, though he clearly pointed out the foundering of Australasia, speaking of it in his famous *Manual of Geology* (page 797) as "a fragment of the Triassic world." The teachings of Dana as to the permanency of continents and oceanic basins have been accepted in some form by all geologists, and lie at the basis of all zoogeography and evolution as well. In Dana's time and to some extent even to-day geologists are swayed by the Wernerian or Neptunian theory of earth history, which postulates a gradual emergence of the land out of the decreasing hydrosphere through loss of water by crustal absorption. Now, however, geologists are holding more and more to the hypothesis that the earth periodically shrinks, and each time it does so some parts or all of the continents rise more or less; but that in the main there is subsidence of the ocean bottoms equal in amount to the rising land-masses, that the water of the hydrosphere is constantly increasing in amount, and that even though the continents are in the main permanent, yet they are partially breaking down into the oceanic basins.

From this we conclude that the enlarging oceanic basins are the most permanent features of the earth's surface. On the other hand, along with the progressive subsidence, the bottom of the Pacific is also built up into many local volcanic cones by outpourings of lava, and further, it rises into more or less long mountain ridges. Some of these elevations of the bottom appear at the surface of the ocean as groups or lines of dead or active volcanoes (see fig. 1). Another general conclusion is that most of the "deeps" of the Pacific Ocean situated between 18,000 and 31,800 feet beneath the surface occur near the continents that exist now or existed formerly, or that they are located on the outer or oceanic side of mountain chains. These,

the "foredeeps" of Suess, are striking tectonic features of the lithosphere. As for the true limits of the Pacific Ocean, Suess states that they are seen in the trends of long mountain folds. "So it is from New Zealand and New Caledonia to the borders of eastern Asia, to the Aleutians, and all along the western coast of both Americas."<sup>2</sup>

*Topography of the Pacific basin.*—So far we have been considering the problem of crustal depressions essentially from the standpoint of hypothesis. Now let us see what is actually known as to the topography of the Pacific Ocean and the geologic history of the Australasian region. An excellent summary of the present geography of the Pacific Ocean and the topography of its bottom is shown on the splendid map by Max Groll, recently published by the Institut für Meereskunde of the University of Berlin (1912). This map is based on Lambert's equal-area azimuthal projection, with a replotting of all geographic and bathymetric data ascertained up to January, 1912, and is therefore more up-to-date and far better than any heretofore published. Groll states that he considered at least 15,000 soundings, made in all the oceans, and that yet there are many areas in the Pacific, hundreds of miles across, that are without a single one. It is therefore natural for him to add: "The greater part of the Pacific Ocean is still unexplored. . . . One is actually frightened at the little that is yet known of the bottom relief of the oceans and at the few data on which our representation of it is based. . . . Even in so relatively well known an area as the East Australasian seas, there are rarely more than from four to six deep-sea soundings to each five-degree field." Our detailed knowledge of the actual configuration of the bottom of the Pacific is therefore seen to be very slight indeed.

#### PALEO GEOGRAPHY OF AUSTRALASIA.

*Formation of two geosynclines* (see fig. 1).—Let us now review the larger features resulting from the ancient cycles of aerial erosion and marine deposition through which has been determined the paleogeography of Australasia. An analysis of this history since the Cambrian seems to show that at least two northeasterly trending troughs of sedimentary accumulation began to form early in the Paleozoic. The western one, which may be known as the Tasman geosyncline, almost wholly of Paleozoic development, is now partially elevated into the plains

<sup>2</sup> Ed. Suess, *Nat. Sci.*, ii, 180, 1893.

FIG. 1.



FIG. 1. Geologic plan of Pacific Ocean and bounding lands drawn on Groll's map. Spaces between dashed lines circumscribe Australasia and the Oceanide arcs. Oceanic deeps in solid black. Closely ruled horizontal lines indicate the areas of the Tasman and New Zealand geosynclines.

Lands ruled vertically indicate the Antarctic system of structures; lines to left, the Asiatic system; lines to right, the American system; horizontal lines, the Atlantic system.

and mountains of eastern Australia, while the rest of it has sunk deep into the present Tasman sea. The other, or eastern trough, which also appeared early in the Paleozoic, maintained itself after this era in diminished extent throughout the Mesozoic and even into Pliocene time. This may be known as the New Zealand geosyncline, a far narrower but longer one than that of Australia; the shorter southern portion has now risen into the mountains of New Zealand, while the much longer northern part has apparently subsided to a depth of not more than 9,000 feet, forming a submerged plateau upon which stand the volcanic islands of the Kermadecs and the Tongas.

*Historical geology of New Zealand* (see figs. 2 and 3).—In the New Zealand trough there appear to be, according to Park,<sup>3</sup> no less than 45,000 feet of Paleozoic and 11,000 feet of Mesozoic sediments, all of which are apparently of marine origin. These are coarse in grain and have much interbedded igneous material, indicating that the adjacent lands were unstable and repeatedly reëlevated into high lands. There appear to be no Cambrian or Triassic strata here, but the remainder of the geologic column is as well represented by marine deposition as is usually the case in geosynclines. There were at least four times when the New Zealand trough was markedly subject to folding and uplift; these were toward the close of the Silurian, Devonian, Jurassic, and Cretaceous periods. During the Cenozoic, the New Zealand trough also appears to have been in continuous subsidence from late Eocene into Pliocene time, when about 9,000 feet of marine sediments had been laid down along the eastern sinking margin. Late in the Pliocene there was marked vertical uplift, probably as much as 4,500 and possibly even 6,000 feet. The nearly horizontal Cenozoic strata are now found in places at an elevation of 3,000 feet, having been depressed 1,500 feet during the time of Pleistocene glaciation. The high condition of New Zealand at this time united into a greater New Zealand all of the present outlying islands of the New Zealand plateau, no part of which is now submerged more than 3,000 feet. It should be added that Captain Hutton and Professor Dana thought that New Zealand was united with Wilkes Land of Antarctica in late Permian time.

*Historical geology of Australia* (see figs. 2 and 3).—In Australia there is no evidence of the Tasman sea during Cambrian time, for the marine invasions at first were from the south and later across the entire medial portion of the con-

<sup>3</sup> Jas. Park, *Geology of New Zealand*, 1910.



continent. The trough began to appear as a sea-way in the Ordovician (?5,000 feet of deposits, according to Süssmilch<sup>4</sup>), with the greatest time of subsidence during the Devonian (27,000 feet); it continued with some interruptions throughout the Carboniferous and Permian (36,000 feet). During the Paleozoic, about 70,000 feet of essentially coarse sediments and interbedded volcanics were laid down in New South Wales, though smaller thicknesses seem to prevail elsewhere in eastern Australia. Here again we see the geologic results of high adjacent and often rejuvenated western lands. The record also shows that there were in Paleozoic time at least three periods of decided crustal folding (Ordovician, Silurian, and Devonian), and one of vertical uplift with faulting (during the close of Permian time).

The marked crustal unrest of eastern Australia is also demonstrated by the vast quantities of extruded volcanics that in the main precede and accompany the deformations, appearing in greatest quantity in the Ordovician, Devonian, and Lower Carboniferous. According to Süssmilch,<sup>5</sup> "Nearly every period belonging to the Paleozoic era had its active volcanoes, from which extensive floods of lava were poured out. The Mesozoic era, on the other hand, appears to have been quite free from volcanic displays. In the Cenozoic era, renewed activity took place." Following the Permian deformation the continent was repeatedly lifted above the embrace of the Tasman sea. It is true, however, that the Cretaceous seas have recorded themselves widely in this continent, but it was a shallow-water flood from the north across medial Australia, and to the west of the high eastern margin, a condition bringing to mind the similar Cambrian invasion. In the Eocene and Oligocene, the sea again overlapped from the south across a part of central Australia, and most markedly so in the Pliocene, when all of eastern Australia was vertically elevated and block-faulted between 1,500 and 7,300 feet above the level of the sea (during the "Kosciusko epoch"). In compensation for this elevation the Tasman sea sank, there being now great depths close to the continent which in one place go down to 18,500 feet.

*Time of severance of Australia from Asia.*—Australasia (Australia, Tasmania, New Guinea) has been the most remarkable asylum among the continents for the preservation to this day of living examples of the plants and animals of the medieval world. Among these in great variety of size, habits, and adap-

<sup>4</sup> C. A. Süssmilch, *Geology of New South Wales*, 1911.

<sup>5</sup> *Op. cit.*, p. 161.



FIG. 2.

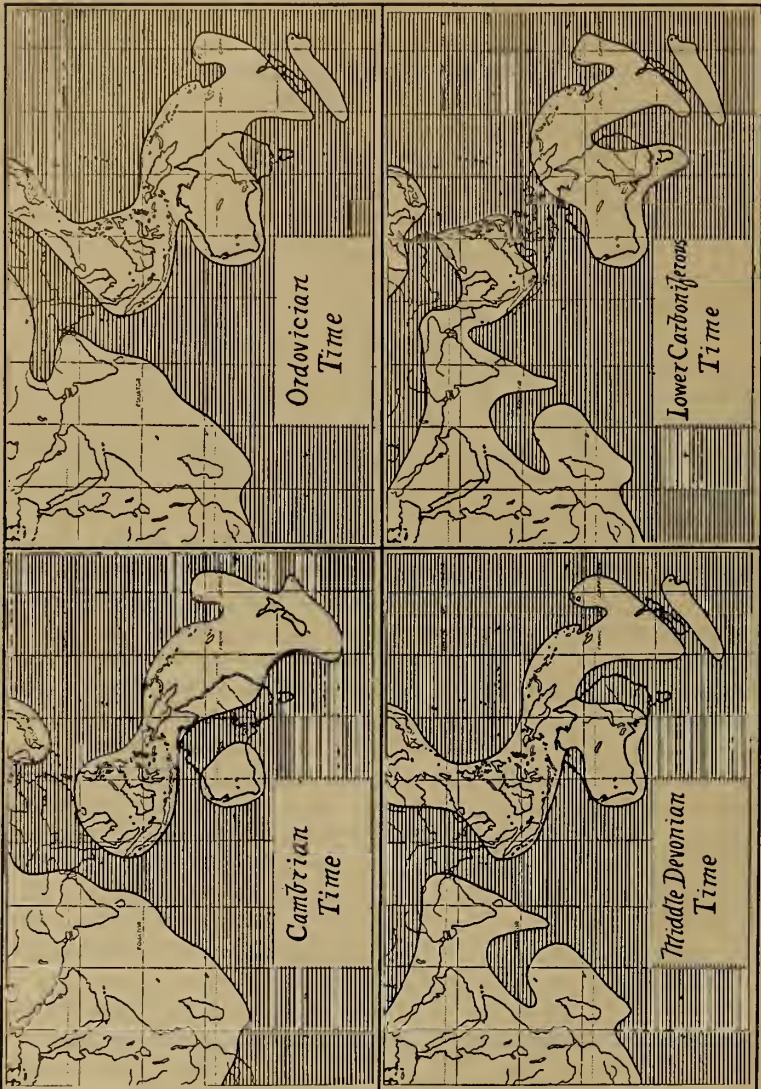


FIG. 2. Paleogeography of Australasia in Cambrian, Ordovician, Devonian, and Mississippian times.

FIG. 3.



FIG. 3. Paleogeography of Australasia in Permian, Triassic, Cretaceous, and late Eocene times.

tations are the marsupial or pouch mammals, which in many ways parallel the placental evolution, and the far less diversified, more primitive, but more remarkable egg-laying monotremes. All seemingly had their origin in the continents of the northern hemisphere. The marsupials were at their culmination in the Pliocene, when forms existed larger than any living rhinoceros (*Diprotodon australis*). From the chronogenesis of these stocks and their diverse evolution in Australia, we learn that they must have been on that continent long before, and that they had been free from all northern invasions and hence escaped destruction by the higher, more intelligent, carnivorous placental mammals. We must, therefore, conclude that Australia has been an island continent at least since late Eocene time, for it is since then that the placental mammals have elsewhere dominated all other land life.

The question next arises, When was Australia severed from Asia? From the paleogeography as now deciphered, we learn that Asia and Australasia were in complete connection during most of the time from the Cambrian to the close of the Devonian. In the Lower Carboniferous, however, southeastern Asia began to be invaded by the Indian and Pacific oceans in the region of what are now the East Indian Islands, and this invasion continued into the Pennsylvanian, after which there was again connection lasting into Triassic time. A greater areal subsidence then occurred in southeastern Asia, New Guinea, New Caledonia, and elsewhere in Australasia; it began in the Jurassic and probably was repeated in Comanchian and Cretaceous times. However, from the fact that carnivorous dinosaurs—land reptiles that arose in the northern hemisphere either late in the Permian or shortly afterward—are known in the Triassic of Australia (none at all occur in New Zealand); we must conclude that there was still at this time an intermittent land-bridge connecting this continent with Asia. The time of more complete severance apparently came in the Jurassic, though intermittent land connections probably persisted to the end of Cretaceous time. The troughs of separation that distinguish the Asiatic land-masses from the Australasian ones seem to be the present Molucca-Banda-Arafura seas, which have depths varying between 4,650 and 21,000 feet (see fig. 1).

The "Asiatic system" of tectonic structures takes in not only the Asiatic continent, but also the outlying series of island arcs and the greater part of the East Indies, as Sumatra, Java, the islands east of and including Timor, Borneo, Celebes, and



the Philippines. The Moluccas, however, appear to be geologically and structurally a part of New Guinea, and are therefore remnants of the foundered continent of Australasia (see fig. 1).

#### THE OCEANIDES AND FOREDEEPS.

*Oceanides*.—Long ago Dana pointed out that there are fifteen chains of islands in the Pacific Ocean, all trending from N.30°W. to N.65°W. These are a part of the Oceanides of Suess, and Dana states<sup>6</sup> that they “are not independent lines, but subordinate parts of island chains. There are three great island chains in the [Pacific] Ocean which belong to the north-westerly [trending] system—the Hawaiian [1,500 miles long], the Polynesian [parallel chains 5,500 miles long], and the Australasian [2,000 miles long].” The first two series are chains of oceanic islands built up largely by volcanoes, while the Australasian and the 2,500-miles-long New Zealand chain, with its northeasterly trend, are but the rising northern and eastern boundaries of the otherwise much broken down and foundered continent of Australasia. Here occur andesitic and other rocks characteristic of continents, and also much compressed and metamorphosed formations not seen on the oceanic islands.

*Foredeeps* (see fig. 1).—In front of the New Zealand chain lies one of the five greatest deeps of the Pacific, the Tonga-Kermadec-New Zealand foredeep (known as the Aldrich deep), whose deeper parts are between 26,000 and 31,800 feet. There are no known foredeeps along the northern outer boundary of Australasia, but just within the outer chains there have been found three deeps ranging between 19,500 and 29,700 feet—the two Solomon Islands deeps (the northern one is known as the Planet deep), and the unnamed deep between the New Hebrides and New Caledonia. To the east of the Philippines is another, more extensive foredeep attaining to 27,800 feet (Swire deep); the Pourtales deep lies 500 miles to the east and the Challenger deep 500 miles still farther east along the eastern side of the Guam-Ladrone or Marianne Islands, with a greatest depth of 31,315 feet. To the east of the Asiatic foredeeps lies the Pacific Ocean proper, whose average depth varies between 15,000 and 18,000 feet, and on its floor rise the more or less submerged Oceanides.

<sup>6</sup> J. D. Dana, *Manual of Geology*, 4th ed., 1895, p. 37.

*Origin of the Oceanides.*—Finally, we must ask, When did the thousands of oceanic islands—the Oceanides—arise? They occur singly, in groups, and most abundantly in linear arrangement. The isolated and the grouped islands probably all represent great volcanic cones that have built themselves up from the ocean bottom through the eruption of rock material. What is the origin, however, of those that are arranged in linear series? Are they ranges of volcanoes that have likewise grown from the depths but are situated on lines of fracture in the lithosphere, or do they rest on the crests of great arches or foldings of the ocean bottoms? Equally important questions are: What is their geological history, and have they simultaneous or successive origins? So far as known, none of the smaller oceanic islands reveals fossils older than the later Tertiary, a condition that appears to be in harmony with the theory that the sum of their movements is negative and thus in keeping with the idea that the oceanic bottoms are in the main subsiding areas. Because of the fact that in the oceans volcanic mountains and folded mountains are protected from erosion by the covering of water, they, unlike the ridges of the dry land, last from one era to another. In fact, the submerged ridges lying at depths of less than 10,000 feet will be built up through the rapid accumulation of organic calcareous débris, while the abysses on either side will receive little solid matter, because of the great solvent power of the water of the deeper parts of the ocean. In the words of Suess<sup>7</sup>: “The result is an exaggeration of the relief.” Because of the inaccessibility of the submerged parts of the Oceanides, we have as yet little evidence showing when they originated, and yet on the basis of the periodically recurring diastrophism it would seem that none is older than the Permian, a time of intense and world-wide crustal deformation. Others may have originated during the late Cretaceous crustal movements, and all may have again been reëlevated and stirred into volcanic activity with the world-wide crustal readjustments that began in the Miocene and continued into late Pliocene time.

*Some objections to continental fracturing.*—The views just presented are those of most paleontologists, but there are geologists and zoogeographers who do not accept the idea of continental fragmentation taking place on so large a scale as is here indicated. They hold firmly to the theory of the permanency of continents and ocean basins, believing that these positive and negative elements of the earth's surface have always retained

<sup>7</sup> Ed. Suess, *Face of the Earth*, vol. iv, p. 326.



the forms they now have. In their eyes, the physical evidence in the areas of fragmentation, and especially in the southern hemisphere, is not of a nature to compel the view that large lands formerly existed here, and they say, further, that there is no process in the mechanics of the earth known to them that would account for such down-breaking of the lithosphere.

Coleman in his presidential address of 1915<sup>8</sup> holds firmly to the theory of the permanency of oceans and continents. He does not believe in a Gondwana Land across the Indian Ocean uniting Africa to peninsular India. His belief is founded on the knowledge that "the earth's crust over large areas . . . approaches a state of isostatic equilibrium," and that "on the broad scale continents are buoyed up because they are light, and ocean bottoms are depressed because the matter beneath them is heavy." In this we agree with Coleman. But he then concludes: "There is no obvious way in which the rock beneath a sea-bottom can be expanded enough to lift it 20,000 feet, as would be necessary in parts of the Indian Ocean, to form a Gondwana Land; so one must assume that light rocks replace heavy ones beneath a million square miles of the ocean floor."

The fallacy of this conclusion is the assumption that the now sunken parts of eastern Gondwana were raised out of the depths of the Indian Ocean after it became very deep, i. e., seemingly since the later Mesozoic and certainly not before Permian time. The paleontologists, on the other hand, postulate the existence of Gondwana at least as early as the Carboniferous, because of the origin and wide distribution in the southern hemisphere of the *Glossopteris* flora (Africa, India, Australia, Antarctica, South America), and the writer has long been holding that the origin of Gondwana goes back into Proterozoic time. It is therefore not a question of raising Gondwana out of the realms of Neptune and of buoying up its rocks and lessening their specific gravity through expansion. These postulates are unnecessary, for Gondwana has always been in existence since there were oceans, or at least since the beginning of Paleozoic time; when the oceans began to deepen markedly in the earliest Mesozoic and since then, these great sinking fields took into themselves the above-mentioned sunken parts of Gondwana and Australasia.

Another erroneous though less significant argument of Coleman's is that because "geodesists are demonstrating that the earth's crust over large areas, and perhaps everywhere,

<sup>8</sup> A. P. Coleman, Dry land in geology, Bull. Geol. Soc. America, xxvii, 175-192, 1916.

approaches a state of isostatic equilibrium," therefore this balance is demonstrated everywhere over the earth's surface. It is true that he writes "perhaps everywhere" but his argument is positive and unqualified when applied to Gondwana. We must therefore ask, What do we know about the detailed isostasy of the oceanic areas? The answer must be that in a broad way we know much, and that the oceanic bottoms are on the average of denser rock than the lands. However, it is not only a question of average densities but the greater one as to what we know of the specific gravity of the entire area of any ocean bottom. The answer in this case must be "Very little indeed," because it is well known to geodesists that no knowledge is more desirable than a complete survey of the oceanic areas as to their detailed specific gravities and bottom relief. The writer therefore concludes that it is *not* "hard to imagine a mechanism that could do the work" because it is the same mechanism that in Mesozoic time made the present channel of Mozambique which separates Madagascar from Africa—a sunken block now a water-way from 240 to 600 miles wide and from 5,000 to 10,000 feet deep.

As for the ancient life found living and fossil in the continents of the southern hemisphere, and especially with regard to the distribution of the Permian *Glossopteris* flora, those who hold to the complete permanency of continents and oceans say that we are still too ignorant of the world's organisms and their histories to conclude from them that their asylums (Australia, India, Africa, South America, Antarctica) were formerly connected one with another; or they hold that the organisms reached these places by accidental dispersal through the air or by being rafted across the intervening water areas. This conflict of views marks one of the greatest outstanding problems of geology and paleontology. The writer, however, is overwhelmed by the facts revealed in the geographic distribution of the ancient land floras and faunas and the marine life, and is compelled to dissent from the rigid view of the permanency of continents.

*Conclusions.*—To sum up, we may say that the bottom of the Pacific Ocean in the region of greater Australasia seemingly became more and more mobile with the Lower Carboniferous and especially during the Jurassic and Cretaceous. During this very long time the eastern half of the Australasian continent, a land about 1,800 miles east and west and 2,200 miles north and south, was folded into a series of parallel ridges trending

northwest and southeast, nearly all of which went down more and more beneath the level of the sea to a maximum depth of about four miles and an average depth of between one and two and a half miles. Small parts of the ridges still protrude above the ocean (at least New Caledonia), but most of what we see are the volcanoes that have built themselves up above the folded rocks to the level of the sea. Further, the entire oceanic area of the Oceanides also subsided during the Mesozoic and Cenozoic, and possibly as much as 7,000 feet; while this was taking place the bottom was apparently folded and built up by volcanic material into many more or less parallel ridges, the Oceanides, a series of arcs extending over an area of about 3,500 miles east and west and the same distance north and south. Finally, we may add that the entire western half of the Pacific bottom, and especially the Australasian region, appears to be as mobile as any of the continents of the northern hemisphere, with the difference that the sum of the continental movements is upward, while that of the ocean bottoms is downward.

ART. X.—*On the Qualitative Separation and Detection (I) of Tellurium and Arsenic and (II) of Iron, Thallium, Zirconium and Titanium*; by PHILIP E. BROWNING, G. S. SIMPSON and LYMAN E. PORTER.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccclxxviii.]

I.

IN a previous paper from this laboratory by one of us\* it was shown that an attempt to separate arsenic and tellurium by the addition of magnesium chloride mixture to a solution of ammonium arsenate and tellurite according to the method of Noyes and Bray† often resulted in some confusion due to the fact that a magnesium compound of tellurous acid was precipitated which interfered with the test for arsenic and removed a considerable part of the tellurium.

The fact that the original hydrogen sulphide precipitate is decomposed by hydrochloric acid and potassium chlorate, and that this oxidation process would probably effect at least the partial oxidation of the tellurium to telluric acid, suggested the investigation of the formation of the telluric acid under these conditions and its effect upon the method. A number of experiments along this line seemed to show that after the treatment of tellurium with hydrochloric acid and potassium chlorate a mixture of tellurous and telluric acids resulted and that the ammonium tellurate gave a precipitate with magnesium chloride mixture as has been shown to be the case with ammonium tellurite. From these results we conclude that any attempt to remove tellurium from arsenic by this method is apt to yield doubtful conclusions. We therefore recommend that the tellurium be removed first by the method of Noyes and Bray, viz. precipitation of elementary tellurium by sodium sulphite in dilute hydrochloric acid solution in the presence of potassium iodide. The filtrate from the tellurium should be boiled to remove excess of sulphur dioxide, then treated with hydrogen dioxide, boiled to remove the greater part of the iodide and then made alkaline with sodium hydroxide and treated with more dioxide to oxidize the arsenic to arsenate. This solution is then acidified to destroy sodium hydroxide and made alkaline with ammonium hydroxide and treated with magnesium chloride mixture which precipitates the arsenate. The filtrate from the arsenate may be tested for molybdenum by potassium sulphocyanide and zinc in hydrochloric acid solution according to Noyes and Bray. This modification of the original method gave satisfactory results when used by a class of about forty.

\* Browning, this Journal, xl, 349, 1915.

† Jour. Amer. Chem. Soc., xxix, 137.

TABLE I.

*Test for Tellurium and Arsenic in Hydrochloric Acid Solution.*Treatment of solution with  $\text{Na}_2\text{SO}_3 + \text{KI}$ .

P. Te	F
Treatment by boiling to remove the $\text{SO}_2$ , by $\text{H}_2\text{O}_2$ to break up the iodide, by boiling to remove iodine, by excess of $\text{NaOH}$ and $\text{H}_2\text{O}_2$ to oxidize the arsenic to arsenate, acidifying to remove excess of $\text{NaOH}$ , by $\text{NH}_4\text{OH}$ and $\text{MgCl}_2$ , $\text{NH}_4\text{Cl}$ mixture, and filtration.	
P. $\text{NH}_4\text{MgAsO}_4$	F
Confirmation by $\text{AgNO}_3$ , forming red brown $\text{Ag}_3\text{AsO}_4$ .	Testing for Mo by $\text{KSCN}$ and $\text{Zn}$ in $\text{HCl}$ . Red $\text{Mo}(\text{SCN})_4$ .

TABLE II.

*Test for Iron, Thallium, Zirconium and Titanium Taken in the Form of Hydroxides.*

Solution of hydroxides in the least amount of  $\text{H}_2\text{SO}_4$ . Treatment with  $\text{H}_2\text{O}_2$ , a red coloration indicating titanium. Treatment with  $\text{Na}_2\text{HPO}_4$  in the presence of  $\text{NaOH}^*$  and addition of  $\text{H}_2\text{SO}_4$  to acidity.

P. $\text{ZrOHPO}_4$	F.
Treatment with $\text{NaOH}$ .	
P. Fe } as hydroxides } or phosphates	F.
Solution in $\text{H}_2\text{SO}_4$ . Treatment with $\text{Na}_2\text{SO}_3$ + $\text{KI}$ and filtration.	Treatment with $\text{H}_2\text{SO}_4$ , $\text{Na}_2\text{SO}_3$ and $\text{Na}_2\text{HPO}_4$ and filtration. P. $\text{TiOHPO}_4$ .
P. $\text{TlI}$	F.
Treatment by boiling (to remove $\text{SO}_2$ ), with $\text{H}_2\text{O}_2$ to break up iodide, by boiling to remove iodine, with $\text{KSCN}$ . Red coloration indicates Fe.	

\* This step is to prevent the excess of acid when sodium phosphate is added which interferes with the ready precipitation of zirconium phosphate. Gentle warming after the addition of the sodium hydroxide gives good results, but in no case should the solution be boiled, and if warmed it should be cooled and treated with hydrogen dioxide before acidifying with sulphuric acid.



## II.

The separation of iron in the ferric condition, thallium in the thallic condition, titanium, and zirconium is made by Noyes and Bray\* by dissolving the hydroxides in hydrochloric acid 1.12 sp. gr. and shaking the solution with ether; the ferric and thallic chlorides dissolving in the ether and the chlorides of titanium and zirconium being left in the water layer. The iron and thallium are separated by sulphurous acid and potassium iodide and the titanium and zirconium by sodium phosphate in the presence of hydrogen dioxide.

This method gives good results but is slow in manipulation and inconvenient and difficult to carry out successfully in the hands of a large class of students lacking experience in such procedures.

As a substitute we present the following method which has given satisfaction and rapidly obtained results:—

The hydroxides are dissolved in sulphuric acid and hydrogen dioxide added, a red coloration indicating titanium. The solution is then made faintly alkaline with sodium hydroxide and sodium phosphate is added. Sulphuric acid containing hydrogen dioxide is added to acidity, the latter reagent serving to keep the titanium in the higher condition of oxidation. The zirconium phosphate remains as a precipitate and is filtered off. After the zirconium is removed the filtrate obtained is treated with sodium hydroxide which precipitates the iron and thallium. After these are removed the alkaline filtrate containing the titanium is acidified with sulphuric acid and treated with sodium sulphite and a little more sodium phosphate, when the titanium phosphate appears. The precipitated hydroxides or phosphates of iron and thallium are dissolved in sulphuric acid, the solution treated with sodium sulphite and the thallic iodide precipitated by potassium iodide. The filtrate from the thallic iodide is boiled to remove sulphur dioxide, treated with hydrogen dioxide and again boiled to remove iodine and oxidize the iron, and then with potassium sulphocyanide to identify the iron.

\* Jour. Amer. Chem. Soc., xxx, 481.

ART. XI.—*The Separation of Vanadium from Phosphoric and Arsenic Acids and from Uranium*; by W. A. TURNER.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxxix.]

In a previous paper\* the determination of vanadium when present in the form of a soluble vanadate has been described. It seemed desirable to make use of this determination for separation of vanadium from some of the common impurities with which it is associated in nature. To this end separations from phosphoric and arsenic acids and from uranium have been attempted and the following pages are a record of these experiments.

In the separations from phosphoric and arsenic acids the procedure was exactly the same as in the simple determination of vanadium with the exception that the precipitates required a more thorough washing. This procedure is briefly as follows:

Portions of about 25 cm<sup>3</sup> of the metavanadate solution, accurately weighed, were diluted to about 150–200 cm<sup>3</sup>. The amount of phosphate or arsenate indicated was added and enough sulphuric acid to make about one per cent of the volume. Cupferron (the ammonium salt of nitrosophenylhydroxylamine) was then added in six per cent solution with stirring until a slight excess was present as shown by the appearance of a white precipitate of nitrosophenylhydroxylamine (formed when cupferron comes in contact with an acid solution). Two or three cubic centimeters in excess are added and the precipitate is filtered without delay and washed with a one per cent solution of sulphuric acid containing a little cupferron. The precipitate after being allowed to drain for a time on the filter is transferred to a platinum crucible, dried, ignited and weighed as vanadium pentoxide.

The vanadium used was a solution of ammonium metavanadate in distilled water which when standardized by the cupferron method gave the following result:

$$25 \text{ grms. NH}_4\text{VO}_3 \text{ sol.} \approx 0.1003 \text{ grm. V}_2\text{O}_5.$$

As sources of phosphoric and arsenic acids disodium hydrogen phosphate and disodium hydrogen arsenate were used. The precipitates were washed fifteen times.

The following table shows how successfully these separations can be accomplished:

Grms. NH <sub>4</sub> VO <sub>3</sub> sol. taken	Impurity added	Grms. V <sub>2</sub> O <sub>5</sub> found	Grms. V <sub>2</sub> O <sub>5</sub> per 25 grms. NH <sub>4</sub> VO <sub>3</sub> sol.	
			Found	Taken
25.0940	1.5 grms. Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	0.1008	0.1004	0.1003
25.0973	“	0.1006	0.1002	0.1003
25.0244	1.5 grms. Na <sub>2</sub> HAsO <sub>4</sub> ·12H <sub>2</sub> O	0.1006	0.1005	0.1003
25.0841	“	0.1007	0.1004	0.1003

\* This Journal (4), xli, 339, 1916.

The separation of vanadium from uranium presents greater difficulty and in fact as yet a good separation has not been accomplished. For this the same ammonium metavanadate solution used in the previous experiments served. As a source of uranium a solution of uranyl nitrate in distilled water was made. This solution, when standardized by the ammonium hydroxide method (in which ammonium uranate is precipitated by ammonium hydroxide in the presence of ammonium chloride, washed with a dilute ammonia solution containing ammonium chloride, ignited first in the Bunsen burner and then in the blast to  $U_3O_8$ ), gave:

25 grms. uranyl nitrate sol. = 0.1991 gm.  $U_3O_8$ .

When these vanadium and uranium solutions are brought together a yellow precipitate of uranyl vanadate is formed. If sufficient hydrochloric or sulphuric acid is added the precipitate will dissolve. The precipitate appears to be insoluble in ammonia.

It is necessary therefore in order to effect a separation of these elements to make the cupferron precipitation in a fairly strongly acid solution. In the experiments recorded about 10 cm<sup>3</sup> of sulphuric acid per 100 cm<sup>3</sup> of solution were used. The wash-liquid also was a sulphuric acid solution of about the same strength containing 1.5 grms. cupferron per liter.

Another expedient adopted to accomplish a more complete separation was to place filter and precipitate after thorough washing back in the original beaker, treat with ammonia (which dissolves the vanadium precipitate) then make nearly acid and cool to 20° before bringing to acidity. After dilution, acidification and the addition of a little more cupferron bring down the vanadium which after filtration and washing is obtained in fairly pure form.

The uranium in the filtrate was determined by the ammonium hydroxide method.

In this way the following results were obtained:

Grms. $NH_4VO_3$ sol. taken	Grms. $UO_2(NO_3)_2$ sol. taken	Grms. $V_2O_5$ found	Grms. $U_3O_8$ found	Grms. $V_2O_5$ per 25 grms. $NH_4VO_3$ sol.		Grms. $U_3O_8$ per 25 grms. $UO_2(NO_3)_2$ sol.	
				Found	Taken	Found	Taken
15.3903	25.1603	0.0683	0.2013	0.1109	0.1082	0.2000	0.1991
20.2137	20.2317	0.0905	0.1610	0.1119	0.1082	0.1990	0.1991
20.2757	19.0602	0.0904	0.1513	0.1115	0.1082	0.1985	0.1991

June 14, 1916.

ART. XII.—*Some Notes on Japanese Minerals*; by SHIM-  
MATSU ICHIKAWA.

I. *Natural Etching of Galena Crystals.*

GALENA crystals with rounded edges from Kuratani, Kaga Province, have been long known. Their rounded edges, however, have not yet been discussed in detail. In 1908 I also observed galena crystals with rounded edges from the Kamioka mine in Iida Province. The natural etching of galena crystals from the above localities is illustrated in the figures of the following plate (I).

Fig. 1 shows the natural etching of a galena crystal from Kuratani. The pits and elevations are given in detail in figs. 2 to 6.

Fig. 2 shows varieties of natural pits on an octahedral face, the three walls of the pit being parallel to the cubic faces. Fig. 3 shows pits on a cubic face, the sides being parallel to the octahedral faces. Fig. 4 shows natural elevations on a cubic face; the sides of these elevations are formed by the faces of an octahedron. Fig. 5 shows the relation between the outlines of the natural pits and the edges of the cubic faces. Fig. 6 gives the relation between pits and the cubic cleavage; the dotted lines of *ab*, *cd*, etc., are innumerable pits in the direction of the cleavage.

Fig. 7 shows the natural etching of a galena crystal, from the Kamioka mine; details are given in figs. 8 and 9.

In fig. 8 the pits and striations on the cubic and octahedron are shown much magnified. Fig. 9 shows the relation between outlines of the different pits and the edges of the octahedron.

Fig. 10 is a cubic crystal with rounded edges, also from the Kamioka mine. The etchings observed on a rounded solid angle are given in fig. 11 (compare fig. 4).

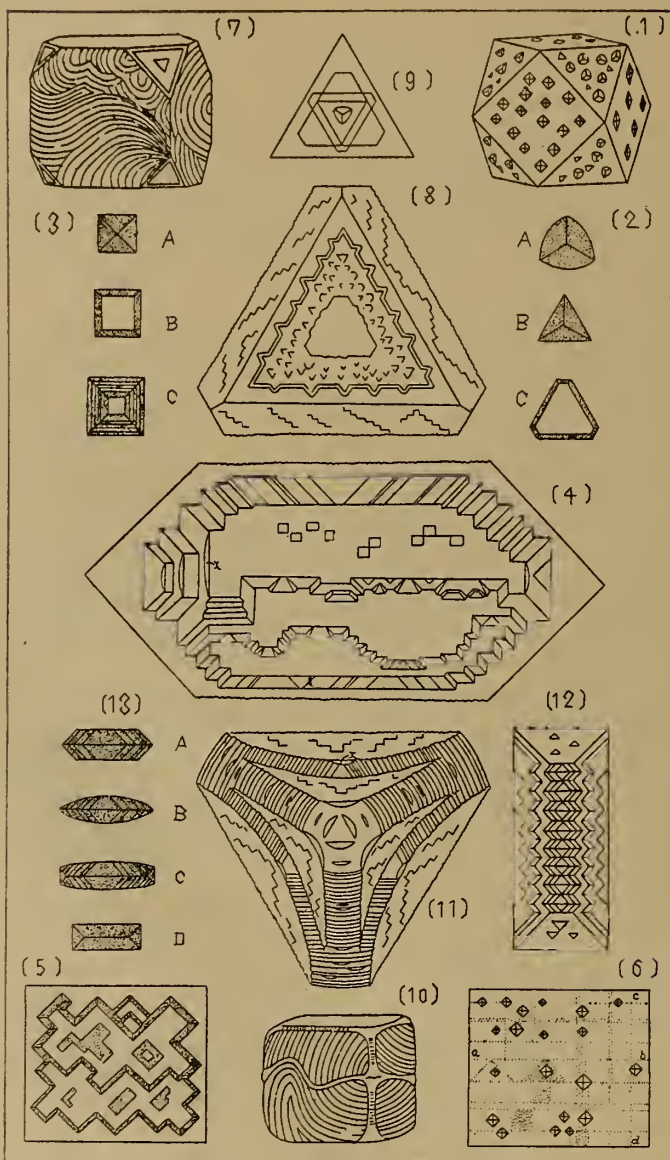
Fig. 12 shows the etchings on a rounded edge of a cubic crystal; and fig. 13 the various forms of natural pits on the rounded-edges of a similar crystal. Both of these are also from the Kamioka mine.

The symmetry of the etched figures on the above crystal faces corresponds to the symmetry of the group to which the given crystal belongs, and the resulting form in the etching is supposed to make up an octahedron (see figs. 4 and 11).

Fig. 1 is magnified 3 times; fig. 7, 1.5 times; fig. 10, 2 times; the other figures from 80 to 140 times.

Reference should also be made to Becker's results on galena crystals published in 1885. (*Min. petr. Mitt.*, vi, 237.)

I.



Natural etching of galena crystals. S. Ichikawa, del.



## II. Natural Etching of Calcite Crystals.

The natural etching of Japanese calcite crystals has already been described by Prof. K. Jimbo and Mr. F. Otsuki, but the etched figures on other faces (except  $mR$ ,  $-mR$ , etc.) and the forms resulting from the etching have not yet been described in detail. In 1907 I observed calcite crystals in Tertiary tuff from Shimoshijo, Shinyokoe-mura, Imatate-gun, Fukui-ken. Since then, I have repeatedly visited the same locality and collected additional crystals more etched than those before described. These specimens are illustrated in the accompanying figures 1 to 7 (II).

Fig. 1, A, shows a short prismatic crystal ( $-\frac{1}{2}R$ ,  $-mR$ ,  $\infty R$ ,  $mRn$ ,  $\infty P2$ , etc.) with natural etchings. B shows the rhombohedral elevations that are observed on the face  $-\frac{1}{2}R$ , in horizontal projection; here the pole-edges of the rhombohedral elevations are parallel with striations on the face  $-\frac{1}{2}R$ . C shows two elevations accompanied by rhombohedral elevations which are rarely found. D shows the relation between the outlines of the pit, striations, etc., and the edges of the faces  $\infty R$ . In the striations the angle BAC is nearly  $140^\circ$ . In the pits the angles are:  $AOB = 120^\circ$ ;  $BOC = 28^\circ$ ;  $COD = 45^\circ$ ;  $DOE = 90^\circ$ . E and F show a group of the pits on the faces of  $\infty R$ . The outlines of the figures A and B are magnified six times, but the pits themselves are magnified 80 to 140 times.

Fig. 2, A, is a long prismatic crystal with the same faces as fig. 1, A. B is a horizontal projection on the vertical axis of the crystal. The outline of the figure is magnified 7 times, but the pits 80 times.

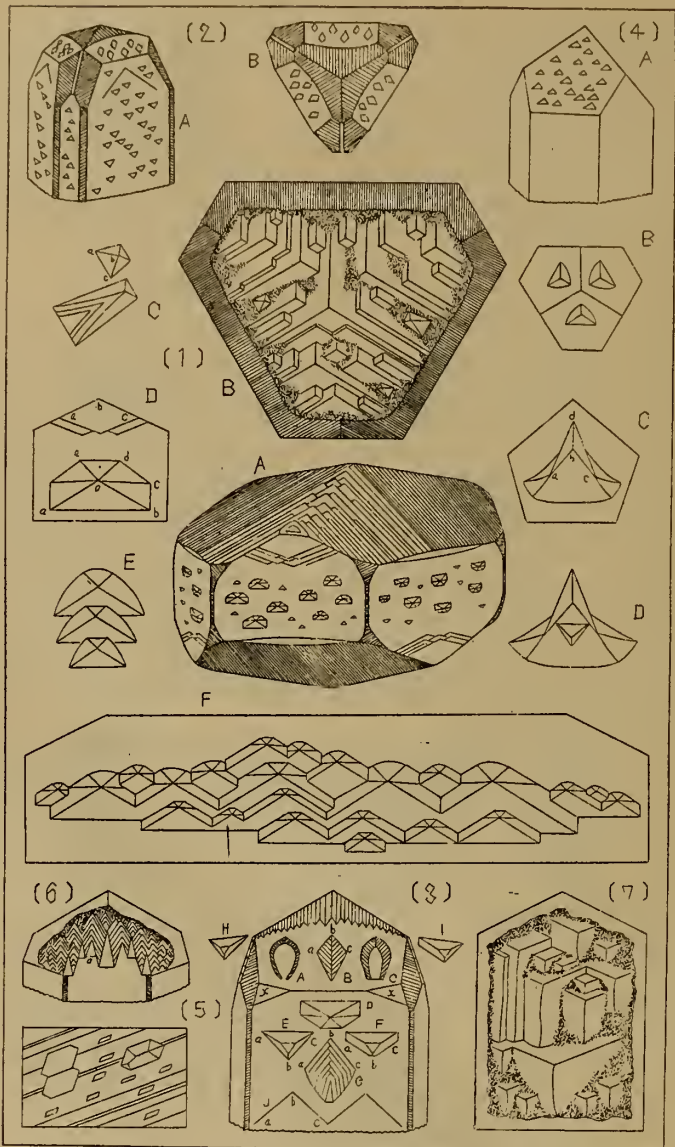
Fig. 3 shows various forms of natural pits on the faces  $-mR$ ,  $\infty R$ , etc., of the above crystals. On the face  $-mR$ , A and C are observed abundantly, but B is very rare. On the faces of  $\infty R$ , D, E, and F are observed abundantly, but G and J are very rare, the angles are:  $E(ABC) = 90^\circ$ ;  $F(ABC) = 110^\circ$ ;  $G(ABC) = 80^\circ$ ;  $J(ABC) = 100^\circ$ . On the face  $X(mRn?)$ , H and I are observed. On the faces  $-\frac{1}{2}R$ ,  $\infty P2$ ,  $mPn$ , etc., striations are usually observed. The outline of the figure is magnified 10 times, but the pits are magnified 80 to 140 times.

Fig. 4 shows natural pits formed on the rhombohedral faces ( $mR$ ) of a prismatic crystal. A is a front view. B is a horizontal projection on the vertical axis. C and D show pits on the rhombohedral face in horizontal position; the angles are:  $ABC = 80^\circ$ ;  $ADC = 40^\circ$ .

Fig. 5 shows natural pits and striations formed on a face of  $\infty P2$  (magnified 360 times).

Fig. 6 shows natural etchings on the solid angles between  $R$  and  $\infty R$ . The figure is magnified 9 times, the etched figures 140 times (angle A =  $30^\circ$ ).

II.



Natural etchings of calcite crystals. S. Ichikawa, del.

Fig. 7 shows rhombohedral elevations formed on a face  $\infty R$  of a short prismatic crystal more etched than fig. 1, A (magnified 70 times).

The symmetry of the etched figures on the above crystal faces corresponds to the symmetry of the group to which the given crystal belongs, and the form resulting from the etching is supposed to be a rhombohedron (see fig. 1, B; fig. 7, etc.).

For Meyer's results on calcite crystals see *Jahrb. Min.* I, 74, 1883; and for those of Lavizzari on a calcite ball etched with sulphuric acid see Naumann-Zirkel's *Elemente der Mineralogie*, p. 200, 1907.

The results of K. Jimbo on the natural etching of calcite crystals from Kitahama, Izumo Province, are described in *Jour. Geogr. Tokyo*, vol. vii. 226, 1899. Also those of F. Otsuki on the natural etching of calcite crystals from Sawadamura, Kamo-gun, Izu Province, in the same journal, vol. viii, 283, 1900.

### III. *Pinite: A Mica Pseudomorph after Cordierite in Trillings from Torihama.*

The trillings of Japanese cordierite crystals and their pseudomorphs have already been described by Prof. A. Kikuchi,\* B. Kotô,† K. Jimbo,‡ Mr. S. Hirose,§ and others. In these papers, however, the structures of the trillings in the crystals and their pseudomorphs have not yet been discussed in detail. In 1908 I personally visited Torihama, Ya-Mura, Mikata-gun, Wakasa Province, which has been long known as a locality of pinite, and collected a few weathered specimens of the mineral. The results of the study of these specimens are mentioned in the accompanying figures (III).

Fig. 1 is an individual of the pinite (natural size). A, shows a part changed into mica.

Fig. 2 shows the structure of the trilling in a section plate cut perpendicularly to the vertical axis of the pinite. The black portion shows the original substance of the cordierite; the remainder is the pseudomorphous mica; parallel lines show cleavage fissures changed into mica (magnified 2 times).

Figs. 3-4 show the structure of the trillings in basal sections; the specimens are wholly changed to mica. The white part in the figure shows micaceous substance, and the rest is an earthy substance produced by the decomposition of the mica (nat. size).

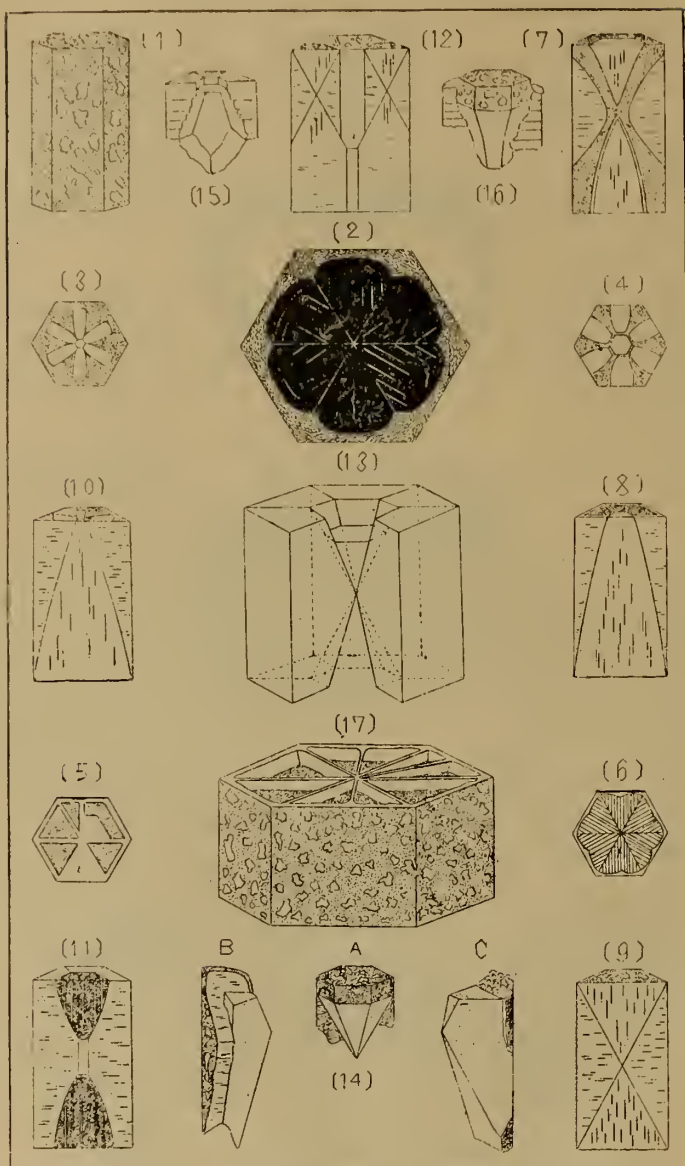
\* Cordierite from Watarasegawa, *Jour. Sci. Coll.*, vol. iii, 1890.

† Cordierite from Doshi, *Jour. Geogr. Tōkyō*, vol. xvi, 224, 1909.

‡ Cordierite pseudomorphs from Tsukuba, Torihama, Doshi, etc., *Beit. Min. Japan*, II, 62, 1906.

§ Cordierite from Sakuratenjin, *Jour. Geogr. Tōkyō*, vol. xxi, 66, 1904.

III.



Trillings of cordierite. S. Ichikawa, del.



Figs. 5, 6 are similar to fig. 2, but only fig. 6 shows the original cordierite-substance (nat. size).

Fig. 7 shows transverse and longitudinal sections of a pinite crystal. The outer part of each changed into mica, the wedge-shaped pieces look as if rounded or hollowed; parallel lines in each piece are cleavage fissure changed into mica (nat. size). Figs. 8 to 12 are the same as fig. 7, but the funnel-shaped portion in fig. 8 is more micaceous than the adjoining portions, and those in fig. 11 is opposite to the former (nat. size).

Fig. 13 is a model figure showing the natural composition of the trillings, separated into eight parts by weathering (magnified 2.5 times).

Figs. 14 to 16 show parts of the trilling separated by weathering, each piece consists of cordierite and the outer parts are somewhat changed into mica (nat. size).

Fig. 17 shows the weathering of a pinite, the radial mesenteries in the center seem to be the secondary sediment of silica which filled the fissures of the trilling and cleavage of the crystal (magnified 3 times).

In the above study, it is proved that the trillings in the cordierite crystals and the pseudomorphs are separated into eight parts by weathering, and also that each portion of the trillings is gradually changed into mica from the outside and their cleavage-fissures by weathering, till finally a completely micaceous pseudomorph results. The funnel-shaped pieces in the trillings are more rapidly separated or decomposed than the adjoining parts. In the entire micaceous pseudomorph, its cleavage is found in the direction of the basal face as mica, and it is easily cleaved by the finger-nail. The micaceous pseudomorphs are decomposed into earth at last.

#### IV. *On the Crystal-Aggregates of Native Arsenic.*

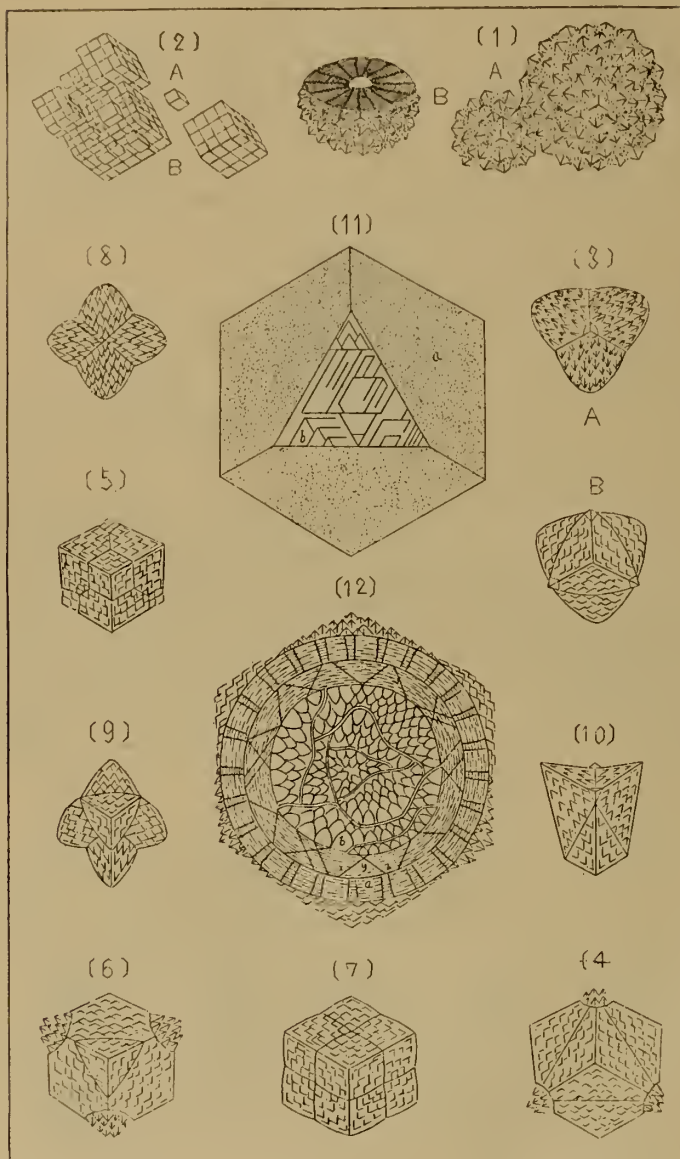
Native arsenic crystals from the Akadani mine, Shimoadinimura, Ono-gun, Prov. Echizen, have been long known by the name of "konpetoishi"; they occur in association with stibnite, realgar and minute crystals of pyrite; the country rock is a liparite. The mineral was first observed by N. Sasamoto,\* who also sent specimens abroad, where they have been examined and in part described. Since 1906 I have repeatedly visited Akadani and collected some interesting specimens showing the crystal-aggregates. A preliminary note has already been published;† the following gives fuller details. The varieties noted are:

\* Jour. Geol. Soc. Tōkyō, vol. ii, p. 461, 1895; see also two notes by T. Hiki, *ibid.*, vol. v, pp. 78 and 167, 1898, and vol. vii, p. 363, 1900; Mr. Wada's "Minerals of Japan," p. 26, 1904; Naumann-Zirkel's "Elemente der Mineralogie," p. 414, 1907.

† Jour. Geol. Soc., Tōkyō, vol. xvi, p. 197, 1909.



IV.



Crystal aggregates of native arsenic. S. Ichikawa, del.

*a.* Concentric radial aggregates about the principal axis of the rhombohedron forming a sphere, this form has long been known by the name of "konpetoishi," they measure 10 to 15<sup>mm</sup> in diameter (fig. 1.)

*b.* Parallel growth of numerous rhombohedrons forming cube-like forms, measuring 5 to 10<sup>mm</sup> in diameter (fig. 2.)

*c.* Complex penetration-twins of four individuals of the *b* type, of many interesting forms, measuring 5 to 10<sup>mm</sup> in diameter (figs. 3 to 10.)

*d.* Irregular-aggregates of the individuals of *b* measuring 20 to 30<sup>mm</sup> in diameter.

Simple rhombohedral crystals, 3 to 4<sup>mm</sup> in diameter, were also found attached to the vein-stone. In the above crystal-aggregates, *a* and *d* are found more frequently than *b*, but the *b* type is very rare.

When fresh, the arsenic is tin-white, but after half a day it is gradually tarnished to a dark color, and after six months becomes dark-gray by oxidation. When decomposed by long exposure to the air, the spherical aggregates sometimes naturally reveal the concentric zonal structure in their fracture, and the spongy structure in their outer part.

The crystal-aggregates, especially the irregular forms, sometimes enclose stibnite and minute crystals of pyrite; this is especially common with the irregular forms. Some specimens are also colored by orange-yellow realgar.

The microscopical structure in the fracture of spherical aggregates or complex penetration twins shows innumerable cleavages in the layers of the concentric zonal structure much resembling that of the bulb of a lily (ex. fig. 12.)

Native arsenic (so-called "konpetoishi") is said to have been recently observed also, in Kochi, Kawada-mura, Imatate-gun near the Akadani-mine.

The above papers, with the accompanying illustrations, were presented to the Twelfth International Geological Congress in Toronto, Canada, in August, 1913.

Kitashinjo-mura, Imitate-gun, Fukui-ken, Japan.

ART. XIII.—*The Algonkian-Cambrian Boundary East of the Green Mountain Axis in Vermont*,\* by T. NELSON DALE.

DURING parts of three summers, 1913–1915, the writer was engaged in tracing the boundary between the pre-Cambrian rocks of the Green Mountain range in Vermont and the Cambrian beds east of them. The work began on the south near Heartwellville, in Readsboro township, Bennington County (lat.  $42^{\circ} 50'$ ; long.  $73^{\circ}$ ), and ended on the north at the southern line of the town of Stockbridge in Windsor County (lat.  $43^{\circ} 42' 30''$ ; long.  $72^{\circ} 49'$ ), the whole latitudinal distance being a little more than 60 miles, of which, however, two stretches were not studied, reducing the distance to 46.7 miles. In this the boundary, measured along its meanders and sinuosities, is 57 miles long.

As many years will probably elapse before the geological mapping of this region is completed and the U. S. G. S. folios of it reach the public, the more important results of these explorations are here briefly outlined. These results concern the structure of the rocks and their origin and composition.

The recent geological literature of the region consists of two papers by C. L. Whittle and an abstract of a note by Arthur Keith.†

The gist of Mr. Whittle's papers is "that immediately below the Lower Cambrian quartzite in Vermont there is a series of more or less metamorphosed elastic rocks of no inconsiderable thickness; the upper member of this series being a dark chloritic mica schist; the lower member a highly metamorphosed conglomerate and between these several pebbly limestones and pebbly micaceous quartzite strata. . . . These rocks are referred to the Algonkian Period." Below the above series "a still older more metamorphosed and more variable series of stratified rocks of Algonkian age occurs, together with gneisses and schists whose origin is unknown, and abundant metamorphic equivalents of old basic rocks."

In his article in this Journal (p. 351) he thus refers to two divergent foliations. "Structurally we have stronger evidence furnished by a conglomerate gneiss at North Sherburne where an anti-clinal axis trending about  $25^{\circ}$  west of north represents

\* Published by permission of the Director of the U. S. Geol. Survey.

† Whittle, Ch. L., The occurrence of Algonkian rocks in Vermont and the evidence for their subdivision, *Journ. of Geol.*, vol. ii, pp. 396–429, 1894.

Whittle, Ch. L., The general structure of the main axis of the Green Mountains, this Journal, 3d ser., vol. xlvii, pp. 347–355, 1894.

Keith, Arthur, A pre-Cambrian unconformity in Vermont, (Abstract) *Geol. Soc. Am. Bull.*, vol. xxv, No. 1, pp. 39–40, Mch. 30, 1914.

the first period of disturbance; a later one induced in the rock the regional schistosity of the range striking N. 10° to 15° E."

The gist of Mr. Keith's note is that the Cambrian quartzite and conglomerate of Vermont unconformably overlies a great thickness of schist, dolomite, graywacke, quartzite and conglomerate and that "these older sediments bounded above and below by conglomerate and unconformities are properly classed as Algonkian."

*Structure.*—While at many points along this boundary the rocks on both sides of it appear to be conformable, at others the divergence between the strike of the foliation of the pre-Cambrian gneiss (and the bedding of the rocks associated with it) and that of the bedding of the Cambrian beds amounts to from 18° to 140°. The pre-Cambrian strike ranges from N. 30°–90° W., averaging N. 70° W. The Cambrian from N. 12° W. to N. 50° E., averaging N. 30° E.

These structural relations can be observed at the following points: In the town of Jamaica, in the deep E.–W. cut made by the West River, two miles north of Jamaica village, the granite-gneiss strikes N. 30° W. and the Cambrian micaceous quartzite a few hundred feet east strikes N. A mile south on the hill west of Ball Mountain the granite-gneiss strikes N. 40° W. and the quartzite near on the northeast strikes N. 20° E.

In the town of Andover, 12–15 miles north of the Jamaica cut, the granite-gneiss of the north and south humps of Terrible Mountain strikes N. 35° to 70° W., but the Cambrian schist along the east base of Terrible Mountain strikes N. 12° W., N. 10° W., N., N. 12° E.

In the town of Ludlow, 5 miles farther north, on the east side of Ludlow Mountain, where the boundary doubles over on itself for several miles, exposing a tongue of pre-Cambrian up to a mile in width, the granite-gneiss strikes N. 45°–90° W., but the Cambrian schist and quartzite east and west of the tongue strike N. 10° to 35° E.

In the town of Sherburne, 13½ miles further north, in the Falls Brook, at the falls two miles E.S.E. of Killington Peak, a pre-Cambrian arkose strikes N. 30°–40° W., but the Cambrian schist and dolomite a little east of it strike N. 40°–50° E. Six miles further north in the same town, 1¼ miles N.N.W. of Sherburne village, in a small tributary of the Ottaquechee River, pre-Cambrian quartzite and arkose strike N. 35°–40° W. but the Cambrian schist at the foot of the falls and also on the east side of the river strikes N. Two miles further north in the mass east of North Sherburne the pre-Cambrian granite gneiss strikes N. 57°–70° W. and various sedimentary rocks associated with it strike N. 30°–70° W., but the Cambrian schist east of them strikes N.



Another structural feature of the region is that the pre-Cambrian gneiss exceptionally has two foliations with strikes corresponding to that of the pre-Cambrian and Cambrian respectively. Thus on the east base of Ludlow Mountain some granite-gneiss ledges have coarse plications striking N. 50°-90° W. but a fine foliation striking N. 20°-30° E.

A pre-Cambrian conglomerate in North Sherburne consists of pebbles arranged in small beds in a schistose cement. The pebble beds strike N. 60° W. with the granite-gneiss but the slip-cleavage foliation of the cement strikes N. 10° W. with the Cambrian schist of the region.

A bed of quartzite 40-50 ft. thick, in the mass east of North Sherburne, has the typical pre-Cambrian strike of N. 70° W. but curves around sharply to strike N. 30°-50° E. with the Cambrian beds. The bending has resulted in much minor faulting. This occurrence indicates that the conformity of strike existing in so many places between the pre-Cambrian and Cambrian may be due to changes produced by the post-Ordovician movement in the pre-Cambrian structure.

*Origin and composition.*—The Cambrian rocks along the boundary studied include: metamorphic arkose, quartzite, albitic muscovite, and muscovite-biotite, also albitic-chlorite schist, and dolomite, both granular and twinned. The quartzite generally includes some beds of sericite schist. Black tourmaline is abundant and in places associated with pegmatite.

The pre-Cambrian rocks include various granite-gneisses, aplite gneiss, metamorphic arkoses, quartzite, conglomerate with pebbles of quartzite, albitic sericite schist and graphitic sericite schist. The age determination of these Algonkian sedimentaries is based entirely upon their strike being conformable to that of the underlying granite-gneiss and unconformable to the adjacent overlying Cambrian beds. Some of these Algonkian schists are petrographically identical with Cambrian and Ordovician ones of the Green Mountain region.

The arkose and quartzite conglomerate call for more detailed description. One of the marked types of arkose is a medium to dark grayish rock, in places with lighter grayish less micaceous bands. It consists of more or less angular grains of quartz, of multiple-twinned plagioclase, of microperthite, in places of microcline, in a cement of muscovite, chlorite, biotite and epidote with accessory zircon, apatite, pyrite, limonite. The quartzite conglomerate in North Sherburne measures roughly not less than 275 ft. in thickness and is separated from an underlying 40-50 ft. thick bed of quartzite by a hundred feet or more of albitic sericite-chlorite schist. At the contact  $1\frac{1}{4}$  miles N.N.W. of Sherburne village the Algonkian schist and arkose include two beds of quartzite, 10-15 and 3-10 ft. thick.



The pebbles of the North Sherburne conglomerate are nearly all quartzite and measure up to two feet in length and eight inches in width. Fig. 1 shows the form of these pebbles. Some of them seem to have been elongated in metamorphism. One from a loose block from the same ledge measures  $15 \times 4-6 \times 2\frac{1}{2}$  inches. The quartzite of these pebbles in thin section shows the presence of a little muscovite, chlorite, siderite passing into limonite, and grains of zircon. A section of

FIG. 1.

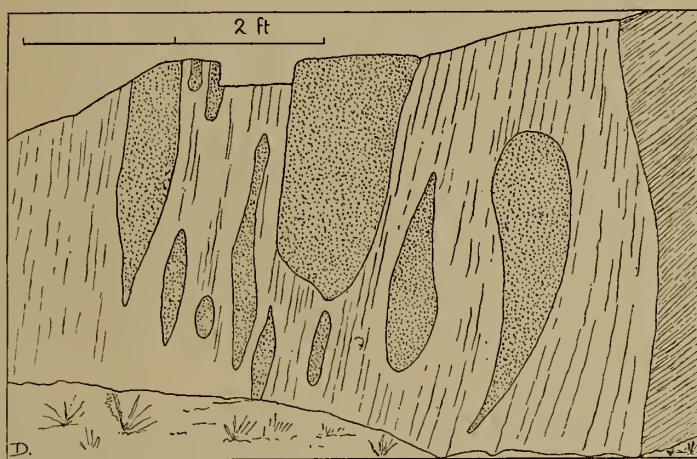


FIG. 1. Diagram-sketch of north side of an E.-W. joint in Algonkian conglomerate showing sections of quartzite pebbles. North Sherburne, Vermont.

the quartzite of the thick bed shows quartz grains much strained and granulated, and a little muscovite and chlorite, and limonite stain of uncertain source. There is thus no marked difference between the material of the pebbles and that of the bed. The cement of the conglomerate is muscovite-quartz-chlorite schist.

*Inductions.*—The original general strike of the pre-Cambrian granite-gneiss and the associated Algonkian sedimentaries in the southern 60 miles of the Green Mountain range in Vermont was probably about W.N.W. and was due to the direction of the post-Algonkian movement. The general strike in the same region of the Cambrian beds east of the pre-Cambrian was about N. 30° E., and was due to the direction of the post-Ordovician movement, but in many places the pre-Cambrian rocks yielded to the later crustal contraction and acquired a

general N.NE. strike. Some pre-Cambrian rocks show the effects of both crustal movements.

Wherever in the Green Mountain region both Cambrian and pre-Cambrian have a N.  $70^{\circ}$ - $90^{\circ}$  W. strike it must be due either to transverse folding in the course of the post-Ordovician movement, or, as surmised by Pumpelly, to compensatory movement due to the resistance offered by rigid granite masses.\*

If the prevalent strike at the close of Algonkian time here was W.NW. then the original orographic features of the Green Mountain region, or at least of the southern half of it, must have trended W.NW.-E.SE., and therefore wherever a ridge of pre-Cambrian rocks with this strike has this trend it may be regarded as a remnant of Algonkian physiography. The two mile long ridge in Andover and Weston, known as Markham Mountain, appears to be such an Algonkian mountain-remnant.

As, along the boundary studied, Cambrian rocks are in some places in contact with Algonkian ones but in others with various granite-gneisses, we must suppose in the latter places either: (1) Denudation in Algonkian time of the Algonkian land surface and the removal of the Algonkian sediments that had transgressed the pre-Algonkian gneisses, or else (2) the exposure of part of the land surface of Algonkian time which was transgressed by Cambrian sediments but never had been by Algonkian ones.

As the Algonkian conglomerate contains pebbles of quartzite and conformably overlies schist and quartzite this conglomerate should be regarded as "intra-formational," i. e., as resulting from the slight and temporary elevation of part of an Algonkian sandstone above sea-level but not from a general great unconformity. The metamorphism that altered the bedded quartz sandstone into quartzite must also have altered the sandstone of the pebbles of the conglomerate into quartzite; and this metamorphism must have been that which accompanied the post-Algonkian movement.

Since the completion of this paper the Bulletin of the Geol. Society of America for March, 1916, has appeared containing a brief abstract (p. 101) of a paper by C. E. Gordon, entitled "Some structural features in the Green Mountain belt of rocks." In this paper he refers to having observed in certain places an east-west trend in the foliation of the ancient gneisses.

Pittsfield, Mass., May 4, 1916.

\* See Pumpelly, Raphael, Geology of the Green Mountains in Mass. General structure and correlation. U. S. Geol. Survey, Mon. 23, p. 21, 1894.

ART. XIV.—*The Thermochemistry of Silicon; Heat of Combination of Silica with Water; by W. G. MIXTER.*

[Contributions from the Sheffield Chemical Laboratory of Yale University.]

THIS article contains experimental work by the writer and a review of the thermochemistry of silicon, which has been regarded as very uncertain. Some of it is undoubtedly good and some of the fundamental values from which others are derived are far from accurate. The writer's results are given first as they are used in discussing the work of others.

There is nothing in the literature bearing on the heat effect of  $\text{SiO}_2 + \text{Aq}$  except the heat of formation of  $\text{SiO}_2 \cdot \text{Aq}$ , 179.6 Cal. and of  $\text{SiO}_2$ , 191 Cal. These indicate that it is endothermic. The problem of finding the heat of union of silica with water is complicated since they do not combine directly and because molecules of silica are complex at temperatures required to dehydrate silicic acid. It is impossible to determine with an approximation to accuracy the quantity of heat required to separate a small quantity of water firmly held, but it appears practicable with silicic acid containing much water. Two methods have been tried, one by fusion with sodium peroxide with unsatisfactory results and the other by solution in hydrofluoric acid.

In order to learn whether or not silicic acid prepared at room temperature differs from that made at  $100^\circ$ , two preparations were made as follows: A solution of sodium silicate was added gradually to hydrochloric acid and the silicic acid which separated after a time was washed with water at room temperature. It was dried in the air, then by a current of dry air under diminished pressure passing through the powder, and in vacuo over oil of vitriol until the water content was reduced to 6.9 per cent.\* Another preparation was made by adding a solution of sodium silicate to an excess of hydrochloric acid and evaporating on a steam bath. The dry residue was moistened with acid and the silicic acid was washed with hot water. It was then left some time in a steam drying oven and then over oil of vitriol. It contained 8.0 per cent of water. The results on p. 126 show that the silica of silicic acid prepared at  $100^\circ$  is in the same molecular condition as that made at room temperature. Hence other lots of silicic acid were made by the second method, as it is somewhat simpler. The water content was found by the common method, heating finally over a large blast lamp to constant weight. The determinations of

\*Since gelatinous silicic acid dries to hard tough lumps it should be pulverized from time to time during the drying process in order to obtain a uniform product.

water were made either before and after the calorimetric tests of a preparation or with a portion weighed at the time of a test, since silicic acid with small water content gains weight rapidly in the air while that having much water may have lost some combined water in a closed vessel if the room is hot. For example, preparation A (Table II) contained 0.3 per cent of combined water and 0.2 per cent absorbed during the necessary exposure to the air. The term "silicic acid" is applied to all preparations having combined water.

The following are the results obtained with fusions of mixtures of silica or silicic acid, sodium peroxide and lampblack:

TABLE I.

Amorphous silica which was heated to a constant weight over a blast lamp: 1218, 1217, 1226: mean 1220 cal.

Silicic acid having

6.9 per cent of H <sub>2</sub> O	1316, 1307, 1301:	mean 1308 cal.
8.0 "	" 1302, 1341	" 1322 "
12.5 "	" 1386, 1390	" 1388 "
21.5 "	" 1230, 1402, 1310, 1204	" 1236 "

The reason for the wide variation in the last results is this. The silicic acid in the dry air of the mixture gives off water which reacts with the sodium peroxide. A thermometer placed in the last mixture before closing the bomb showed a slight rise in temperature. The silicic acids with 6.9 and 8.0 per cent of water have vapor pressures too low to affect the determinations. Any of the results may be low owing to a little silica left unchanged in a fusion which can not be determined since it would dissolve in the water solution of the fusion.

From the results with the silicic acids containing 6.9 and 8.0 per cent of water we have the equations

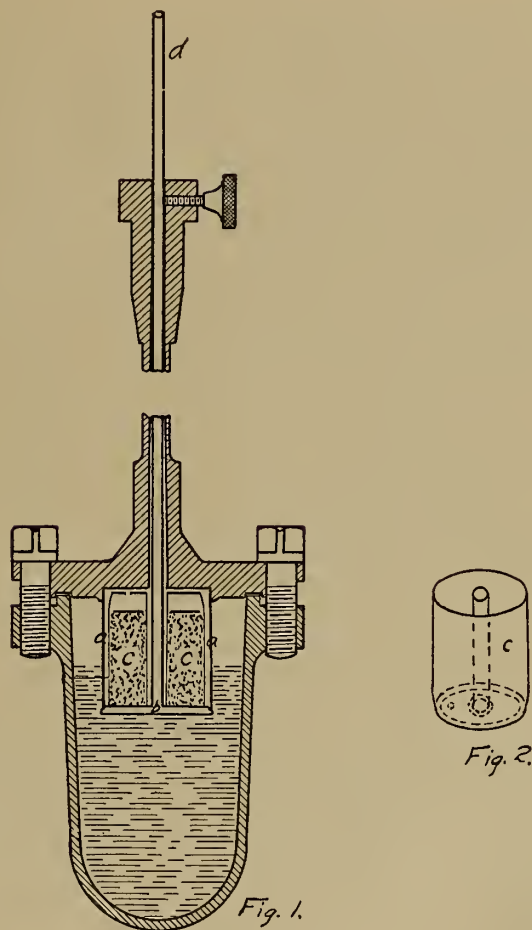
$$0.931x + 0.069y = 1308$$

$$0.92x + 0.08y = 1322$$

in which  $x = 1250$  and  $y = 2100$  cal., in which  $x$  equals the heat effect for 1 gm. SiO<sub>2</sub> and  $y$  is the heat effect for 1 gm. of water. The value for  $y$  is 200 cal. higher than the heat of the reaction of solid water, ice, with sodium oxide. These derived values are only approximations. They indicate, however, that little energy is required to separate water from silica. For the heat of polymerization of silica we have  $1250-1220 \times 60.4 = 1800$  cal. or about 2.0 Cal. This small value accords with the fact that silica does not glow when heated.

The apparatus in which silicic acid was dissolved in hydrofluoric acid is shown in fig. 1. It is an old sterling silver bomb with a new silver-plated brass top and fixtures. The disc *b* is held in place by the rod *d*. The cup *c*, shown better

FIGS. 1 AND 2.



in fig. 2, is made of thin sheet silver. The small hole in the bottom allows air to escape so that *c* may sink in the acid. The hole is covered by a disc of silver. The silicic acid for an experiment is placed in *c* which is closed by a cover not shown in the figure. The weight is taken and *c* is at once placed in *a*. The cover is removed and *a* is closed by *b* and the joint is made



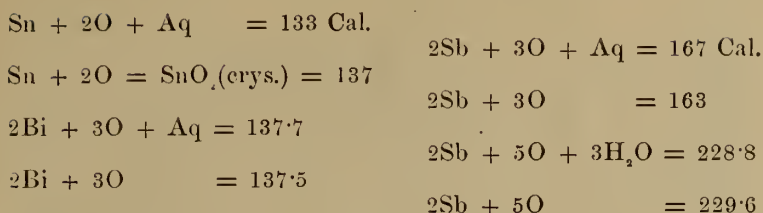
tight with bees-wax. The hydrofluoric acid is weighed in the open bomb and then the top is put on. After the preliminary observations of temperature in the calorimeter the disc *b* is pushed down, thus allowing the silicic acid and cup *c* to fall into the acid. The mixture is stirred by moving *d* and *b* up and down.

Hydrofluoric acid having a density of 1.079 and containing approximately 22 per cent of HF was used in the work. The specific heat of it was found by cooling about 200 g. in a platinum bottle in snow for hours, in one case over night, and then placing it in the calorimeter used for the work. Two determinations gave 0.80 and 0.81. The method is not a good one, but the result is sufficiently accurate for the work as shown by 0.994 found for the specific heat of water. The heat capacity of the hydrofluoric acid solution was so small compared to the total heat capacity, that an extremely accurate value is unnecessary. The calorimetric experiments were made under fairly uniform conditions and hence the results are comparable. One source of a small error was the undetermined specific heat of the solution of hydrofluosilicic acid.

The line *e* of Table II shows the heat effect of 1 g. of  $\text{SiO}_2$  if the water is combined with the silica without heat effect. These *e* values indicate that little energy is required to separate the water. The heat effect of 1 g. of  $\text{SiO}_2$  derived algebraically from the *d* values of B and C is 594 cal.; from E and F, 588; E and G, 587; F and G, 588 cal. Now the heat of combination of water in B is calculated thus:

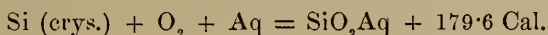
$592 - (594 \times 0.99) = 4$  cal. That is 4 cal. are required to separate 0.01 g. of water from 0.99 g. of silica and for 1 gram molecule, 7200 cal. Likewise we find that 7000 cal. are required to separate 18 g. of water in preparation C. These results are within the experimental errors, but they indicate that energy is required to separate the small quantity of water retained by silica at a red heat. The values found algebraically for the heat of solution of the silica in E, F and G in hydrofluoric acid are the same as the *e* values. This indicates that water is combined without heat effect in silicic acid containing 7.5 to 21.4 per cent. It should be understood that the silicic acid giving this result was made at  $100^\circ$  and may have contained capillary water. Such water would not affect the result essentially.

Silicon dioxide in its union with water with small or no heat effect resembles the anhydrides of weak metallic acids. The oxides given below are more or less polymerized, hence the difference between the heat of formation of an acid or hydroxide and that of a corresponding oxide is not in all cases the heat effect of the combination of water.



The heat of solution of 1 g. of silica in hydrofluoric acid found in experiments E, F and G, Table II, is 588 cal. or 35.5 Cal. for 1 gram molecule. (Si = 28.4.) Guntz\* obtained 33.6 Cal. (Si = 28.) Thomsen† found in the reaction of hydrofluoric acid on a solution of silicic acid that the heat effect rises regularly until eight molecules of acid are added and ceases with the tenth. With 6HF it is 32.3 cal. In the writer's experiments 12 to 17 HF were used to 1SiO<sub>2</sub>. It may be stated that anhydrous silica dissolves too slowly in hydrofluoric acid for a calorimetric test.

The heat of formation of silicic acid is most important, as other values may be obtained from it. Berthelot‡ derived from the heat of the reaction of SiCl<sub>4</sub> with water

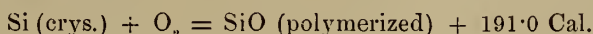


The only uncertain value used is that for the heat of formation of SiCl<sub>4</sub>. Troost and Hautefeuille§ burned impure amorphous silicon in chlorine and gave as the result 157.6. B corrected for an error in the water equivalent given by T and H for the mercury calorimeter used, and for Si (amor.) → Si (crys.) and states that



The heat effect of SiCl<sub>4</sub>(liq.) + Aq is, according to Berthelot, 69.0 cal. : to Thomsen, 69.3 Cal.

The heat of oxidation of silicon has been determined by two methods with fairly concordant results. The writer|| burned crystalline silicon, 99.95 per cent pure, carbon and silicon carbide in sodium peroxide, and the last two in oxygen, and from the results derived



von Wartenburg¶ burned amorphous silicon, containing 2.5 per cent of SiO<sub>2</sub>, in oxygen and from nine experiments obtained a mean of 194.9 Cal. ± 4.1 Cal. He also found by dissolving

\* Ann. Chim. Phys. (6), iii, 60.

† Ber. deutsch. Gesellsch., iii, 575.

‡ Thermochemie, II, 123 and 151.

§ Ann. Chim. Phys. (5), ix, 77.

|| This Journal, xxiv, 120, 1907.

¶ Nernst Festschrift, 459; Chem. Zentralblatt, 1912, II, 1095.



TABLE II.

	A		B		C		D	
	SiO <sub>2</sub> 99.5	H <sub>2</sub> O 0.5	SiO <sub>2</sub> 99.0	H <sub>2</sub> O 1.0	SiO <sub>2</sub> 98.2	H <sub>2</sub> O 1.8	SiO <sub>2</sub> 98.2	H <sub>2</sub> O 1.8
Substance (a) .....	3.406	3.540	2.677	2.691	3.003	2.890	3.261	3.457
Hydrofluoric acid, 22% HF .....	69	66	60	62	70	76	62	65
Water equiv. of system (b) .....	1357	1366	1366	1325	1315	1330	1345	1349
Temperature interval (c) .....	1.465	1.502	1.168	1.200	1.358	1.273	1.427	1.516
Observed heat effect, <i>b</i> × <i>c</i> .....	1988	2051	1585	1590	1786	1697	1919	2044
Heat effect of 1 g. of <i>a</i> .....	584	581	592	591	595	586	588	591
Average (d) .....		580	592	592	590	590	590	590
<i>d</i> ÷ % of SiO <sub>2</sub> (e) .....		583	598	598	601	601	601	601

	E		F		G		H		I		J	
	SiO <sub>2</sub> 92.5	H <sub>2</sub> O 7.5	SiO <sub>2</sub> 87.5	H <sub>2</sub> O 12.5	SiO <sub>2</sub> 78.6	H <sub>2</sub> O 21.4	D 74.5	ads. H <sub>2</sub> O 25.4	D 81.0	ads. H <sub>2</sub> O 19.0	D 83.4	ads. H <sub>2</sub> O 16.6
3.644	3.635	3.139	2.771	3.860	3.871	3.914	3.914	2.315	3.680	3.803	3.680	3.803
69	71	57	65	50	74	64	64	50	65	72	65	72
1502	1367	1300	1336	1330	1367	1341	1341	1329	1327	1343	1327	1343
1.497	1.446	1.240	1.223	1.345	1.306	1.259	1.259	0.804	1.303	1.352°	1.303	1.352°
1980	1977	1612	1634	1788	1785	1688	1688	1.069	1727	1807 cal	1727	1807 cal
543	544	513	516	463	461	431	431	462	470	478	470	478
544		515		462	462	431	431	462	474	474	474	474
588		589		588	588	578	578	570	568	568	568	568

A, Silicic acid heated 3 hours at about 1000°; B, Silicic acid heated about one hour at 800-900°; C, Silicic acid heated one day at about 500°; D, Silicic acid heated 6 days at about 400°; E, F, G, Dried at 100° and in desiccator; H and I, Weighed amounts of preparation D exposed in the silver cup of the calorimeter to air saturated with water vapor at room temperature; J, A thin layer of D was exposed as described, then thoroughly mixed. This treatment was repeated several times and then the substance kept in a tube closed with a rubber stopper. The adsorbed water was derived from the total loss on ignition, D containing 1.8% of water.

Evidently the values for hydrofluosilicic acid and silicon tetrachloride are subject to the uncertainty in the value for silicon tetrachloride from which the value for silicic acid is derived and also to the unestablished heat effect of  $\text{Si}(\text{crys.}) \rightarrow \text{Si}(\text{amor.})$ . Nevertheless the writer's results indicate that the thermochemistry of silicon, excepting the tetrachloride and silicic acid, is fairly well established.

Table II, under H, I and J, contain experiments with silica holding 1.8 per cent of combined water and considerable adsorbed water. The results indicate that more energy is required to separate adsorbed water and convert it into the liquid state than to melt ice. This is what would be expected. The molecular condition of adsorbed water has not been found. Such water is known to have a lower freezing point than ordinary water and Foote & Saxon\* have shown that it is different from combined water.

ART. XV.—*Composition of the Selensulphur from Hawaii*;  
by GLENN V. BROWN.

IN the course of an investigation of the chemical reactions of selenium, the writer had occasion to look up the occurrence of this element in nature. It is usually found combined in selenides of the heavy metals, but also occurs free, especially in volcanic regions. One of its most frequent forms is as an isomorphous mixture with sulphur, named selensulphur in the books on mineralogy. Selensulphur is classed by Dana† as a mineral species, No. 4, and is described as "an orange-red or reddish brownish mineral containing sulphur and selenium, but in unknown proportions." It seemed incredible that no quantitative analysis had ever been made of a mineral known since 1825 and reported to occur at a number of localities, yet such appears to be the case, for no analysis could be found in any available book on mineralogy or chemistry. On talking over the matter with Dr. Edgar T. Wherry, Assistant Curator, Division of Mineralogy and Petrology, United States National Museum, the writer learned that at least one authentic specimen of selensulphur was included in their collection, and through the kindness of Richard Rathbun, Assistant Secretary in charge of the Museum, a small fragment of this specimen was received for investigation. This specimen was collected

\* Jour. Am. Chem. Soc., xxxviii, 588, 1916.

† System of Mineralogy, 6th edition, 1892, p. 10.



by James D. Dana while mineralogist to the Wilkes Exploring Expedition at Kilanea in 1840.

The fragment (U. S. N. M. Cat. No. 12901) consisted of a slaggy, vesicular lava, almost a pumice in structure, impregnated with an orange-red to sulphur yellow crystalline mineral, and contained minute needle-like crystals in the cavities. It yielded the following reactions:

Before the blowpipe: Bluish flame, odor of burning sulphur plus the pungency and odor of burning selenium (suggesting scorching cabbage); residue reddish-brown, non-magnetic.

In closed tube: Sublimate, similar to that of pure sulphur; banded appearance while hot; on cooling, lower portion clear, light yellow merging into a darker, grayish upper portion. The yellow portion of the sublimate was insoluble in carbon disulphide, but readily soluble in bromine.

Qualitative analysis of the rock and mineral showed the presence of silicon, phosphorus, sulphur, selenium, iron, aluminium, titanium, calcium, magnesium, sodium and potassium. Tests on the largest amounts which could be spared failed to show even traces of tellurium or of arsenic.

The specimen was crushed to a coarse powder and the yellow to orange-red portions, high in selensulphur, were picked out. The selected material was then finely powdered, and amounted to 8.2 grams. Determinations were made of the specific gravity with a pyknometer, loss at 103°, sulphur content and selenium content.

The selensulphur was extracted from the finely powdered mixture of rock and mineral with bromine and the selenium determined by the method of W. Smith,\* as follows: the bromide of selenium was decomposed by the addition of successive small amounts of bromine water, the solutions were filtered and the selenium precipitated from the combined filtrates by potassium iodide and hydrochloric acid. The solution was then boiled to convert all of the selenium to its black modification, filtered through a Gooch crucible, the precipitate washed with hot water, and the selenium finally weighed as the element. In another portion of the mineral the sulphur was oxidized to sulphuric acid by fusion with sodium peroxide, the melt treated with hydrochloric acid and the insoluble residue filtered off. Upon boiling the solution, red selenium separated, and after standing over night the separation of the selenium was complete. The selenium was then filtered off, and the sulphuric acid in the filtrate precipitated and weighed as barium sulphate.

In determining the loss at 103° traces of sulphur and selenium were vaporized, as shown by the odor present when

\* *J. Ind. Eng. Chem.*, vii, 849, 1915.

the air bath was opened to remove the samples. The amounts lost were, however, too minute to cause appreciable difference in the determinations. The lava discarded as showing practically no selensulphur must have contained some as an invisible impregnation, for an analysis of this material showed selenium, 0.07 per cent, and sulphur, 3.32 per cent.

The composition of the handpicked sample is given in column 1, the same after deducting the material other than selenium and sulphur recalculated to 100 per cent in column 2, and the ratio of selenium to sulphur in column 3.

	1	2	3	
Loss at 103° (moisture) . . .	3.16%			
Sulphur . . . . .	12.44	94.82%	2.956	45.5
Selenium . . . . .	0.68	5.18	.065	1
Remainder (lava) . . . . .	(83.72)			
	<hr/>	<hr/>		
	100.00	100.00		

Specific gravity 2.378.

Alloys of sulphur and selenium containing from 35 to 66 per cent of the latter have been described,\* but the mineral selensulphur is here found to contain such a small amount of selenium that it can hardly be considered more than a variety of the main substance, sulphur. It is therefore suggested that "seleniferous sulphur" would be a more appropriate term than selensulphur to apply to this mineral.

Bucknell University, Lewisburg, Pa.

\* Browning, Introduction to the Rarer Elements, 2d ed., p. 145.

ART. XVI.—*Insects in Burmese Amber*; by T. D. A.  
COCKERELL.

I AM greatly indebted to Mr. R. C. J. Swinhoe, of Mandalay, Upper Burma, for the loan of some specimens of burmite, or Burmese amber, containing well-preserved insects. Mr. Swinhoe writes that "there is no reason to doubt that the stratum in which the amber is found is Miocene." Thus we have for the first time a record of Miocene insects from Burma; and it need hardly be said that this amber fauna, as it becomes better known, will prove of the greatest interest and importance for the understanding of insect evolution and migrations. The material now submitted, which will eventually be placed by Mr. Swinhoe in the British Museum, includes three species suitable for description, an Hemipteran, a Termite and a Psocid. In the Records of the Geological Survey of India (vol. xxv, Part 3, p. 130, 1892 and vol. xxvi, Part 1, p. 31, 1893), Dr. Fritz Noetling describes the occurrence of amber in Upper Burma, and gives particulars of the localities. The amber-bearing beds, which he considers probably lower Miocene, consist of a soft blue clay, which is superficially discolored brown. The amber appears to be limited to the upper part of this clay, and was certainly not produced where it is found, but must have been washed down the rivers to the sea, where the deposition of the clay was going on. In the same Records (xxv, p. 180) Dr. Otto Helm discusses the Burmese amber, and decides that it differs from all other fossil resins known to him. In the next volume (xxvi, Part 2, p. 61) he returns to the subject, and gives a lengthy account of the physical and chemical properties of the amber, for which he proposes the name Burmite. Burmite differs from succinite (Baltic amber) in lacking succinic acid; and is further distinguished by its hardness and toughness, its vivid colors, and its fluorescence. It resembles Sicilian amber in its frequently red color.

*Enicocephalus fossilis* n. sp. (Enicocephalidæ).

Dark brown; legs and antennæ dull ferruginous; wings dusky hyaline. Wings broadly rounded at end, extending some distance beyond tip of abdomen; discal cell closed. Form and structure of body, legs and antennæ essentially as in *E. culicis* Uhler, except in the following points: last antennal joint a trifle longer than penultimate; anterior tibiæ longer, much more slender basally; anterior tarsi with only one claw, which is long; hind tarsi longer and more slender. The following measurements are in microns: total length 3040; length

of beak 370; second antennal joint 496, third 352, fourth 368; base of anterior legs to base of antennæ about 800; length of anterior wing about 2080. This agrees with the type of the genus (*E. flavicollis* Westw.) in the closed discal cell and single claw on anterior legs. The venation is more complex than in the living species of which I have any information, and is therefore apparently more primitive. Possibly a distinct genus is indicated, but existing species differ greatly in venation, which also appears to vary a good deal within the species. The second vein from the stigma is rather weak, and appears

FIG. 1.

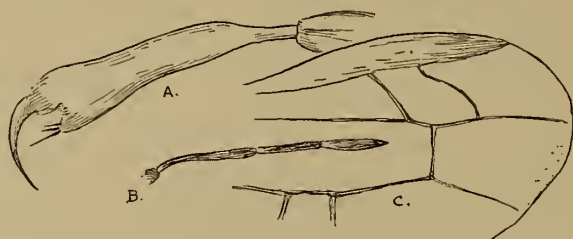


FIG. 1. *Enicocephalus fossilis*. A, anterior tibia, tarsus and claw; B, antenna; C, end of wing.

to represent a cross-vein proper. The closed quadrate cell below the discal cell appears to be a primitive character; it is found in *Scytinoptera* from the Permian, one of the Palæohemiptera. The species of *Enicocephalus* swarm in the air like gnats, so it is easy to see how they might be trapped in the resin forming amber. Handlirsch records no fossil species, but when Westwood originally described the genus in 1837 he included four species, of which two were from "gum animé," which I suppose to be copal, of posttertiary age. Ashmead remarked in 1892: "The genus is evidently an ancient phylogenetic type, now nearly extinct." The few living species are widely scattered over the world.

*Psyllipsocus* (?) *banksi* n. sp. (Psocidæ).

Black, with dark brown legs; wings ample, broad, extending far beyond abdomen, hyaline, spotless, without scales, the veins not hairy. Antennæ very long, and (except the base) excessively slender, thread-like. Anterior tarsi three-jointed, the first joint considerably longer than the other two combined, and having a row of short oblique bristles on its lower side. Hind tibiæ and tarsi very long and slender. Head large;

abdomen short. Venation of anterior wings: stigma with its lower side nearly straight, not bulging; radial sector forked below basal half of stigma; media with stem (after leaving radial sector) nearly straight, and with two forks as usual in related forms; fork of cubitus with the lower branch well-developed though short, directed downward to the margin. Hind wings with a cubital fork; the hind wings on the two sides

FIG. 2.

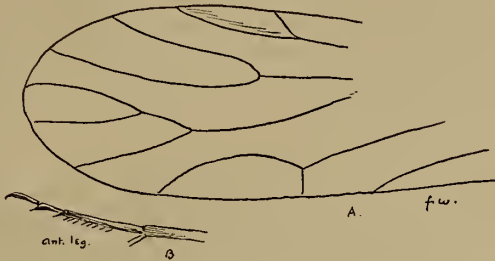
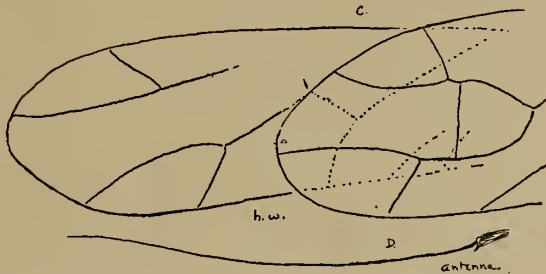
FIG. 2. *Psyllipsocus banksi*. A, anterior wing; B, anterior leg.

FIG. 3.

FIG. 3. *Psyllipsocus banksi*. C, hind wings of both sides; D, antenna.

have very different venation, as shown in the figures, one having a closed cell absent from the other. The following measurements are in microns: length, about 1600; length of anterior wing about 1840; width of anterior wing 720; length of anterior tarsus about 320; hind femur about 370; hind tibia 670; hind tarsus 465; length of stigma 340.

This minute insect could not be identified with any genus described from European amber or in the modern fauna in the scanty literature on Psocidæ at my command, so I sent a sketch to Mr. Nathan Banks, asking his advice. This he very kindly gives as follows: "The Psocid you figure must be close to



*Psyllipsocus* de Selys; that is the only one I know of with the hind wing showing a forked vein near hind margin. In the fore wing the media varies from two to three branched in the same species. In *Psylloneura* Enderl. the fore wing is just about the same, but hind wing has not the forked vein; in both, and other *Psyllipsocinae*, the stigmal vein is fairly straight." *Psyllipsocus* is a living European genus; *Psylloneura* was based in 1903 on a species from New Guinea, and no other species have been added since. *Psyllipsocus ramburi* is sometimes injurious in houses, according to Bertkau. The straight lower edge of stigma and the cubital fork of hind wing appear to be primitive characters. The fossil may be generically distinct from *Psyllipsocus*, but it seems best to provisionally refer it to that genus.

FIG. 4.

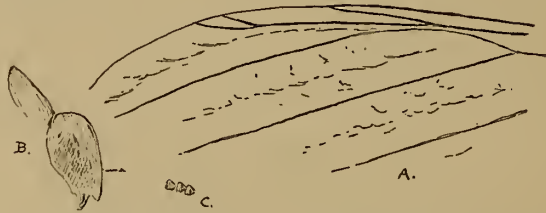


FIG. 4. *Termopsis swinhoi*. A, Costapical part of wing; B, side view of head; C, joints of apical half of antenna.

*Termopsis swinhoi* n. sp. (Termitidæ).

Length 3.8<sup>mm</sup>; black; wings about 4.5<sup>mm</sup> long, hyaline, with brown costa; head of moderate size, the face flat and vertex not conspicuously elevated; antennæ with the joints beyond the middle much broader and larger than those near the base; legs rather small; cerci small. Radius running close to costa, giving off two branches above, one very close to the end, the other not far from it. Media running very close to radius, and giving off oblique branches.

So far as can be seen, the structure of the wings resembles that of *Termopsis procerus* Heer (the type of *Termopsis*), from the Miocene of Croatia. The radius is however less complicated than in Heer's species.

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ART. XVII.—*The Preparation and Properties of Lead-Chlor Arsenate, Artificial Mimetite*; by C. C. McDONNELL and C. M. SMITH.

THE mineral mimetite, the composition of which as first shown by Wöhler in 1825 is  $3\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{PbCl}_2$  or  $\text{Pb}_4(\text{PbCl})(\text{AsO}_4)_3$ , was made artificially, first by Lechartier,\* and also by Michel,† by fusing together lead arsenate and lead chloride. Weinschenk‡ accomplished the same by heating a mixture of water, ammonium chloride, lead chloride and ammonium arsenate at a high temperature in a sealed tube. Its preparation in the wet way at ordinary temperature has never been recorded, although it was observed by H. Rose§ that when a solution containing arsenates and chlorides is precipitated with lead nitrate or acetate, “lead chloride is also precipitated with the lead arsenate and forms a double compound with the latter which cannot be decomposed by washing with a large volume of water.” The nature of this compound was not further studied by him and has apparently been overlooked by later investigators.

During an investigation of the arsenates of lead, while endeavoring to produce crystallized dilead arsenate ( $\text{PbHAsO}_4$ ), various media were tried as solvents. It was found that a boiling 40 per cent solution of ammonium chloride dissolved dilead arsenate to the extent of about  $\frac{1}{2}$  per cent of the ammonium chloride present. When such a solution was poured into a large volume of cold water a gelatinous precipitate was produced, which on analysis was found to contain 74.54 per cent  $\text{PbO}$  and 23.00 per cent  $\text{As}_2\text{O}_5$ , leaving 2.46 per cent unaccounted for. Qualitative tests revealed the presence of chlorine, and another sample of the material prepared in the same way, and washed free from soluble chlorides, was analyzed with the following results:

	Found	Theory for mimetite $\text{Pb}_4(\text{PbCl})(\text{AsO}_4)_3$
Lead oxide, $\text{PbO}$ .....	74.64%	74.97%
Arsenic pentoxide, $\text{As}_2\text{O}_5$ .....	22.81	23.18
Chlorine, $\text{Cl}$ .....	2.72	2.38
	<hr/>	<hr/>
	100.17	100.53
O, equivalent to Cl ... ..	0.61	0.53
	<hr/>	<hr/>
	99.56	100.00

\* Comptes Rendus, lxxv, 172, 1867.

† Bull. Soc. Min. de France, x, 133, 1887.

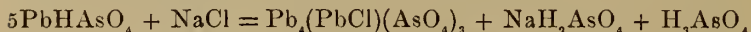
‡ Zeitschr. Kryst. Min., xvii, 489, 1890.

§ Ausführliches Handbuch der Analytischen Chemie, II, 406, 1851.

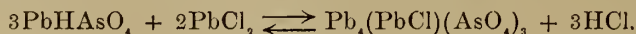
It was found that a chlor compound was also formed (slowly in the cold, and very rapidly on warming) when a mass of dilead arsenate was digested with ammonium, sodium or potassium chloride. Sodium chloride seemed to be particularly effective in forming a product of nearly theoretical composition. Two samples resulting from the digestion of dilead arsenate for 5 minutes at boiling temperature with (a) 2 per cent and (b) 10 per cent sodium chloride\* solutions analyzed as follows:

	a	b
Lead oxide, PbO .....	74.75%	74.56%
Arsenic pentoxide, As <sub>2</sub> O <sub>5</sub> .....	23.25	23.39
Chlorine, Cl .....	2.39	2.39
	100.39	100.34
O, equivalent to Cl .....	0.54	0.54
	99.85	99.80

These transformations are accompanied by the solution of 40 per cent of the total arsenic in the dilead arsenate,† the supernatant liquid showing a distinct acid reaction toward methyl orange. The reaction may be expressed by the following equation:



A particularly interesting reaction is that between dilead arsenate and a solution of lead chloride, which substances were found to react readily on warming, giving a solution containing free hydrochloric acid and a residue corresponding closely to theory for mimetite. This may be expressed by the following reaction:



In all of these reactions we have the rather strange phenomenon of the transformation of one lead arsenate into a *more basic* one with liberation of a strong acid.

\* Dilead arsenate boiled for about 5 hours with solutions of potassium bromide, potassium iodide or sodium fluoride (35 grams to 1 l.) gave products similar in composition. The bromine compound contained 5.79 per cent Br (theory 5.22) and 21.92 per cent As<sub>2</sub>O<sub>5</sub> (theory 22.51); the iodine compound 23.57 per cent As<sub>2</sub>O<sub>5</sub> (theory 21.84); and the fluorine compound 23.71 per cent As<sub>2</sub>O<sub>5</sub> (theory 23.44). The reaction with KI apparently did not proceed as rapidly as the others, and did not go to completion during the time of the digestion.

† It was noted by Headden (Colorado Agricultural Experiment Station Bulletins, 131, 22, 1908; 157, 30, 1910), and by Haywood and McDonnell (Bur. Chem. Bull. No. 131, 46, 1910), that water containing sodium chloride extracts a greater amount of arsenic from commercial lead arsenates than does pure water. This also explains why greater injury to foliage occurs when lead arsenate is applied with water containing chlorides in solution, as has been shown by the latter authors (*ibid.*, p. 49).

The precipitates resulting from the preceding experiments, when examined under the microscope, were seen to consist in the main of amorphous material, but many crystals were observed, usually small prismatic forms, apparently hexagonal, though too small for definite determination. After many attempts, we were successful in obtaining crystals sufficiently large to permit of the determination of their optical properties. Uniformly crystalline material was first obtained by dissolving pure dilead arsenate in hydrochloric acid (30° of concentrated acid to 860° of water) adding ammonia until a precipitate was just about to form and then pouring the solution into 10 liters of cold water. A precipitate formed immediately and when examined with the microscope was found to consist mostly of very small crystals with numerous long prismatic ones, apparently hexagonal prisms doubly terminated by pyramids of the same order, or a combination of the pyramid and basal pinacoid. Two such preparations were made and gave when analyzed the following results :

	a	b
Lead oxide, PbO .....	75.06%	74.83%
Arsenic pentoxide, As <sub>2</sub> O <sub>5</sub> .....	25.84	22.76
Chlorine, Cl .....	2.66	2.96
	<hr/>	<hr/>
O, equivalent to Cl .....	100.56	100.55
	60	67
	<hr/>	<hr/>
	99.96	99.88

Considerably larger crystals (see fig. 1\*) were obtained by treating a solution of PbHAsO<sub>4</sub> in dilute hydrochloric acid with lead acetate to incipient precipitation and allowing it to cool to room temperature. In one such preparation many crystals were obtained .07 by .01<sup>mm</sup>, while a few measured .13 by .03<sup>mm</sup>. The chlorine content of products prepared in this way varied from 2.52 to 2.83 per cent.

When lead-chlor arsenate crystallizes from a solution containing hydrochloric acid it is sometimes accompanied by dilead arsenate or lead chloride. In one case crystals of all three compounds were obtained from the same solution.

Dilead arsenate is slightly soluble in concentrated sodium chloride solutions (probably because of the acid liberated) but only a few crystals were obtained from a solution of 150 grams of salt in 500° of water, which had been boiled in contact with dilead arsenate for one hour and the clear filtrate allowed to

\* Photomicrographs made by G. L. Keenan, micro. analyst, Bureau of Chemistry.

cool. However, by first adding arsenic acid to the boiling salt solution, followed by lead acetate just short of a permanent precipitate and allowing the solution to cool, a slightly greater precipitate was obtained. The crystals so produced differed from those obtained from dilute hydrochloric acid solutions in that they were terminated by pyramids of the second order (fig.

FIG. 1.

FIG. 1. Lead-chlor arsenate, artificial mimetite ( $\times 234$ ).

2). Sodium and potassium chlorides were the only media from which crystals with pyramids and prisms of different order were obtained. A few attained the dimensions  $.06 \times .04^{\text{mm}}$ .

The filtrate from the experiment just described was kept at about  $15^{\circ}\text{C}$ . for 5 weeks, when a mass of sodium chloride containing a small amount of lead-chlor arsenate had separated out. The salt was removed by washing with water and the lead-chlor arsenate remaining was examined with the microscope. It consisted of small crystals, showing no abrupt transition from lateral to end faces, resembling prolate spheroids.



Crystals of this form are very frequent when produced by slow growth. They resemble more nearly natural mimetite, which rarely shows clear cut crystals but almost always characteristic "barrel-shaped" forms.

In the preceding experiments the resulting products in every case (except where dilead arsenate was transposed by boiling

FIG. 2.

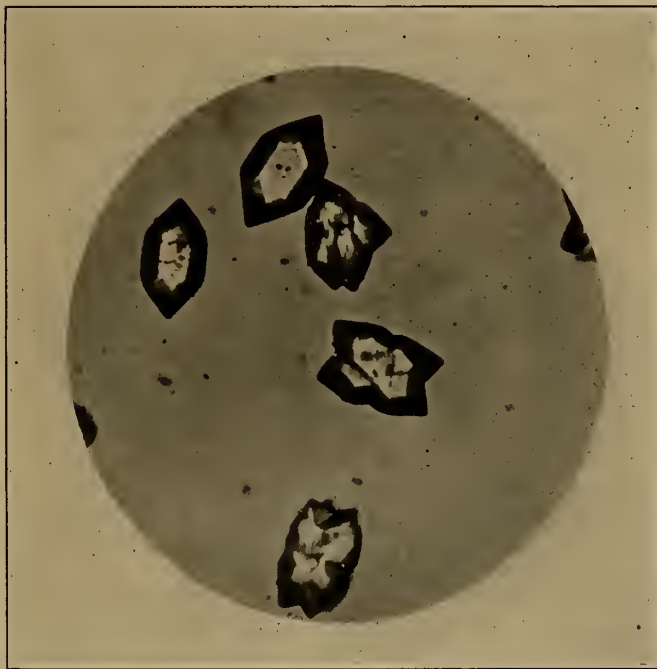


FIG. 2. Lead-chlor arsenate, artificial mimetite ( $\times 238$ ).

with sodium chloride solutions) contained chlorine in excess of the theoretical amount for mimetite.\*

\* This suggested that there might be other lead-chlor arsenates containing relatively more lead chloride. In fact a natural mineral (Georgeadisite) has been reported (*Comptes Rendus*, cxlv, 783, 1907) the analysis of which corresponds to the formula  $Pb_3(AsO_4)_2 \cdot 3PbCl_2$  or  $(PbCl)_3AsO_4$ . We have succeeded in producing another compound of this class, having a chlorine content of 3.4 per cent, which is referred to later, and evidence of a third containing about 4 per cent.

A lead-chlor arsenate is formed by double decomposition between dilute solutions of di- and trisodium arsenates, or even arsenic acid, and lead chloride, and also when dilute solutions of sodium and potassium dihydrogen

It was found, however, that a product of practically theoretical composition was obtained by diluting a boiling saturated solution of sodium or potassium chloride, to which had been added arsenic acid and lead acetate, with a small amount of boiling water: To 2000<sup>cc</sup> saturated sodium chloride solution at boiling temperature were added approximately 30 grams of arsenic acid, then lead acetate solution until a permanent precipitate remained, filtered and added 600<sup>cc</sup> of boiling water to the clear filtrate. A precipitate formed almost immediately and settled rapidly, leaving a clear solution. This was decanted after a few minutes and the precipitate washed by decantation with boiling water until no reaction for chlorine was obtained in the wash water. The precipitate recovered weighed 4.8 grams and consisted of beautiful crystals similar in appearance to those shown in fig. 2. In size they averaged about  $\cdot 015 \times \cdot 01 \text{mm}$ , but some were observed as large as  $\cdot 10 \times \cdot 05 \text{mm}$ .\*

Analysis:

Lead oxide, PbO.....	73.90%
Sodium oxide, Na <sub>2</sub> O.....	.64
Arsenic pentoxide, As <sub>2</sub> O <sub>5</sub> .....	23.18
Chlorine, Cl.....	2.46
	100.18
O, equivalent to Cl.....	0.55
	99.63

arsenates are added to lead chloride. However when a solution of lead chloride is added to sodium or potassium dihydrogen arsenate, the latter remaining in excess, dilead arsenate is formed. A chlor arsenate will be precipitated by lead acetate or nitrate from a solution of disodium arsenate containing sodium chloride.

\*The same compound was formed, but in much smaller crystals, when the boiling saturated sodium (or potassium) chloride solution, prepared as described, was added quickly to three to six times its volume of boiling water. However, when a portion of the same solution was added, at boiling temperature, to five times its volume of *cold* water (28–30° C.), a crystalline precipitate was produced which analyzed:

Lead oxide, PbO.....	73.80%
Sodium oxide, Na <sub>2</sub> O.....	.32
Arsenic pentoxide, As <sub>2</sub> O <sub>5</sub> .....	22.30
Chlorine, Cl.....	3.42
Water (expelled on ignition).....	.97
	100.81
O, equivalent to Cl.....	0.77
	100.04

This corresponds closely to the formula:  $2\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}$ , or  $\text{Pb}_5(\text{PbCl})_2(\text{AsO}_4)_4 \cdot \text{H}_2\text{O}$ . This experiment was repeated a number of times and always resulted in the production of this compound, which differs from mimetite in containing a greater proportion of lead chloride and also a small amount, apparently one molecule, of water of crystallization.

Compounds prepared in this way from saturated sodium chloride solutions generally contained a small amount of sodium, replacing, apparently, an equivalent amount of lead.

The following physical properties of the artificial mimetite, prepared as just described, were determined:

*Color.*—In bulk this material had a slight yellow tint, but the color varied with the different preparations, which suggests that it is probably due to traces of impurities.

*Specific Gravity.*—7.15 at 15° C. (determined by the use of a 10<sup>cc</sup> specific gravity bottle with 4 grams of material and water as the medium). This agrees with the value for the natural mineral, which according to Dana\* varies from 7.0 to 7.25.

*Optical Properties.*†—Parallel extinction, apparently uniaxial (if biaxial the axial angle is very small); approximate refractive indices,  $\epsilon = 2.13$ , and  $\omega = 2.16$ , and therefore optically negative. These observations and the general form of the crystals indicate that they belong to the hexagonal system.

It will be noted that the artificial mimetite which we have prepared is, in so far as we have been able to determine from the examination of a number of preparations, uniaxial. Natural mimetite, the occurrences of which, as stated by Clarke,‡ indicate formation by hydrochemical reactions, is generally biaxial. Specimens from Johannegeorgenstadt, examined by Bertrand,§ had an axial angle in air of 64°. Jannettaz|| found an axial angle of 39° in air on a specimen from the same locality. A variety of uniaxial mimetite has been reported by Jeremejew.¶ The optical properties of the artificial mimetite prepared by Lechartier, Michel and Weinschenk are not recorded. The anomalous optical behaviour of natural mimetite may be due to the presence of other chlor arsenates such as we have here briefly referred to. We have not been able, however, to prepare any of the higher chlor arsenates in sufficiently large crystals to determine their optical properties.

Insecticide & Fungicide Laboratory,  
Bureau of Chemistry, Washington, D. C.

\* System of Mineralogy, 6th ed., p. 772, 1892.

† Determinations made by F. E. Wright, Geophysical Laboratory, Carnegie Institution of Washington.

‡ U. S. Geological Survey Bull. No. 616, p. 682, 1916.

§ Bull. Soc. Min. de France, iv, 36, 1881; v, 254, 1882.

|| Ibid., iv, 39, 1881.

¶ Verh. Russ. min. Ges., (2), xxii, 179, 312, 332, 1886; through Zeitschr. Kryst. Min., xiii, 193, 1888.

ART. XVIII.—*The Effect of a Magnetic Field on the Initial Recombination of the Ions Produced by X-Rays in Air* ;  
by G. E. M. JAUNCEY.

§ 1. *Introduction.*

ASSUMING a given number of ions to be distributed uniformly throughout a gas and using the known coefficient of recombination and the known mobilities of the ions, the saturation voltage can be calculated for an ionization chamber of known dimensions. This calculated saturation voltage is much less than the observed saturation voltage when the gas is ionized by  $\alpha$ -rays. It, therefore, appears that ions, produced by  $\alpha$ -rays, recombine at an abnormally high rate when first formed. This abnormal recombination is known as initial recombination.

The generally accepted explanation of this fact is that conditions are abnormally favorable for recombination along the path of an  $\alpha$ -particle where the ions are much crowded together.

W. H. Bragg\* has pointed out that the recombination of ions may be complicated or influenced by the fact that when a pair of ions is first formed the ejected electron may not have sufficient velocity to break away from the parent atom and a strong electric field would tend to complete this incipient ionization. Thus one effect of the electric field would be to actually increase the rate of formation of ions and under these conditions there may be no such thing as saturation voltage. A gas ionized by X-rays shows to a small degree the effects of initial recombination. In this case the excessive density of the ions in the region of formation cannot be used as an explanation for initial recombination. The only available explanation seems to be the above hypothesis of Bragg.

If a magnetic field is applied to a gas ionized by X-rays then the electron which is ejected from an atom by means of the ionizing agent will follow a curved path and will therefore remain for a longer time near the parent atom and so there will be a greater chance of it being drawn back into the atom.

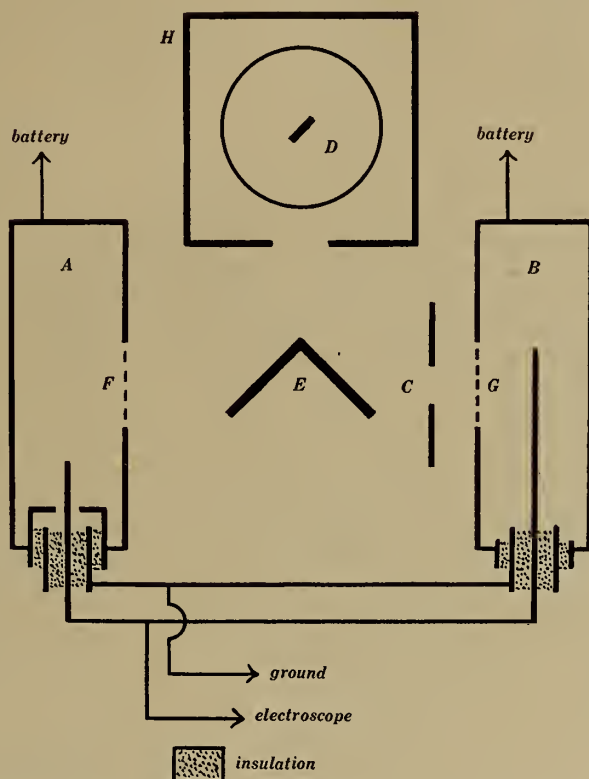
Furthermore Bragg in his "Studies in Radioactivity" cites many experiments which support the hypothesis that a gas is not to any great extent directly ionized by the X-rays but by the secondary high-speed cathode rays which are produced by the direct action of the X-rays. In contradiction to this, Kleeman† concluded from one of his experiments that as much as half the ionization in an air-filled chamber was due to the

\* Studies in Radioactivity, p. 73.

† Cambridge Phil. Soc., Proc. 15, pp. 169-177.

direct action of  $\gamma$ -rays on air. In this experiment Kleeman passed the  $\gamma$ -rays from radium through an aluminium plate and then through a window of thin paper into an ionization chamber, the distance between the aluminium plate and the paper window being a few centimeters. On applying a magnetic field to the space between the plate and the window

FIG. 1.



Kleeman found that the ionization in the chamber was decreased to about 55 per cent of its original value. The magnetic field deflected the secondary  $\beta$ -rays produced in the aluminium so that these  $\beta$ -rays no longer entered the ionization chamber.

It seems, therefore, that Kleeman's conclusion is invalid. The secondary  $\beta$ -rays which are scattered from the atoms of the gas in the ionization chamber are not, according to Bragg,\* prevented from producing ionization by a magnetic field.

\* "Studies," p. 166.



The present work was undertaken with the object of testing the direct effect of a magnetic field on the ionization current in air at atmospheric pressure when the applied voltage is either above or below the saturation voltage.

§ 2. *Experiment I. Voltage above Saturation.*

Homogeneous secondary X-rays from copper were used. Fig. 1 shows the connections. Primary X-rays from the X-ray tube D, which was enclosed in the lead box H, fell upon the sheet of copper E which was bent into the shape of a V. This copper was caused to emit secondary X-rays, part of which entered the chamber A through the paper window F and part entered the chamber B through the slit C and the paper window G. The ionization chamber A was placed between the poles of an electromagnet and the other chamber B was outside the magnetic field. The opening of the slit C could be varied by means of a micrometer screw. The ionization chamber A was connected to a positive and the chamber B to a negative voltage or vice versa, the voltage being such as to give the saturation current for both chambers. The inside electrodes of both chambers were connected together and to a Wilson tilted electroscope as shown. The chamber A was made of lead, the inside being coated with paper in order to cut out the effect of secondary cathode rays from the lead. The dimensions of A were  $7.5 \times 2.30 \times 1.0$  cm<sup>3</sup>, the X-rays entered through a window  $1.0 \times 1.5$  cm<sup>2</sup> and travelled for a distance of about 2.3 cms. in the chamber. The inside electrode was a wire which could be extended to various lengths along the middle line of the chamber A in order to vary the saturation voltage. With this arrangement the reading of the slit opening when there was no deflection of the electroscope was taken as a measure of the ionization current in the chamber A. Any variation in the primary X-rays produced proportional changes in the total ionization in the two chambers and thus any fluctuation in the strength of the primary X-rays was compensated. The electromagnet being necessarily near the X-ray tube, the bright spot on the anti-cathode was deflected by the magnetic field. This was partially overcome by means of a compensating magnet. The strength of the magnetic field was found by means of an exploring coil and a ballistic galvanometer in the usual way.

In this experiment the effect of a magnetic field on the total ionization produced by X-rays was examined. The results are shown in Table I.

This table shows that the magnetic field, and consequently the bending of the secondary cathode rays into curvilinear paths, does not alter the total ionization produced in a gas by X-rays.

TABLE I. EXPERIMENT I.

Ionizing agent	: Homogeneous X-rays from copper	
Strength of magnetic field	: 4200 gauss	
Gas ionized	: Air at atmospheric pressure	
Voltage across the ionization Chamber A	Ionization Current (slit readings)	
	Without magnetic field	With magnetic field
Above saturation voltage	641	631
	627	629
	634	621
	637	637
	Mean .... 635	Mean .... 629

§3. *Experiment II. Voltage below Saturation.*

The compensation arrangement of Experiment I was abandoned because the saturation voltage was less than 7 volts which was too low and because a compensation method is not desirable when the voltage-current relation is being determined, the shape of the curve depending upon the absolute value of the ionization-current.

In this experiment primary X-rays entered the lead chamber A directly, the distance between the electromagnet and the X-ray tube being such that the bright spot was not noticeably deflected by the magnetic field. The reciprocal of the time for a given deflection of the gold leaf of the electro-scope was taken as a measure of the ionization current.

In this experiment the effect of a magnetic field on the relation between the voltage and the ionization current was examined. The results are shown in Table II.

TABLE II. EXPERIMENT II.

Ionizing agent	: Primary X-rays		
Strength of magnetic field	: 4200 gauss		
Gas ionized	: Air at atmospheric pressure		
Voltage across chamber	Ionization Current		
	Without magnetic field	With magnetic field	With magnetic field (corrected values)
15.0	52	---	---
22.5	79	80	77
45.0	141	148	142
67.5	180	199	191
120.0	250	268	257
187.5	310	324	310

In this table each of the values of the ionization current in columns 2 and 3 is a mean of four or five readings, which were taken alternately with and without the field. It is seen that in the given set of readings the ionization current was always slightly greater with the field than without. By changing the positions of the bulb this effect could be reversed, thus showing that the effect is probably due to the field having a small action on the cathode stream in the X-ray tube. When 187.5 volts was put across the chamber the reading was 310 without the field and 324 with the field. Since the results of Experiment I have shown that the total ionization is unaltered by a magnetic field if the strength of the ionizing agent remains constant and since the ionization currents of 310 and 324 are nearly the saturation currents, the readings with the field were all reduced in the ratio of 324 to 310 and these corrected values are shown in the fourth column.

From Table II it is seen that the corresponding numbers in the second and fourth columns are almost identical, the small differences observed not being greater than those due to experimental errors. Hence it is concluded that a magnetic field has no effect on the saturation curve and therefore no effect on the initial recombination of the ions.

#### § 4. *Summary.*

1. A magnetic field of the intensity here used has no effect on the total ionization produced by X-rays.

2. A magnetic field of the intensity here used has no effect on the initial recombination of the ions produced by X-rays.

In conclusion, the author wishes to thank Professors Franklin and MacNutt for their interest and help in this research.

Physics Laboratory, Lehigh University,  
South Bethlehem, Pa., April 29, 1916.

ART. XIX.—*The Separation of Thorium from Iron with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine* (“Cupferron”); by WILLIAM M. THORNTON, Jr.

THE ammonium salt of nitrosophenylhydroxylamine, which was first introduced into analytical chemistry by O. Baudisch,\* has been made a subject of study by several chemists.† Because of its selective action as a precipitant many clean cut separations have been effected; thus solving a variety of analytical problems which without the use of the reagent would involve much difficulty. Bellucci and Grassi‡ have shown that in solutions decidedly acid with either sulphuric or hydrochloric acid, the substance precipitates quantitatively titanium and that under like conditions titanium can be completely separated from aluminum in one precipitation. Following the work of Bellucci and Grassi, the author§ has demonstrated 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. Pursuing a similar technique, E. M. Hayden, Jr. and the author|| succeeded in separating zirconium from both iron and aluminum. During the same year,¶ Ferrari, by means of the “cupferron” reagent, separated zirconium from aluminum; but did not consider the more complicated case of iron being present as a third ingredient. Owing to the fact that thorium bears a marked resemblance to zirconium in its chemical relations, the author has seen fit to study the former element with respect to the “cupferron” reagent. The outcome of this investigation has been to establish conditions under which thorium is quantitatively precipitated by the reagent

\* Chem. Zeitung, xxxiii, 1298, 1909; xxxv, 913, 1911; Baudisch and King, Jour. Ind. Eng. Chem., iii, 629, 1911.

† Nissenon, Z. angew. Chem., xxiii, 969, 1910; Chem. Zeitung, xxxiv, 539, 1910; Biltz and Hödtke, Z. anorg. Chem., lxvi, 426, 1910; Hanus and Soukup, *ibid.*, lxviii, 52, 1910; R. Fresenius, Z. anal. Chem., 1, 35, 1911; Bellucci and Grassi, Gazz. chim. Ital., xliii, 1, 570, 1913; Rodeja, Anal. Fis. Quim., xii, 305, 1914; xii, 379, 1914; Ferrari, Annali Chim. Appl., ii, 276, 1914; iv, 341, 1915; Turner, this Journal, xli, 339, 1916.

‡ Loc. cit.

§ This Journal, xxxvii, 173, 1914; *ibid.*, xxxvii, 407, 1914.

|| This Journal, xxxviii, 137, 1914.

¶ Loc. cit.

and also to accomplish the indirect separation of thorium from iron.

A standard solution of thorium sulphate was employed for these experiments. This was prepared by dissolving the Welsbach Light Company's thorium nitrate in boiling water and precipitating the thorium with a boiling solution of sebacic acid according to the method of Smith and James.\* The thoroughly washed precipitate was dried and ignited to thorium oxide in a platinum dish. The residue was then subjected to a prolonged digestion with hot sulphuric acid. After cooling, the semi-solid mass was poured into cold water and the solution filtered from an insoluble residue of unattacked thorium oxide. The filtrate was made nearly neutral with redistilled ammonium hydroxide and the thorium precipitated with recrystallized oxalic acid. The thorium oxalate, after complete washing, was dried at 110° C. and the sample preserved. Of the oxalate thus obtained 8.5 grams was digested with 50 cm<sup>3</sup> of sulphuric acid (made by diluting acid of sp. g. = 1.84 with an equal volume of water), adding a little nitric acid to oxidize traces of organic matter which discolored the liquid, and warming until nitric acid could no longer be detected by its odor. On pouring the residue into cold water the thorium sulphate dissolved completely and the solution was made up to a volume of one liter. Two experiments were made in order to set the standard of this solution. Weighed portions were treated with redistilled ammonium hydroxide at the boiling temperature, the resulting thorium hydroxide was ignited to the oxide, and the latter was brought to constant weight over the blast lamp. Duplicate determinations gave the following result:—

Thorium sulphate solution		Thorium oxide	
(a) 25 cm <sup>3</sup>	25.740 grm.	0.0922 grm.	0.3582%
(b) 25 cm <sup>3</sup>	25.757 grm.	0.0925 grm.	0.3592%

The mean of these two values was taken as correct.

Preliminary experiments soon revealed the fact that even with small concentrations of free sulphuric acid the precipitation of thorium by the "eupferron" reagent is incomplete. The author, therefore, resorted to the expedient of throwing out the thorium from a medium containing acetic as the only free acid. Accordingly weighed portions of 25 cm<sup>3</sup> of the standard thorium sulphate containing also about 1.25 cm<sup>3</sup> of sulphuric acid (1 : 1) were taken and treated with 15 grm. of ammonium acetate in the form of a strong solution and the volume made up with water to 500 cm<sup>3</sup>. A 5 per cent "cup-

\* *Jour. Am. Chem. Soc.*, xxxiv, 281, 1912.



ferroun" solution was then added gradually with constant stirring till present in some excess—15 cm<sup>3</sup> being the volume actually used. The precipitate, after having been thoroughly coagulated by stirring, was thrown onto a paper filter and washed with a 1 per cent solution of ammonium acetate. The moist paper with its contents was then placed in a tared platinum crucible, dried at 100–110° C., and ignited first with the Bunsen burner and then with the blast lamp to constant weight. In this way the results of Table I were obtained, which are within the limit of error for ordinary analytical work.

TABLE I.

The Estimation of Thorium by Means of the "Cupferron" Reagent.

No.	ThO <sub>2</sub> taken gram.	ThO <sub>2</sub> found gram.	Error gram.	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> NH <sub>4</sub> gram.	Vol. of Solution cm <sup>3</sup>
1	0.0925	0.0924	–0.0001	15	500
2	0.0923	0.0917	–0.0006	15	500

The thorium salt of nitrosophenylhydroxylamine\* differs a good deal in properties from the corresponding compound of either titanium or zirconium. In the case of the two last elements a high concentration of free sulphuric acid is consistent with total precipitation; while in the case of thorium extremely small concentrations of the same acid exert a marked solvent effect on the precipitate. Although very similar in appearance to the zirconium precipitate, the thorium precipitate is rather different in texture. Whereas the former permits filtration by suction, the latter passes through the paper in small quantities under the influence of very light pressure. This is unfortunate from a manipulative standpoint, since the precipitate cannot be drained at the pump—necessitating the removal of included water by slow drying.

In the second series of experiments thorium was separated from iron. Known quantities of iron were taken by weighing off portions of pure dry ferrous ammonium sulphate. The solution (about 150 cm<sup>3</sup>), containing sufficient tartaric acid to hold up the bases in ammoniacal solution, was made slightly alkaline with ammonium hydroxide, and colorless ammonium sulphide was added in moderate excess. After settling, the ferrous sulphide was filtered off and washed ten times with water containing a little colorless ammonium sulphide. Five cubic centimeters of sulphuric acid (1 : 1) was then added and the hydrogen sulphide thus liberated was removed by boiling. After cooling to room temperature, 25 grams of ammonium

\* [C<sub>6</sub>H<sub>5</sub>(NO).N.O]<sub>4</sub>Th, assuming a formula analogous to the one proposed by Bellucci and Grassi for the titanate derivative.

acetate was added, the volume made up to 400 cm<sup>3</sup> or 500 cm<sup>3</sup> and a 5 per cent "cupferron" solution added in decided excess. From this point on the determination was made just as in the case of thorium alone. Table II contains the results of three experiments.

TABLE II.

The Separation of Thorium from Iron.

No.	ThO <sub>2</sub> taken gram.	Fe <sub>2</sub> O <sub>3</sub> taken gram.	ThO <sub>2</sub> found gram.	Error gram.	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> NH <sub>4</sub> gram	Vol. of Solution cm <sup>3</sup>
3	0.0924	0.1018	0.0922	-0.0002	25	400
4	0.0924	0.1018	0.0916	-0.0008	25	500
5	0.1846	0.1018	0.1840	-0.0006	25	400

A separation of thorium from iron with the aid of the "cupferron" reagent has been satisfactorily worked out and the experimental data show a fair degree of accuracy. Let the reader distinctly understand, however, that the above process is not offered as an analytical method for practical purposes. The well-known oxalate\* precipitation is satisfactory and separates thorium from nearly all the common elements with which it is likely to be associated. But another link has been added to the chain of "cupferron" results and some comparative data on titanium, zirconium and thorium with respect to this remarkable reagent have been brought to light, which it is hoped will prove of interest.

Finally the author wishes to state that the experimental part of the work on thorium was carried out in the laboratory of the College of the City of New York and to thank Professor Charles Baskerville for fostering the investigation.

Wilmington, Delaware,  
June 6, 1916.

\* See E. Benz, Zs. angew. Chem., xv, 297, 1902.

ART. XX.—*On the Quantitative Estimation of Small Quantities of Sulphide Sulphur*; by W. A. DRUSHEL and C. M. ELSTON.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxxx.]

THE methods of estimating sulphide sulphur in common use depend (1) upon oxidation of the sulphur to the sulphate condition and weighing it as barium sulphate, (2) upon oxidation by means of standard iodine and titration of the excess of iodine with standard sodium thiosulphate, and (3) upon the precipitation of the sulphur by an excess of standard sodium arsenite as arsenious sulphide and titration of the excess of arsenite with standard iodine. These methods all require considerable time for execution, and the first and second methods are not entirely reliable for quantities of sulphide sulphur much smaller than 0.04 per cent. The third method is said to be accurate for quantities of sulphide sulphur as small as 0.0003 per cent, but it is necessary to allow the mixture, after treatment with sodium arsenite, to stand for twelve hours in order that the precipitated arsenious sulphide may be removed quantitatively by filtration before the excess of arsenite is titrated back with iodine.

The object of the present investigation was to develop a rapid method of estimating very small amounts of sulphide sulphur with a fair degree of accuracy. The method is a colorimetric method and consists essentially of the comparison of the depth of color of lead sulphide stains obtained from the sulphide sulphur of a given weight of a sample to be analyzed with a standard series of stains prepared from sulphide solutions of known sulphur content. A set of stains varying in depth of color from a faint yellowish brown to black representing from 0.0002 per cent to 0.004 per cent of sulphide sulphur may be prepared and used indefinitely for comparison. With a set of standard stains at hand the method has the advantage that within the range given the sulphide sulphur of a sample may be determined with a fair degree of accuracy in less than ten minutes.

*Preparation of standard set of sulphide stains.*—The apparatus used for preparing standard stains and for making analyses is very simple. The inner tube of a Liebig condenser with its larger end about 18<sup>mm</sup> in internal diameter was cut off 15<sup>cm</sup> in length. The smaller end was drawn down somewhat, rounded and fitted to a sound cork stopper which in turn was fitted to a 100<sup>cm<sup>3</sup></sup> round-bottom flask. The condenser tube then served as a sort of reflux condenser. To the upper and larger end of

this tube a filter paper moistened with a dilute solution of lead acetate was smoothly fitted and tied, so that the steam passing up through the tube and carrying hydrogen sulphide was required to pass out through the lead acetate paper. A similar tube with the internal diameter of its larger end about 36<sup>mm</sup> was also prepared and used for sulphide sulphur samples containing 0.001 per cent or more of sulphur.

A solution of sodium sulphide was made up with pure distilled water and carefully standardized. The solution was then diluted to contain exactly 0.01 per cent of sulphide sulphur. This solution was used for making up standard solutions containing 0.0002, 0.0004, 0.0006, 0.0008, 0.001, 0.002, 0.003 and 0.004 per cent of sulphide sulphur respectively, taking care to use distilled water free from traces of nitrites in making the dilutions. It was found that the more dilute sulphide solutions when made up with ordinary distilled water lost their sulphide content either wholly or in part on standing for several hours in stoppered bottles. This difficulty was obviated by using nitrite free distilled water in making up the solutions.

Carefully measured portions of 1<sup>cm</sup><sup>3</sup> to 5<sup>cm</sup><sup>3</sup> of the standard solutions were pipetted into the 100<sup>cm</sup><sup>3</sup> flask and 25<sup>cm</sup><sup>3</sup> of hydrochloric acid of about 0.5 per cent strength were added. The flask was immediately attached to the condenser tube fitted with moistened lead acetate paper as previously described. The mixture was then gently boiled for a few minutes at such a rate that the steam issued not too rapidly from the upper end of the condenser tube. In this way the sulphide sulphur was quantitatively liberated as hydrogen sulphide and evenly deposited as lead sulphide on the moistened lead acetate paper. The undecomposed lead acetate was then washed out, the paper dried and labeled with the amount of sulphide sulphur present as one of the set of standard stains. In the same way complete sets in duplicate were prepared ranging in sulphide sulphur from 0.0002 per cent to 0.004 per cent.

In order to determine the accuracy with which sulphide sulphur may be estimated in this way one of us made up a series of sodium sulphide solutions which the other estimated by the method outlined. The results are given in Table I. The first column shows the amount of sulphide sulphur in the solutions as made up. In the second column are the estimated amounts of sulphide sulphur.

In making these estimations the larger condenser tube was used where a preliminary trial indicated that the amount of sulphide sulphur was equal to or greater than 0.001 per cent. In all other cases the smaller tube was used. The maximum error, depending upon the amount of sulphur present, with the larger tube was 0.001 per cent and with the smaller tube 0.0003

TABLE I.

	Sulphide sulphur taken per cent	Sulphide sulphur found per cent	Error
1.	0.0025	0.0020	0.0005
2.	0.0015	0.0012	0.0003
3.	0.0006	0.0006	----
4.	0.0004	0.0003	0.0001
5.	0.0004	0.0004	----
6.	0.004	0.005	0.001
7.	0000	0000	----
8.	0.0002	0.00015	0.00005
9.	0.008	0.009	0.001
10.	0.002	0.0025	0.0005
11.	0.001	0.0015	0.0005
12.	0.0001	0.0001	----

per cent. These errors may be reduced by repeating the determination and taking the mean of several values found. In this way in the practical applications of the method the errors may be kept within reasonable limits.

*Practical applications.*—(1) In gas analysis. The method was used for the estimation of the hydrogen sulphide in the laboratory atmosphere and in illuminating gas. On a day when no hydrogen sulphide generator was being used in the laboratory the air contained barely a perceptible trace of sulphur; on another day when a class two floors below was using a hydrogen sulphide generator the amount of hydrogen sulphide in the air of the upper laboratory was found to be 1 part in 5,000,000. Twenty-five liters of air were slowly drawn through a Geissler bulb of the most modern type containing dilute potassium hydroxide solution. This solution was then washed into a measuring flask and made up to the mark with nitrite free distilled water and aliquot portions of this solution were used for determining the sulphide sulphur as previously described. The same procedure was used for estimating the hydrogen sulphide in illuminating gas. The colorimetric method gave 1 part of sulphur in 1,000,000 of gas. The same result was obtained by oxidizing the larger portion of the solution from the Geissler absorption apparatus with bromine water and weighing the sulphur as barium sulphate. Duplicate determinations on the same illuminating gas gave precisely the same result.

(2) In coke analysis. The simplest method of estimating sulphur in coke given by Fresenius is to boil 5 grams to 10 grams of powdered coke in dilute hydrochloric acid, and to absorb the hydrogen sulphide evolved in dilute potassium hydroxide solution. The sulphur is then oxidized to the sul-



phate condition by chlorine water or bromine water and weighed as barium sulphate. This method was used as a control to check up the results obtained by the colorimetric method. In this method the hydrogen sulphide was liberated and absorbed as suggested by Fresenius and aliquot portions of the sulphide containing potassium hydroxide solution were transferred to the distillation flask and the previously described procedure was followed. A comparison of the results obtained by the two methods on several samples of coke is found in Table II.

TABLE II.

## Coke Analysis.

Sulphide sulphur found	
by Fresenius gravimetric method	by colorimetric method
0·049%	0·050%
0·050	0·050
0·026	0·025
0·025	0·026
0·027	0·025

(3) In paper analysis. Another practical application of this method of determining sulphide sulphur is in paper analysis. In order that tissue paper may be used for wrapping polished metal without producing a tarnish the paper must be relatively free from sulphide sulphur. A weighed amount of paper, 1 gram to 2 grams, is cut into small pieces and transferred to the distilling flask and digested with gently boiling 0·5 per cent hydrochloric acid, collecting the hydrogen sulphide as lead sulphide on lead acetate paper as previously described. A number of samples of tissue paper were examined and in those samples which contained sulphide sulphur the amounts varied from 0·0002 per cent to 0·001 per cent. Papers which contained the larger amounts of sulphide sulphur when used for wrapping polished silver pieces usually produced a marked tarnish in the course of two or three weeks.

This colorimetric method of estimating very small quantities of sulphide sulphur is very rapid, fairly accurate, and has a number of practical applications.

ART. XXI.—*Margarosanite, a New Lead-Calcium Silicate from Franklin, N. J.*; by W. E. FORD and W. M. BRADLEY.

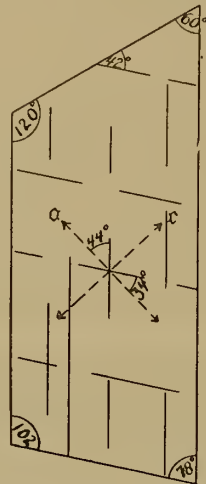
THE new mineral to be described in the following paper was originally observed on specimens from Franklin, N. J., that came from about the 1000 ft. level of the Parker shaft on North Mine Hill and were collected during the year 1898. It was partially investigated by S. L. Penfield and C. H. Warren during their study of Franklin minerals which resulted in the description of the other new species, hancockite, glaucochroite, nasonite and leucophœnicite.\* Partial analyses were made by both Penfield and Warren, but the investigation was never carried to a conclusion and the results obtained were not published. Their material has remained in the Brush Mineral Collection since that time and was added to several years ago by a few more specimens presented by the Foote Mineral Co. of Philadelphia. It is only recently that a complete and satisfactory investigation of this mineral has been possible. The results have shown that we have here another new species to add to the already long list of those peculiar to the Franklin locality.

Margarosanite, as the new mineral is called, is a silicate essentially of lead and calcium. It occurs in lamellar masses composed of thin plates packed closely together and which in general show a rhombic outline due to cleavages. It is colorless and transparent, showing a distinct pearly luster. It has a hardness of 2.5–3; specific gravity of 3.991. In the oxidizing flame it fuses with some difficulty, the fragment assuming an amethyst color, but in the reducing flame, it fuses easily and quietly at about 2 to an opaque grayish glass. In the reducing flame it gives a pale azure-blue flame with an outer border of pale green. With fluxes on charcoal it gives a metallic globule of lead accompanied with the lead oxide coating. It gives the characteristic color tests for manganese when fused in the sodium carbonate or borax beads. It is decomposed by treatment with nitric acid, yielding separated silica.

The mineral shows three good cleavages. The principal cleavage is parallel to the tabular development of the mineral and is so perfect that it almost gives a micaceous character to the material. There are two other well-developed cleavages which are nearly, but apparently not exactly, perpendicular to the first. These are shown by the characteristic rhombic outlines of the broken plates of the mineral and by the numerous cleavage cracks existing within the sections. The traces of these latter cleavage directions upon the surfaces of the plates make angles with each other which are closely approximate to  $102^{\circ}$  and  $78^{\circ}$ . On a few of the plates an oblique terminal edge

\* This Journal, viii, 339, 1899.

was observed which was due, apparently, to the presence of a crystal face, as no interior cleavage cracks parallel to it were observed. The trace of this face upon the surfaces of the plates made angles of about  $120^\circ$  and  $60^\circ$  with one of the cleavage directions and  $42^\circ$  and  $138^\circ$  with the other. This crystal form is not perpendicular to the chief cleavage but cuts across the edge of the cleavage plate at some oblique angle. These various relations are shown diagrammatically in the figure.



The two extinction directions in the sections make angles of about  $44^\circ$  and  $46^\circ$  with one of the cleavage directions and of  $34^\circ$  and  $56^\circ$  with the other. The faster of the two rays nearly bisects the smaller angle ( $78^\circ$ ) of the rhomb, formed by the two cleavages which are nearly perpendicular to the surface of the sections. In convergent light the sections show a biaxial figure with one optical axis revolving just outside the field of the microscope. The axis lies along the vibration direction  $\alpha$ , so that the cleavage plates are at least nearly perpendicular to the optical axial plane. These optical facts are also summarized in the figure. The indices of refraction of the two rays vibrating in the section were determined by immersion in high refracting oils and low fusing solids with the following results:  $1.730 \pm .002$  and  $1.795 \pm .005$ . Of these the value  $1.795$  must be close to that of the intermediate index of refraction,  $\beta$ . From a consideration of the above facts, it is probable that the mineral belongs in the triclinic crystal system.

Upon the specimens, on which the margarosanite was found, the following species were also observed: light and dark-brown garnet (almandite), hancockite, rœblingite, nasonite, franklinite, willemite, yellow axinite, datolite and a biotite-like mica

which gave the characteristic reactions for manganophyllite. In some cases the margarosanite was found lying immediately upon barite. The cleavages and general characters of these two minerals are so similar, that it became necessary to separate the margarosanite with great care before analyzing it. This was done by crushing the material and picking it over grain by grain under a lens. In this way material of undoubted purity was obtained for the analysis.

The method of the analysis was simple and was briefly as follows. The mineral was decomposed by treatment with nitric acid with the consequent separation of silica. The solution was evaporated to dryness and after taking the residue up in dilute acid the silica was filtered off. The filtrate was again evaporated to dryness to remove the nitric acid and the residue treated with water to dissolve the nitrates. During this evaporation a small amount of basic lead nitrate was formed which was insoluble in water. This was taken up in a very little nitric acid. The lead was precipitated and weighed as the sulphide. The manganese was precipitated as a sulphide and, after precipitation as the basic carbonate, was weighed as  $Mn_3O_4$ . The calcium was determined as usual and the amount of water found by a direct determination, according to the Penfield method.

A number of complete and several partial analyses were made by Bradley, the majority of which showed close agreement with each other. Several of the better determinations in each case are given below :

	Average						Ratios			
SiO <sub>2</sub> . . .	33.73	33.73	33.98	33.39	33.71	.5581	3.00	} .5986	1.07	
PbO . . . .	40.15	43.30	43.89	43.67	43.50	.1951	1.04			
CaO . . . .	21.61	21.62	21.97		21.73	.3873	} .4035	2.16		
MnO . . . .	0.98	1.01	1.29	1.30	1.14	.0162				
H <sub>2</sub> O . . . .	0.48	0.68			0.58					
	100.66									

These results are in substantial agreement with those of the partial analyses made earlier by Penfield and Warren. Since the water is in small amount and since it is driven from the mineral at a low temperature, it is thought to be hygroscopic in character and is not considered in the calculations. The analysis points clearly to a metasilicate formula for the mineral. The various bivalent oxides may be considered as isomorphous with each other and the formula given as  $RSiO_3$ , or in view of the ratio existing between the lead oxide and the calcium-manganese oxide, it may be written as  $Pb(Ca,Mn)_2(SiO_3)_3$ .

Below are given the theoretical composition of the last formula and the results of recalculating the present analysis

with the elimination of the water and the substitution of calcium oxide for the small amount of manganese oxide present:

	Theory for PbCa <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub>	Analysis recalculated
SiO <sub>2</sub> .....	35.10	33.77
PbO .....	43.17	43.57
CaO .....	21.73	22.66
	100.00	100.00

The name margarosanite, which is proposed for this new species, has been derived from *μαργαρίτης*, a *pearl*, and *σανίς*, a *tablet or board*, in reference to its pearly luster and lamellar structure.

Mineralogical Laboratory of the Sheffield Scientific School  
of Yale University, New Haven, Conn.,  
April 18th, 1916.

ART. XXII.—*On the Paleozoic Alcyonarian, Tumularia*; by  
W. I. ROBINSON.

THE new name *Tumularia* is here proposed for the forms which are now placed in the genus *Stylaræa* Seebach (1866),\* since that name was preoccupied by Milne-Edwards and Haime (1851),† for a hexacoral from an unknown locality. A single species, *S. mülleri*, was described by these latter authors and is therefore the genotype. Later Milne-Edwards‡ found this species to be identical with *Porites punctata* (Linnæus)§ and as the only species of the genus was thus removed to *Porites*, the name *Stylaræa* disappeared, because under the rules of nomenclature the same name can not be used for two different genera of animals. It was, however, inadvertently again applied by Seebach|| to a single species, *Stylaræa ræmeri*, from the Silurian of Esthonia. This form is closely related to *Protaræa*, but is distinct in several important characters, and since the name given by Seebach is preoccupied, the name *Tumularia* is here proposed.

\* Zeit. deutsch. geol. Ges., vol. xviii, pp. 304-310.

† Polyp. foss. d. Terr. Pal. Arch. Mus., vol. v, p. 143.

‡ Hist. nat. d. Coral., vol. iii, 1860, pp. 181-182.

§ Syst. Nat., 10th ed., 1758, p. 1277.

|| Loc. cit.



Family Heliolitidae

Genus *Tumularia*, nom. nov.

- 1859 *Columnaria* (partim) Billings. Can. Nat. Geol., vol. iv, 428.  
1866 *Stylaræa* Seebach. Zeit. deutsch. geol. Ges., vol. xviii, 306.  
1878 *Stylaræa* Nicholson and Etheridge. Mon. Sil. Foss. Girvan Dist., 60.  
1879 *Stylaræa* Zittel. Handb. d. Pal., vol. i, 239.  
1883 *Stylaræa* Roemer. Leth. Geog., Pt. I, Leth. Pal., 456.  
1899 *Stylaræa* Lindström. K. Svenska Vetens.-Akad. Handlingar, vol. xxxii, 110.  
1899 *Stylaræa* Lambe. Cont. Can. Pal., vol. iv, Part I, 91.

A free translation of the original generic description is as follows:

Vermicular, perforate sclerenchyma forming encrusting masses surrounded by a thin epitheca. Cells polygonal; moderately deep, with a strongly developed spongy columella. Walls massive. Spines occur at the corners of the cells. Septa strongly crenulated; descending abruptly to the calyx floor.

A summary of the genera *Protaræa* and *Stylaræa* (= *Tumularia*) was given by Lambe,\* who described and figured as *Protaræa vetusta* a form which differs from other figures and descriptions of that species. The form described by him differs from *Protaræa* in that it has a parietal or pseudo-columella, the calices are far apart, and there are small tubules in the intervening areas. It varies from *Tumularia* in that it has twelve septa while *Tumularia* has but eight, or rarely sixteen; it has tubules between the calices while *Tumularia* has not; the columella is parietal, that of *Tumularia* is essential.

Excluding this form because of the differences mentioned, *Protaræa* is clearly distinct from *Tumularia*. The original description of *Protaræa* is not definitive, but the genus was redescribed by Nicholson† as follows:

“Corallum forming thin crusts, about one-third of a line in thickness, which grow parasitically upon foreign bodies. Calices nearly equally developed, usually hexagonal, about one line in diameter or rather less, shallow, the bottom of the cup being tuberculated. Septa twelve in number, sub-equal, extending but a short distance inwards towards the center of the visceral chamber. Walls of the calices thick.”

The points of distinction upon which is based the retention of *Tumularia* as a distinct genus are:

1. Eight or sixteen septa; *Protaræa* has twelve.
2. An essential columella; *Protaræa* has a parietal columella or none at all.

\* Cont. Can. Pal., vol. iv, Part I, p. 89. † Pal. Ohio, vol. ii, p. 221.

3. Broad and petalliform septa; those of *Protaræa* are lamellar.

*Coccoseris* Eichwald 1860 (= *Lophoseris* Eichwald 1857) is evidently a synonym of *Protaræa* and not of *Stylaræa* as suggested by Lindström.\* The illustrations in *Lethæa Rossica* are very clear and show twelve septa in both the genotype, *Coccoseris ungeri*, and the only other species listed, *C. approximata*.

LIST OF SPECIES.

*Tumularia parva* (Billings).

*Columaria parva* Billings. *Cau. Nat. Geol.*, vol. iv, 428, 1859.

*Stylaræa parva* Lambe. *Cont. Can. Pal.*, vol. iv, Pt. I, 91, pl. 5, figs. 9-9b, 1899.

Locality and horizon: Mingan Islands, Quebec, and the Champlain-Montreal area, Canada; Virginia and Tennessee. Ordovician (Chazy).

*Tumularia ræmeri* (Seebach). Genotype.

*Stylaræa ræmeri* Seebach. *Zeit. deutsch. geol. Ges.*, vol. xviii, 306, 1866.

Locality and horizon: Wesenberg in Esthonia. Middle Ordovician.

*Tumularia occidentalis* (Nicholson and Etheridge).

*Stylaræa occidentalis* Nicholson and Etheridge. *Mon. Sil. Foss. Girvan Dist.*, 62, 1878.

Locality and horizon: Craighead, near Girvan, Scotland. Silurian.

\* Index to generic names, K. Svenska Vetensk.-Akad. *Handl.*, viii, No. 9. 1883.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY.

1. *Organic Agricultural Chemistry*; by JOSEPH SCUDDER CHAMBERLAIN. 12mo, pp. 319. New York, 1916 (The Macmillan Company. Price, \$1.60).—This is a text book of general agricultural chemistry or of elementary biochemistry for use in colleges. A companion volume on inorganic agricultural chemistry covering the subject of soils and fertilizers is being prepared by an associate of the author in the Massachusetts Agricultural College. The volume under consideration is interesting in being novel in its scope and in its manner of treating the subject. It aims to give to students of practical agriculture a general scientific knowledge of organic and physiological chemistry, but it does not attempt to present agricultural analysis. The first section of the book, comprising nearly one-half of it, deals systematically with organic chemistry. The treatment is confined to fundamental principles and a discussion of the more important compounds occurring in plants and animals. In spite of this limitation the course appears to be an excellent one, and to be very modern in its presentation. The second section dealing with physiological chemistry gives a very satisfactory discussion of enzymes and fermentation, the composition of plants and animals, the living cell and its food, animal food and nutrition, digestion and absorption, milk, blood and urine, and plant physiology. The last section, which is the most practical one from the point of view of the student of agriculture, deals with the food constituents of plants, and animal food and feeding. As a whole the book seems to be very well devised for its purpose. H. L. W.

2. *Outlines of Industrial Chemistry*; by FRANK HALL THORP, with Assistance in Revision from WARREN K. LEWIS. 8vo, pp. 665. New York, 1916 (The Macmillan Company. Price, \$3.25).—This is the third edition of a well known and widely used text book which made its first appearance in 1898. The rapid progress that has been made in chemical industry in recent years has made necessary considerable changes in the present issue, so that many sections have been re-written. The book is elementary in its character, and the processes are usually described quite briefly in connection with their fundamental principles and their important features. The number of topics taken up, however, is very large, so that the book gives an extensive view of the industry, including the inorganic, the organic, and the metallurgical branches. The work is not only a useful text book for students in colleges and technical schools, but it should be of interest to many general readers, who need have only a moderate knowledge of general chemistry in order to understand nearly all of it, as it is largely descriptive, contains no extended mathematical and theoretical discussions, and is clear in style. H. L. W.

3. *A Method for the Identification of Pure Organic Compounds*, Vol. II; by SAMUEL PARSONS MULLIKEN. Large 8vo, pp. 327. New York, 1916 (John Wiley & Sons, Inc. Price, \$5 net).—Eleven years have elapsed since the appearance of the first volume of this monumental work, a volume which classified and described about 2300 of the more important compounds of carbon with hydrogen, and carbon with hydrogen and oxygen. Meanwhile, however, the third volume, dealing with the identification of commercial dyestuffs, has been published, so that a fourth volume, now in preparation, will complete the set. The second volume, now being considered, contains classified descriptions of about 4000 of the more important compounds of carbon with the elements nitrogen, hydrogen and oxygen. This volume will be particularly useful, since it includes a great many compounds whose identification may be of great practical importance, such as all of the alkaloids, a majority of the most important drugs of other classes, many of the most interesting components of animal and vegetable organisms, the high explosives, and a considerable part of the "intermediates" of the dyestuff industry. All of the compounds in this volume are classed as "Order II." In order to identify an individual compound, it is necessary to find, in the first place, whether it is colorless or colored. If colorless, it is placed in three "genera," according to its acidity, basicity or neutrality. In each of these genera the compounds are separated into solid and liquid divisions. In these final "divisions" the compounds are arranged according to melting points or boiling points, and finally tests and miscellaneous properties are given for each individual. The book gives 43 numbered "tests," which have general application, and many special tests are given for the individual compounds. This important work makes it possible to identify many compounds much more easily, and in many cases more satisfactorily than by the usual method of analysis, molecular weight, and the resulting empirical formula. The book is of much importance to chemists in general, and much praise is due to Professor Mulliken for his labors of many years and his success in producing this work. H. L. W.

4. *Annual Reports of the Progress of Chemistry for 1915*. 8vo, pp. 268. London, 1916 (D. Van Nostrand Company, New York. Price \$2 net).—This is the twelfth volume of these reports, which are issued by the London Chemical Society. It contains nine e-says by as many authors, who are specialists in the different branches of chemistry that are reported. The subjects dealt with are General and Physical Chemistry, Inorganic Chemistry, three divisions of Organic Chemistry, Analytical Chemistry, Physiological Chemistry, Agricultural Chemistry and Plant Physiology, and Mineralogical Chemistry. As the reports are short, varying in length from 16 to 43 pages, it follows that the matter is very much condensed, particularly in the extensively investigated branches, and that the authors have been compelled to confine themselves to such topics as appeared to be

most important and interesting. The work appears to have been very well done, and the volume is valuable as a means of giving chemists who are specializing in their own branches of the science, some information in regard to the important achievements in the other branches. It is interesting to observe that the references to American researches are numerous in several of the reports. This indicates that chemical investigation is being well conducted in our country.

H. L. W.

## II. GEOLOGY.

1. *The Origin of the Earth*; by THOMAS C. CHAMBERLIN. Pp. xii, 272. Chicago, 1916 (University of Chicago Press).—Geologists have long been looking forward to this book and to a restatement of the planetesimal theory by its creator. As the book was written “not only for the specialist but for the educated layman” as well, the subject is presented “in as summary a manner and with as little technical detail as is consistent with sound method.” The educated layman will find the book highly profitable and fairly easy to master if the author’s advice is taken that it were well if the reader were deliberate. The specialist will also find much that is new and helpful to a better understanding of the planetesimal theory. This hypothesis, the author tells us, had its origin many years ago in an endeavor to explain the climatic conditions of the Pleistocene deposits of Wisconsin. “Strangely enough, the cold trail of the ice invasion had led by this long and devious path into the nebulous field of genesis” (9).

The book begins with a discussion of the Gaseous and Laplacian theories of earth origin. A ring of gas “such as the Laplacian hypothesis postulates as the parent of the earth, with a temperature high enough to keep the refractory substances that make up most of the earth in the form of a gas, could not have held itself together by its own gravity.” Further, it “could not have held in gaseous relations the waters of the oceans or the constituents of the air, nor perhaps even the rock substances of the earth” (36).

The planetary system of the sun “must clearly have had a biparental origin” as it clearly betrays a birth through the close approach of two bodies whose tidal interactions resulted in the sun taking on the form of a spiral nebula. The juvenile earth began to form through the infall of the planetesimals upon the earth-knot of the nebula. The shaping agencies were primarily (1) gravitation, (2) the adjustments due to the periodic shrinking of the earth mass, (3) the adjustments following the periodic acceleration in rotation, and (4) the pull of the moon upon the earth manifested in the twice-daily tides.

The newest feature of the book relates to the process of earth shaping during the juvenile stages, a process that may be called the *conic hypothesis of earth structure*. This theory states that



the earth is divided into six primary, positive, rigid, conic segments of crystalline substance but non-crystalline major structure, whose apices unite at the center of the earth, and between which lie the more or less irregular, laterally crowded, weaker, negative and lighter continental wedges. Two of the master cones occupy the Pacific depression, two the Atlantic, one the Indian, and the sixth takes in the more or less positive Mediterranean-Black Sea-Caspian Sea region. The segments move upon one another along "yield tracts" or fissure tracts that radiate from each pole at angles of about  $120^\circ$ . This hypothesis appears to be diametrically opposed to the working hypothesis of isostasy and the latter's postulate that the relief of the earth's surface is compensated for by corresponding variations in sub-surface density which cease at a depth equal to a fiftieth or a hundredth part of the radius of the earth. The book, however, does not follow the digressions in discussions which are necessary in pursuing the method of multiple working hypotheses. The popular nature of the book was doubtless regarded as a bar to such thorough discussion and comparison of conflicting hypotheses.

The inner reorganization of the earth is due to compression, generation of heat, and, through atomic dissociation, the birth of radioactive elements. "Radioactive heat was thus added to the heat of compression. . . . It is therefore assumed that there was only a sparse distribution of radioactive elements in the parent nebula, and hence in the original material of the earth, but that there was progressive concentration of these at the surface as effusive igneous action went on" (227-228). In the course of time the metals and metallic alloys probably concentrated toward the center of the earth and the silicates toward the surface (237).

C. S.

2. *Jointing as a Fundamental Factor in the Degradation of the Lithosphere*; by FREDERICK EHRENFELD. Proc. Amer. Philos. Soc., vol. lv, 1916, pp. 363-399, pls. vi-viii.—A very suggestive paper the conclusions of which are as follows: "Law of joints.—1. The lithosphere is subject by its nature to the development of lines of weakness or fracturing which in turn develop into actual movable segments. These segments or joint lines develop in such regularity of arrangement that they may be said to occur in 'joint-systems' which are shown at the surface as controlling agents in land erosion and land shaping; and they act beneath the surface inducing tectonic movements which are independent of atmospheric or marine contact.

"2. Degradation of the lithosphere is fundamentally a factor in its own structure and will occur wherever an agent capable of transporting the movable joint blocks is in contact with the lithosphere. This applies to those portions of the land or rock mass below sea level.

"3. Atmospheric erosion and marine planation are two separate phases of a general process of lithosphere degradation which are

frequently connected into consecutive stages by the presence of joint lines which extend from beneath sea level up into the mass of the lithosphere above sea level; these lines are also horizontal and thus act to produce flat surfaces.

"4. Degradation of the lithosphere surface may occur also by the vertical displacement of these joint segments irrespective of atmospheric or marine contact.

"5. Joint control of lithosphere degradation has been active since the period when the lithosphere possessed a solidified structure and has been a fundamental factor in the evolution of the lithosphere, or geomorphology." c. s.

3. *The Fauna of the Chapman Sandstone of Maine, including Descriptions of Some Related Species from the Moose River Sandstone*; by HENRY SHALER WILLIAMS, assisted by Carpel Leventhal Breger. U. S. Geol. Surv., Prof. Paper 89, 1916, pp. 347, 27 pls., 2 text figs.—This excellent monograph consists of a very detailed description of the genera and species of one of the Lower Devonian faunas of Maine, the Chapman sandstone, and comparisons are made with the related forms from all parts of the world. The fauna consists of 125 species, chiefly bivalves and brachiopods, of which 70 are new (10 brachiopods, 42 bivalves, 11 gastropods, 2 cephalopods, 5 crustacea). Of new genera there is one of brachiopods, *Antispirifer*; of bivalves, *Grammysioidea*, *Nuculoidea*, *Preanicula*, *Sphenotomorpha*; and of ostracods, *Zygobeyrichia*. The work was completed in 1910 and unfortunately has remained unpublished until now. It therefore does not consider the later publications by the New York and Maryland State Surveys.

The Chapman fauna, Professor Williams holds, "is intimately related on the one hand to the Tilestone fauna of England and on the other hand to the so-called Hercynian fauna of the Continent" (296). Its age "seems to be strictly Lower Devonian" and agrees best "with that portion of it below the Upper Coblenzian. It is a later fauna than the Tilestone or Downtonian of Great Britain or the terminal marine fauna of Arisaig, Nova Scotia" (297). On the basis of the brachiopods alone "the Chapman fauna is to be correlated with the Helderbergian fauna of the interior seas" of the United States (298). With this latter conclusion the reviewer does not agree because of the presence of *Hipparionyx unguiformis*, *Cyrtina rostrata*, *Megalanteris*, *Beachia*, *Rensselaeria*, and *Eunella*, all of which are more or less decisive indicators of Oriskanian time; the fauna seems to the reviewer to be not older than the early Oriskanian.

c. s.

### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *A Comprehensive Plan of Insurance and Annuities for College Teachers*; by HENRY S. PRITCHETT. Bulletin Nine of the Carnegie Foundation for the Advancement of Teaching. Pp. xiii, 67. New York City, 1916.—Ten years of experience in

the administration of the accepted plan of the Carnegie Foundation for providing pensions for college teachers has revealed certain serious defects in the system. Briefly stated, these include the fact that no provision is made, either in the case of disability or death, until the individual is well advanced in life; or, in other words, teachers under perhaps sixty or sixty-five years can receive no benefit from it. Again although the original endowment was large and has been added to, its income is nevertheless limited, the demands upon it are increasing and, therefore, at best but a part of the country's institutions and their teachers can come under its provisions.

The realization of these and other shortcomings in the present plan has led to the development of a new system of insurance and annuities to be available for "all college teachers of sound qualification" in the United States, Canada and Newfoundland. The essential feature of this system is that it shall be contributory, the individual and his college sharing the pecuniary responsibility from the beginning of his career as a teacher. Further, The Carnegie Foundation, with its large capital, would administer the system, guarantee a good rate of interest on the accumulated funds, and assume other responsibilities involved. For the details of the plan reference must be made to the present bulletin; it is, perhaps, enough to say that, while its basis is "socially wise, economically sound and permanently secure," the contributions called for from the individual would be small compared to the benefits to be received.

The Foundation is now committed to the existing pension system as applied to some seventy-three institutions in the United States and Canada. Obviously the older teachers must remain under it, but for men of some definite age, to be settled upon, it will be profitable to pass from the existing system to that now proposed. This point, with the details of the whole scheme, will come up for consideration by the trustees toward the end of the present year.

#### OBITUARY.

SIR WILLIAM RAMSAY, the distinguished English chemist, died at his home in Hazlemere, Bucks, England, on July 23 in his sixty-fifth year. His career was remarkable alike for the extent and the brilliancy of his original scientific work. His discovery and investigation of the atmospheric gases argon, krypton and neon alone would have established his reputation; while his identification of helium both in the atmosphere and in many minerals, his investigation of radium, and his discovery, as he believed, of the transmutation of the elements, rank with the most brilliant contributions to chemical science.

PROFESSOR ELIE METCHNIKOFF of the Pasteur Institute, famous the world over for his investigations and discoveries in bacteriology and for their application to the prevention and cure of human diseases, died in Paris on July 15, at the age of seventy-one years.

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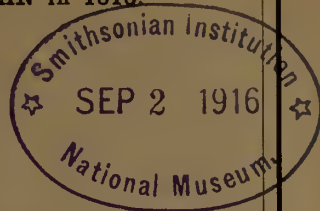
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[FOURTH SERIES.]

ART. XXIII.—*The Geological History of the Australian Flowering Plants*; by E. C. ANDREWS, Sydney, New South Wales, Australia.

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## VI. Summary

## INTRODUCTION.

The earlier botanists explained the Australian plants as a special creation. It is safe to say that were the flowering plants of Europe and Australia to be fossilized, and were it possible for a botanist unacquainted with the Australian plant types to see the two groups for the first time, he would conclude that they did not belong to the same geological period.

It is fitting, in a report such as the present, to direct attention to the conclusion of Bentham as to the probable origin of the indigenous flora of Australia. It had been the intention of the great systematist to discuss the subject in detail, but advanced age and declining health followed on the accumulation of the botanical data necessary for such discussion and he simply wrote the accompanying note in the concluding preface to the *Flora Australiensis* (vol. VII, 1878): "The predominant portion appears to be strictly indigenous. Notwithstanding an evident though very remote ordinal, tribal, or generic connection with Africa, the great mass of purely Australian species, or endemic genera, must have originated or been differentiated in Australia, and never have spread far out of it."

It is fitting also at this stage, to acknowledge the great help received from Mr. R. H. Cambage during the past twelve years in the accumulation of data necessary to write the present paper. Indeed it is difficult to indicate just where his influence and his help ceased in the preparation of the report. The original intention had been to prepare a joint report either on the genus *Eucalyptus* or on the flowering plants in general of Australia. Increased professional duties, however, have prevented Mr. Cambage from coöperating in the preparation of such a work, hence the present brief statement by myself.

Special thanks are due also to Mr. J. H. Maiden, Director of the National Herbarium, and to Messrs. E. Cheel and A. A. Hamilton, of the Herbarium.

As the study of the angiosperms in Australia is considered more and more in detail, it becomes evident how unsafe it would be to accept the evidence of any one family, or order, alone, as regards the possibility of former land connection with Australia. As examples may be quoted the papers on

the Distribution and Development of the plants in the groups Leguminosæ<sup>1</sup> and Myrtaceæ.<sup>2</sup> The distribution of these groups alone, considered without reference to the distribution of other families of animals and plants, suggested that the great tropical lands had been connected directly with each other as from Tropical America to Tropical West Africa, thence through Madagascar and Asia through the Malay Archipelago to Australia. But the study of the Amentales, the Compositæ, the Ericaceæ and many other families, and orders, suggested that the discussion of the legumes and myrtles alone had shown only one aspect, out of several possible, of the story of angiospermous distribution. The distribution of animals suggested another line of evidence and it was decided finally to obtain the independent testimony of various witnesses as to the possibility of land connections since the early Cretaceous and to coördinate the evidence so secured. Thus the student either of isostasy or of insular floras and faunas is driven to accept the doctrine of the permanence of the larger features of the ocean basins since the dawn of the angiosperms. For example, it is known that the rock structures underlying the ocean basins are heavier than those of the continental areas considered with respect to unit columns lying above a certain plane about 100 miles below the sea-level and such a peculiar adjustment of structures has not been attained in a hurry. Again Wallace has observed<sup>3</sup> that the sedimentary deposits of the land areas are suggestive of shallow-water conditions, while there is an absence of continental areas of deposits such as are found to-day on the bottom of the deep sea.

Throughout these pages the idea of a great two-period differentiation of climate has been made prominent, nevertheless it must not be forgotten that the distribution and development of almost all of the plant types considered in the present report could be explained satisfactorily on the assumption of the co-existence of waste places, of barren sandy tracts and of subarid to arid regions with the widespread mild and moist conditions of the Cretaceous and Eocene, such waste, barren, and desert areas increasing in size at various periods, notably since the Eocene or Miocene. Indeed it is necessary to postulate the uninterrupted existence of such desert conditions or of barren soils throughout the later history of the angiosperms, say, since the Lower Cretaceous, otherwise it is difficult to

<sup>1</sup> E. C. Andrews, Proc. Roy. Soc. N. S. Wales, vol. xlvi, pp. 333-407, 1914.

<sup>2</sup> *Idem.* Proc. Linn. Soc. N. S. Wales, vol. xxxviii, pp. 529-568, 1913.

<sup>3</sup> *Island Life*, 1892, pp. 103-105.



explain the existence of so many cosmopolitan forms of xerophytic tendency which appear to have spread to the various continents while yet these were all connected. Examples are *Acacia*, *Senecio*, *Lobelia*, *Campanula* with *Wahlenbergia*, *Gnaphalium*, *Helichrysum*, and many others. Indeed the student of geography who has traveled widely feels the necessity for postulating waste places, deserts and barren sandy areas, even during the Cretaceous which was a period of base-leveling, and of great spilling over of the ocean basins on to the continents. Sandy seashores must have existed as well as sandy tracts of Triassic, Permian, and other rock types, and these must have been relatively barren, while areas well-removed from the sea in certain latitudes, would surely have been sub-arid to arid as high mountain ranges were rare. Siliceous sands whether along the seashore or inland must have produced xerophytic growths even if subject to moist seasons.

Nevertheless in the present report it has been thought advisable to emphasize the apparent zoning of climate both before and after the isolation of Australia from the world generally.

#### I. *The Problem Stated.*

In Australia the flowering plants comprise from 10,000 to 11,000 species, distributed between about 150 families. Eight small families are almost confined to Australia, namely Goodeniaceæ, Candolleaceæ, Brunoniaceæ, Casuarinaceæ, Tremandraceæ, Stackhousiaceæ, Phillydraceæ and Pittosporaceæ (with the exception of *Pittosporum*, which occurs throughout the Old World tropics).

Australia has an area of about 3,000,000 square miles, and is composed mainly of a broad, low, western plateau, a low-lying central area, a belt of plateau following the eastern and southeastern periphery of the continent much like an intramarginal vein sympathises with the general curvature of the leaf margin, and a narrow coastal strip in Eastern Australia. The eastern plateau area is relatively narrow and relatively high and is separated from the ocean by a well-watered coastal area possessing a mild climate. To the coast the eastern plateau, with a height varying from 1,700 to 7,000 feet, above the sea, presents a rugged front dissected with profound gorges, thus forming a decided barrier locally to direct communication between the inland and coastal plants. On the other hand relatively-low gaps occur in the plateau masses and these permit a moderate amount of communication between the coastal

and inland plant types. The greater portion of Australia, west of the Eastern Australian plateaus, possesses really only two well-marked seasons, namely summer and winter. The highest shade reading recorded is about 127 degrees Fahrenheit, and the lowest winter reading from 10 to 15 degrees; moreover, the humidity is remarkably low in these great plains or low plateaus. Exceptions occur in the southwestern corner of Australia and in the Port Darwin area in the Northern Territory. The eastern plateaus are well watered but are subject to desolating winds both in summer and winter and temperatures considerably below zero Fahrenheit have been recorded from southern localities. These plateaus, however, afford shelter to the coastal region from the desolating winds of summer and winter, especially to those portions immediately under the escarpments and in the gorges. This narrow coastal strip supports an assemblage of plants of the jungle habit crowded together, interlaced with vines, and having a great similarity to Malayasian types, and to a lesser degree with types found distributed over the whole of the fertile tropics.

In the subarid to arid regions which comprise so great a proportion of the Australian area, there exist numerous specialized xerophytes of the families Leguminosæ, Myrtaceæ, Myoporaceæ, Euphorbiaceæ, Verbenaceæ, Labiatae, Compositae, Santalaceæ, Rhamnaceæ, Graminaceæ, Chenopodiaceæ, Malvaceæ, and Stereuliaceæ.

But the most instructive feature in the distribution of the Australian flora is the great number of genera and species, and the individuals innumerable of such genera and species on the large and excessively sandy areas lying mainly between 28° and 42° south latitude, and especially in the southwestern corner of West Australia between 29° and 34° south latitude where the rainfall is fair in amount but not great, where the summers moreover are very hot and the continental winds from the center are very dry. Large patches of sandy soil occur in the Sydney-Blue Mountain area, and in the northeastern portion of New South Wales, but there the rainfall is greater, the temperature more uniform, and the effect of the desiccating continental winds much less pronounced than in the western area. Nevertheless the numbers of genera and species are greater in the sandy southwestern area of Australia than in the well-watered sandy tracts of eastern New South Wales.

On these sandy wastes are to be seen not only the great proportion of the endemic genera of Australia, but also the *large* genera of Australia. Certain important subgenera or see-

tions of cosmopolitan tropical genera are here also to be found, but so modified as to present an appearance very different to their tropical or sub-tropical relations. Examples are the phyllodineous acacias, *Phyllanthus*, and a section of *Cassia*. From County Cumberland, which has an area of about 1,500 square miles surrounding Sydney, there have been recorded more species of Vasculares than from New Zealand or the whole of the British Isles. And the district of Perth in West Australia is perhaps even more remarkable in this respect.

In the Sydney district, the name being used in the larger sense, there are sheltered areas or pockets of volcanic soil or shales, on which dense luxuriant plant growths abound forming canopies of dark and glossy green, which exclude a great proportion of the sun's rays. Surrounding these patches of rich soil are the hungry sandstones forming so much of the large Sydney and Blue Mountain district, whose vegetation is in striking contrast with that of the rich soils. Here is to be seen no luxuriant foliage, no twining nor towering canopy to the jungle, but instead merely an array of *Eucalyptus*, phyllodineous acacias, banksias of somber hue and casuarinas, pine-like in appearance—with all the vivid green dissolved out of the leaves—to all appearance a type of vegetation ancient, dilapidated, rusty and weather beaten, some of whose members indeed are little better than skeletons. Whole areas of heath-like growths occur in the open places with leaves terete, cylindrical, involute, revolute, linear, acicular, or pungent. The most skilful paleobotanist would fail here to discover the "Open Sesame" to the generic classification of the types in the absence of flowers and fruits, for in these acicular and linear types of leaves there is no venation to be seen: there is little to distinguish them from each other. Many "traps for beginners" are to be found in the study of this sandstone flora and yet, despite their appearance of pauperism, they are all the "children of a great king," their noble ancestry being apparent directly the keen winter winds have gone, and the warmth of returning spring unfolds their beautiful and brilliant blooms. Here both upon shrubs and undershrubs with acicular, terete, involute, or revolute leaves, various brilliant pea blossoms proclaim the glows and glories of the legumes (*Pultenæa*, *Dillwynia*, *Aotus*, in the tribe Podalyriæ). Alongside these golden bushes another type with linear leaves bears myrtle blooms (*Bæckea*).

Other shrubs, undershrubs, or small trees with circular, pine-like, or linear leaves, and associated with the xerophytic

legumes and myrtles are *Ricinocarpus* (Euphorbiaceæ), *Westringia* (Labiatae), *Persoonia* (Proteaceæ), *Grevillea* (Proteaceæ), *Hakea* (Proteaceæ), *Acacia* (Mimosaceæ), *Kunzea* (Myrtaceæ), *Melaleuca* (Myrtaceæ), *Viminaria* (Papilionaceæ), *Casuarina* (Casuarinaceæ), *Banksia* (Proteaceæ), *Leucopogon* (Epacridaceæ), *Candollea* (Candolleaceæ), *Eriostemon* (Rutaceæ), all easily classified once they have burst into flower, but all riddles to the foreign botanist until they have flowered.

Again, the vast genera of the world generally, such as *Piper*, *Eugenia*, *Cassia*, *Euphorbia*, *Senecio*, *Carex*, *Psychotria*, and *Phyllanthus*, rarely possess numerous species in Australia. The exceptions are *Acacia* (450 species), *Phyllanthus* (50 species), *Cassia* (30 species), and a few others, but these have been so modified to suit the Australian soil and climate that they appear as distinct genera in the great majority of instances, so far as their foliage is concerned. *Acacia* indeed, of the phyllodineous type, and some *Cassias*, would never be recognized as such by extra-Australian students, in the absence of fruits and flowers. The few members of the great cosmopolitan genera which occur within Australia on the hungry sandstones mostly retain traces of their ancestry in the possession of pinnate leaves, dwarfed, battered and bedraggled, it is true, but nevertheless standing in striking contrast with their surroundings, like broken-down aristocrats ill at ease among hungry and unclothed savages, but still clinging to the rags and shreds of respectability (Examples, *Breynia*, *Panax* and *Cupania*).

Again, the great genera of Australia, that is, the genera, or sub-genera, peculiarly Australian, such as *Eucalyptus*, the phyllodineous *Acacias*, *Grevillea*, *Hakea*, *Hibbertia*, *Goodenia*, *Candollea*, *Pimelea*, *Pultenæa*, *Leucopogon*, *Malaleuca*, *Bæckea*, *Daviesia*, *Persoonia*, *Banksia*, *Dryandra*, *Eremophila*, *Bossia*, and many others, do not occur in the sheltered jungle areas, but are to be found most abundantly on the hungry sandy and extremely siliceous soils, especially in southwestern Australia, where not only are the endemic species most numerous but many genera are endemic to that region in addition to possessing more than their share of species in the genera endemic in Australia generally.

All this being so, with our knowledge concerning these specialized xerophytes, which are all endemic in Australia, but absent from the areas of mesophytic and jungle growths, which are all, moreover, vigorous, large and aggressive genera, almost all confined to or, at least, in their true home, on the hungry



siliceous sands and rocks of Australia, whose seedling stages also proclaim their recent derivation from forms very different to their present ones—how are the facts named to be reconciled with the statement by paleobotanists that they formerly existed as luxuriant types in the mild and moist climate of the Cretaceous and Eocene? It is not that Australian botanists would deny the existence of Myrtaceæ, Proteaceæ, and allied families in Europe, during Cretaceous and Tertiary time; what they would deny, however, is that the endemic *genera* of Australasia ever did form a part of the Cretaceous and Tertiary flora of the Northern Hemisphere. This is the first portion of the problem to be approached.

Other portions of the problem deal with the hypothecated land connections between Australia and South Africa, South America, New Zealand, and the Northern Hemisphere, respectively.

Thus the Proteaceæ, and the Restiaceæ, are practically confined to Australia and South Africa, while certain genera such as *Helichrysum*, *Helipterum*, and *Cassinia*, in Compositæ. *Bulbine*, *Wurmbia*, and *Casia* in Liliaceæ, are almost confined to these two countries.

In Southern South America and Australia, there are many genera and species confined almost entirely to the two areas. New Zealand and Australasia show even greater affinities, while striking similarities exist between the floras of Australasia and those of the great temperate areas of the Northern Hemisphere especially in the families Ranunculaceæ, Geraniaceæ, Stellatæ (Lindley), Compositæ, Cruciferæ, Lobeliaceæ, Umbelliferæ, and Boraginaceæ.

There is also the interesting problem to be faced of the evident closer connection, in former times, between the western and eastern Australian floras.

One of the most interesting of the questions raised also by this knowledge of the broader relations of the Australian plant types to the generalized types of the tropics and of the world at large is that which is connected with the xerophytic forms such as *Acacia*, many *Cassias*, *Senecio*, *Lobelia*, and others. These forms apparently were world-wide in their distribution before the isolation of Australia from the rest of the world, and they are xerophytic types in nearly every country. Do they connote deserts existent with the supposed mild and moist climate during the cosmopolitan distribution in the Cretaceous and the Eocene; do they imply the existence of a differentiation of climate at the close of the Cretaceous;



or do they imply merely a response by the plants to their environment of extremely poor soil?

Before proceeding to the general discussion of these points, however, it will be advisable to mention briefly the significance of the general relationships existing between the families and orders of the flowering plants, the significance of the Cretaceous and post-Cretaceous geography and climate, of the transporting agency of man, animals, and the sea, of vigorous and aggressive plant genera, of the distribution of mammals, and of the theory of multiple origins.

## *II. The Significance of the present Relationships existing between Families and Orders of the Flowering Plants.*

The angiosperms are divided into about two hundred and fifty families, according to the various classifications proposed by systematists. These families are fairly distinct from each other but they may be grouped into series yet more distinctive known as orders. With a few exceptions the many orders are quite distinct from each other. If now the orders be taken individually it will be found that, in most cases, they possess some families characterized by tropical arborescent forms, generally also of luxuriant appearance, while other families in the same order are mainly herbaceous and confined to the cooler, or colder, regions of the earth. This is most pronounced in the more highly specialized types such as the Sympetalæ and the more specialized of the Dialypetalæ types, while it is less pronounced in the more primitive types of the Monochlamydeæ, such as the catkin-bearing groups. Thus the Araliaceæ and the Umbelliferæ with the Cornaceæ form an order, in which the Araliaceæ, for the most part, are luxuriant trees suggestive of the tropics or sub-tropics while the Umbelliferæ are herbs, for the main part, in the cooler portions of the globe, their extremely compound leaves, however, suggesting an ancestry flourishing under mild and moist conditions. The Rubiaceæ, the Stellatæ (Lindley), and the Caprifoliaceæ, form another distinctive group, in which, however, the Caprifoliaceæ have preserved their woody nature even though acclimatized to the cold. For the Leguminosæ, which embraces the Papilionaceæ, Cæsalpiniaceæ, and Mimosaceæ, an ancestry of large trees is suggested with luxuriant pinnate foliage, with a tendency to adapt itself to temperate climates on the part of the Papilionaceæ, especially in the cases of the herbaceous tribes Viciæ, Trifoliæ, and Loteæ. The Gruinales, comprising families such as Rutaceæ, Geraniaceæ, Oxalidaceæ,

Malpighiaceæ, Simarubaceæ, Zygophyllaceæ, and Meliaceæ, is another splendid example. The Ranales form another good example of this principle, Magnoliaceæ, Anonaceæ, and Ranunculaceæ, being taken as types. The Myrtales is another good example with Myrtaeæ, Combretaceæ, Melastomaceæ, Rhizophoraceæ, Haloragchaceæ, Lythraceæ, Leeythidaceæ, and Onagraceæ, taken as types. The Sapindaceæ, Acerraceæ, and Hippocastanaceæ, furnish another example. The eatkin-bearing families are peculiar in that they suggest an ancestry of large and luxuriant trees with compound leaves dwelling in a mild and moist climate, which still are large trees in the main although confined for the most part to the cool and cold temperate regions. Many families again may be divided into tribes which have relations one to another somewhat similar to those which the various families bear to one another in the orders. Thus Papilionaceæ has the tribes Sophoreæ and Dalbergiæ, which are mainly large trees, with luxuriant pinnate leaves in warm moist regions, Galegeæ and Phaseoleæ, mainly trees and twining plants in warm and temperate regions, while the tribes Vieiæ, Loteæ, and Trifoleæ, are mainly herbs in cool temperate regions. Many other examples might be cited.

Again, in many of the more highly organized families, there is not only a tendency to become herbaceous in the colder regions but also in the warmer parts of the earth. Cueurbitaceæ, Lobeliaceæ, Campanulaceæ, Compositæ, Solanaceæ, Liliaceæ, and Orchidaceæ, may be cited as examples.

The significance of this remarkable arrangement into groups as they are seen to-day appears to be that a response was made to some widespread mild and moist condition of climate in the far past by a great development of large luxuriant trees fertilized by winds and clothed with dense foliage, the leaves being pinnate, compound or toothed. Jungles were rare, but great forests were common, to suit the fertilization by winds. Later, as a result of another widespread climatic factor came a great and rapid deployment of luxuriant trees with symmetrical flowers which began to supplant the older anemophilous types. Then by the introduction of an additional factor came the development of the zygomorphic corolla and the tendency for such types to crowd together and to push the forest growths to the less favored spots, inasmuch as the crowding and clinging habit tended to prevent wind fertilization. Then came a zoning of climates with the development of deserts in both tropics and temperate regions with mild moist conditions in local areas. This is suggested first, by the long-established

development of herbs among the old luxuriant tree forms in the temperate regions; second, by the great development of herbs and undershrubs in the warm arid and subarid regions, and third, by the development of vines and herbs and epiphytes in the mild and moist regions.

An alternative explanation may be found by admitting the existence of deserts of limited area even in the Cretaceous and Eocene and in the presence of large areas of rocky barren soils such as those now found in South Africa and Australia.

A much later period of climatic zoning throughout the world is evidenced by the development of deciduous trees in the northern lands and the great development of xerophytic tribes, subtribes, genera and species in both the northern and southern hemispheres.

In other words the present classification of the flowering plants suggests that the great alliances of orders are of long standing, that the families are due to an early world-wide differentiation of climate, and that the present xerophytic and deciduous development is due to the later and local modification of old and well-established families and tribes.

### *III. The Difficulty attendant on the Determination of Fossil Flowering Plants by Leaf Remains only.*

It is necessary for true progress in paleobotany that the proper determinations of the angiosperms should be agreed upon both by botanists and paleobotanists. In this connection it seems peculiar that the leaders of the botanical world, past and present, both were and are accustomed, respectively, to demand full and abundant material before referring a plant, previously undescribed, to its proper genus and species.\* Paleobotanists, on the contrary, seem content with fossil leaves alone for generic determinations of flowering plants although those fossil remains may date back to the Cretaceous. It is not that the plants so named may be referred to new genera for stratigraphic purposes, or that they are referred to genera whose names suggest a general likeness in leaf characteristics to certain types of modern genera, which causes the confusion, indeed upon first thought this may seem a procedure unlikely to lead to serious error, but the application of this method has led paleobotanists on the evidence of leaves alone to refer many

\* See also a paper by A. A. Hamilton on "The Instability of Leaf Morphology in its relation to Taxonomic Botany," Proc. Linn. Soc. N. S. W., vol. xli, pp. 152-179, 1916, and references therein.—[This note was received after the article was put into type—Eds.]

*fossils* of the Cretaceous and Tertiary beds to *modern genera* straight out even when those particular genera no longer exist either in or near the regions considered. The particular cases which come to the mind of the Australian geologists in this connection are the well-known references of Cretaceous and Eocene leaf remains in North America and Europe to the modern genera *Eucalyptus*, *Hakea*, *Grevillea*, *Banksia*, *Dryandra*, *Callistemon*, and other types now found only in Australia, and of various Tertiary leaf remains in Australia to *Quercus*, *Alnus*, *Acer*, and other genera, not now existent in Australia.

These determinations, moreover, appear to be opposed to the general evidence available on the subject because:—

*First.*—The vitality, vigor and aggressiveness of the genera, such as *Eucalyptus*, *Grevillea*, *Hakea*, *Persoonia*, *Banksia*, and *Dryandra*, is very decided. Anyone who has made a close study of *Eucalyptus* must have observed its adaptation to all varieties of moisture, climate and soil in Australia, exclusive of jungle areas. All round Australia it extends, flourishing on the actual sands immediately behind the sea beaches, swarming up the sides of the mountain gorges, defying the desolating winds of the cold plateaus and the desiccating influence of the arid to subarid climate of the plains and straining at its fetters, as it were, as though eager to conquer other areas than Australia. In other words it acts as though it were a genus which has not yet reached its prime.

On the sandy areas, especially in West Australia, the same remarks are true, although in a measure somewhat slighter, of the vast genera *Grevillea* and *Hakea*, and the large genera, *Persoonia*, *Banksia*, and *Dryandra*. Nevertheless, vigorous and aggressive as are all these types to-day in Australia, it is stated that in extra-Australian regions they became so unfitted, one and all, to survive that they were driven out of the last trench even in Africa, a country whose soil and climate is similar in many ways to that of Australia.

This difficulty is accentuated especially when the apparent saltation of *Eucalyptus*, in the eastern portion of Australia, is considered, many disputes having arisen as to specific determinations by highly-trained Australian botanists of certain forms found in that region.

*Second.*—These types, *Eucalyptus* (300 species), the *phylloclineous acacias* (420 species), *Grevillea* (200 species), *Hakea* (110 species), *Persoonia* (62 species), *Banksia* and *Dryandra*, each about 50 species, are all xerophytic. Their ancestors



were not xerophytes, nevertheless the fact seems incontrovertible that they are xerophytic as genera, and that the actual genera were developed as xerophytic adaptations, and that in almost all instances the genera, during their existence as these particular genera, never had an earlier mesophytic existence.

This is strongly opposed to the idea that such genera were part and parcel of the luxuriant growths of the mild and moist Cretaceous in Europe and America.

*Third.*—These types are almost entirely confined to the hungry, sandy soils of Australia, exceptions being some of the *more recent* species of *Eucalyptus*, and acacias. Soil conditions such as these could scarcely be matched in Europe.

*Fourth.*—The morphology and earlier history of the genera considered are against the idea of matching leaf remains of the mild and moist Cretaceous and Eocene in the Northern Hemisphere, with modern Australian genera. Thus certain lanceolate leaves, in the Northern Hemisphere, possessing a venation not much akin to any recent *Eucalypt* have been referred to the genus *Eucalyptus*, whereas all the botanical evidence<sup>4</sup> indicates that this particular form of leaf lanceolate more or less falcate and with twisted petiole, is only a recent development and that the earlier form of leaf was more like many *Myrtæ*, being opposite, penniveined, generally sessile, and more or less orbicular in shape. The venation also is peculiar, and the earlier types had closely-set secondary veins, arranged to the midrib at an angle approaching the right-angle.

*Grevillea*, besides being a vigorous and hardy xerophyte, has a very irregular perianth, and a follicular fruit. It is mainly a shrub or undershrub, a dwarfed individual, a very specialized type, far removed from the primary type of the *Proteaceæ* as generally conceived, which should have had a regular perianth and should have had a luxuriant arborescent form. Two of the species, however, are large trees, namely *G. robusta* and *B. striata*. The same remarks apply to the cases of *Hakea*, *Banksia*, and *Dryandra*. *Persoonia*, by some botanists, with its regular perianth, and its drupaceous fruit, might be considered as a primary type, but its vigor, its xerophytism, and its choice of the most hungry coarse sandy soils proclaim its recency as a genus within the Australian States. *Callistemon* is a highly specialized genus among the *Myrtaceæ*, closely allied to *Melaleuca* (120 species approximately) and one which, even to Australian botanists, would be difficult to describe from

<sup>4</sup>E. C. Andrews, *Myrtaceæ*, Proc. Linn. Soc. N. S. Wales, vol. xxviii, p. 555, 1913.



leaves alone, especially if mixed up with certain *Melaleuca* leaves.

It seems peculiar also, if it be assumed that a great and vigorous genus like *Quercus* (250 species) once flourished in Australia, that some trace of it should not exist now, as the climate of Tasmania and Southeastern Australia is adapted to its growth, or at least that it made no xerophytic response to its environment in much the same way as it has done in America.

#### IV. *General Geographical Conditions. Transport of Plants and Distribution of Mammals.*

##### (a) CRETACEOUS AND POST-CRETACEOUS GEOGRAPHY AND CLIMATE.

The accompanying notes on the general geographical conditions of the world are abbreviations from Vol. III of Chamberlin and Salisbury's *Geology*. In the lower Cretaceous there was a general sea transgression and very little diversity in the world's climate so far as can be gathered from a study of the fossils. Newberry<sup>5</sup> suggests that in the upper beds, the angiosperms belong to familiar genera such as *Sassafras*, *Laurus* and *Eucalyptus*.

In the Upper Cretaceous there was a very great sea transgression in America (both North and South), Europe, Asia, and Australia, and doubtless in Africa, the climate appears to have been mild and warm, and is supposed by Neumayr<sup>6</sup> to have been comparable with that of Malayasia at the present time. Angiosperms were in marked ascendancy.

*Eocene.* Mild climate as told by fossils. Large epicontinental seas.

*Miocene.* Great terrestrial aggradation. Great terrestrial degradation also. Floras become more suggestive of temperate climates. Deciduous trees make their appearance.

*Pliocene.* Differentiation of climate and heralding of the approaching Glacial Period.

*Pleistocene.* Great Glacial Periods and repeated revivals of glaciation. Lowering of temperature simultaneously over the globe. Interglacial periods. Great increase of land area since the Cretaceous, Eocene, Miocene, and even Pliocene Periods with development of deserts, high mountains, and marked zoning of climate.

<sup>5</sup> United States Geol. Survey, Monograph XXVI, p. 23, 1895.

<sup>6</sup> *Erdegeschichte*, vol. ii, p. 383.

To this epitome may be added a few notes on the topography and climate of Australia as bearing directly on the development of the local flora.

In the Lower Cretaceous the sea transgressed a portion of central Australia.

The Upper Cretaceous sea covered nearly the whole of the central portion of Australia and it is probable that this epicontinental sea extended from the Malayan area in the north to the Southern Ocean on the south.

The Eocene sea was not large and was confined to small areas in the north and south of the continent. Indeed the continent as a whole appears to have been growing in size subsequently to the close of the Cretaceous although a very recent submergence, post-dating the Glacial Periods, appears to have isolated New Guinea and Tasmania from the mainland.

The land history of Australia in Cretaceous and post-Cretaceous times is full of interest and throws a considerable amount of light on biological problems. It is as if there has been a general tendency in Australasia and New Zealand to move in a vertical direction in post-Cretaceous time, the movement being subject to two great laws, namely:—

*First.*—That elevation, or vertical movement, of the land was emphasized in an easterly direction, due allowance being made for the lagging behind of the two great and relatively heavy portions, namely, Central Australia and the sub-oceanic mass between Australia and New Zealand.

*Second.*—That the uplifts after the widespread peneplanation of the Cretaceous Period did not proceed continuously, but were saltatory in their action and, moreover, the periods of time punctuating these uplifts became less as the present time approached, but the amount of individual vertical uplift became greater as the periods separating the uplifts became less in duration. This has given rise to great "valley-in-valley" structures owing to the interrupted work of the streams.

Thus during the Cretaceous Period great peneplains were formed and only the hardest rock structures remained to show the existence of former plateaus or hills. In the various Tertiary divisions of time the streams carved valleys with widths so great as to appear as local peneplains, nevertheless they are only very broad shallow valleys, in whose bases other broad and shallow valleys have been excavated. The great uplifts of the later Kosciusko Period allowed the streams to form profound canyons receding along these older shallow valleys. In other words the main Tertiary land history has consisted of

repeated elevations with stream revivals. During one or more of the Tertiary divisions of time, especially the Miocene, the land appears to have sunk somewhat with the formation of lake-like expanses along the stream courses and the burial, later, of deep river deposits beneath basalt floods covering thousands of square miles in Eastern Australia. This led to great modifications in stream drainage, but the great and dominating lesson of repeated stream revival cannot be overlooked, the modifications due to basalt floodings being only an incident in the establishment of the great geographical unity of Eastern Australia in Tertiary and post-Tertiary time.

Two glacial visitations at least during the Pleistocene have been recorded for Australasia.<sup>7</sup> As the various geographical changes were contemplated in Australia, such as the increase in height of the plateaus, the approach of the Glacial Period, and the succession of the milder interglacial periods, it may be understood how vast a change such influences would have induced in the flora of East Australia and of New Zealand, especially in the extinction of weak types and the saltation of vigorous and aggressive genera such as *Eucalyptus*, *Acacia*, *Veronica*, *Pultenaea*, and *Coprisma*.

(b) THE TRANSPORT OF PLANTS AND THE DISTRIBUTION OF MAMMALS.

(1) *The Transport of Plants.*

*By sea currents, by birds, by winds.* The works of Charles Darwin, Guppy, Schimper, Hemsley, and others, are full of instances showing the great power of transportation of plants by the agencies here enumerated, and not only so but of the vitality of many seeds thus transported. The example of Krakatoa populated with many species of plants between the years 1883<sup>8</sup> and 1908, is very significant in this connection. If Krakatoa, a small island, has received such a large flora as it possesses at present from the action of currents, birds, and man, what may have been accomplished during the progress of ages in the way of plant transport by similar agencies from one great land block to another, such as from America to Africa, to Australia, or to New Zealand? Here again we have also the cumulative action of time and the long-continued

<sup>7</sup> David (T. W. Edgeworth). *Geological Notes on Kosciusko*, with special reference to the evidence of Glacial Action, *Proc. Linn. Soc. N. S. Wales*, vol. xxxiii, pp. 657-660, 1908. David (T. W. Edgeworth), Pittman (E. F.), and Helms (R.), *Geological Notes on Kosciusko*, *Proc. Linn. Soc. N. S. Wales*, xxvi, pp. 26-27, 1901.

<sup>8</sup> Ernst, "New Flora of Krakatoa," Cambridge University Press, 1908. Quoted from letter by Dr. H. B. Guppy.

action of isolation from the ancient home, in producing great changes in the nature of the evolution of new genera, subgenera, and species. Two examples may be taken, namely, Hawaii and St. Helena. From the geological evidence, neither of these appears to have been in direct connection with the great land blocks, such as North America in the case of Hawaii, and of West Africa in the case of St. Helena. Nevertheless their endemic flora is so rich and varied as to suggest the cumulative action of time and of evolution, under isolation, in producing numerous endemic species, if not genera, from the waifs brought to them by the sea, by birds, or by man since their existence as islands.

In this connection attention may be drawn to the magnificent work of Wallace,<sup>9</sup> Guppy,<sup>10</sup> and Hemsley,<sup>11</sup> on Insular Floras. The study of these volumes is of the utmost service in clearing the way for a proper discussion of the population of islands by various agencies.

*Man.* The importance of this agent, in the transport of plants from land to land across the sea, appears to have been almost always underestimated. Anyone who has lived with native races of men must have noted their belief in the necessity of certain plants to their well-being, either as articles of food or as medicines. Man has had a long history on the globe, and in his many wanderings, both in the primitive and civilized state, he must have been the means, consciously or unconsciously, of carrying many plants from the northern hemisphere to the southern or from the east to the west and so on. Certain of the Compositæ, Cruciferae, Labiatae, Umbelliferae, Caryophyllaceae, Rosaceae, and other families, may be conceived as having been transported in this way, for example, *Taraxacum officinale*.

## (2) *The Distribution of Mammals.*

Inasmuch as it is necessary to apply the testimony of independent witnesses, whenever possible, as to supposed land connections during particular periods of the earth's history, it would, in the case of the angiospermous distribution, be advisable, if possible, to apply the testimony of the animals.

The distribution of reptiles, birds, worms, and invertebrates generally does not concern us, necessarily, in the distribution of the flowering plants, inasmuch as they had their origin long before that of the angiosperms, and they, therefore, may have

<sup>9</sup> Island Life, 1892.

<sup>10</sup> A Naturalist in the Pacific, Plant-Dispersal, vol. ii, 1906.

<sup>11</sup> The Voyage of the Challenger, Botany, vol. i, Introduction.



been distributed over the earth during land connections prior to the Cretaceous Period. The discussion of their distribution in this connection, therefore, would be liable to result in confusion.

The distribution of the mammals, however, specially the placentals, may be taken as independent testimony in the discussion of the distribution of the flowering plants.

The accompanying notes are abbreviations from Chamberlin and Salisbury's *Geology* (vol. III, 1906).

Marsupials and monotremes appear to have been in existence in the Upper Cretaceous. The earliest actual records of the placentals are from the early Tertiary. Among them were undifferentiated sloths, rodents, lemurs, edentates, and carnivora. Before the close of the Eocene, the Ungulata, Carnivora, Edentata, Insectivora, Rodentia, Quadrumana, Cetacea, and Sirenia, were distinctly defined.

*Oligocene.* No living genera recorded.

*Miocene.* Still no living genera, unless some doubtful *Canis* and allied types be allowed.

*Pliocene.* Many strange genera, but there were also many modern genera in existence.

*Pleistocene.* Many extinct genera, but also very many modern genera, in existence.

In the chapters on the Tropical, the African, the South American, and the New Zealand problems, it will be seen how valuable is the testimony of these independent witnesses, the mammals.

#### V. *The Development of the Australian Angiosperms.*

If, now, the data supplied in the foregoing chapters be correct, it is permissible, perhaps, to suggest along which lines the population of Australia by angiosperms has moved. In this connection it must be remembered that, vast as is the number of species existing still in Australasia, the mere existence of types such as *Casuarina*, *Fagus*, *Epacris*, *Philydrum*, *Stackhousia*, *Pleurocarpæa*, *Tetralthea*, *Eucalyptus*, *Angophora*, *Brunonia*, and many others, implies a wholesale extinction of genera and species, intermediate between these types and their nearest living allies.

For the sake of simplicity, the problem may be considered under six heads, namely, The Tropical Problem, the South African Problem, the South American Problem, the Northern Hemisphere Problem, the New Zealand Problem, and the West and East Australian Problem.



In the succeeding sections the information supplied already in the earlier pages is assumed.

(a) THE TROPICAL PROBLEM.

(1) *Distribution of Acacia, Cassia, Xanthoxylum, Vernonia.*

In the fertile tropics there are many large families of flowering plants containing a great wealth of genera and species, which are more or less luxuriant in habit, primary or generalized in character, and having a cosmopolitan range in the fertile tropics. In the neighboring extratropical areas many types occur secondary to the primary forms of the tropics. These secondary forms are mainly xerophytes, and occur both as modifications of the cosmopolitan genera of luxuriant type and as local genera grouped round the local forms which the main cosmopolitan genus may have assumed. These secondary sections, subgenera, or groups of genera, considered as distinct local groups, appear to have relations more intimate with the cosmopolitan tropical type than with each other. The secondary types in the southern hemisphere are mainly undershrubs, shrubs, or dwarfed trees, more rarely herbs, the leaf surfaces are reduced and the evidence is that the specialization has been in the direction of providing against excessive transpiration of moisture. The secondary types in the northern hemisphere are peculiar in that they generally are herbs, either annual or perennial, more rarely trees, while the primary forms in the tropics most frequently are trees of beautiful appearance and luxuriant habit, with pinnate leaves.

Examples are to be found in families such as the Myrtaceæ, Leguminosæ, Rutaceæ, Rubiaceæ, Sapindaceæ, Euphorbiaceæ, Solanaceæ, Verbenaceæ, Orchidaceæ, Labiataæ, Malvaceæ and Sterculiaceæ.

Before discussing any of these families individually it would be advisable perhaps to consider the distribution of a few of the most important genera in these and allied groups, genera, for example, such as *Acacia* (or better still *Mimosa* in the Linnean sense) *Cassia*, *Vernonia*, and *Xanthoxylum*.

Of these *Acacia* is a peculiar type. Its primary form is suggested by the section *Gummifera*, which is spread over the tropics and subtropics of the world, but occurring not so much in the fertile tropics, as on the plains and wastes of the warmer world. Indeed it is one of those remarkable types which suggest strongly that in the days when some great connection existed between all the great land blocks of the world within the region of warm climate, that xerophytes had already come

into existence. This may be placed tentatively in the later Cretaceous.

In Australia *Acacia* and its allies are represented by modifications of the genus, as local subgenera or sections, which have a general appearance very different from that of the worldwide section *Gummiferæ*. One of the Australian sections, namely *Phyllodineæ*, with about 420 species, is leafless, but possessing a development of phyllodes remarkable for their variety of form and structure.

*Vulgares*, another great section, or subgenus, is plentiful in Asia, Africa, and America, but is absent from Australia. Another subgenus is endemic in Tropical America.

No local genera grouped around *Acacia* occur in Australia, but in America there is the vast genus *Mimosa* (400 species) with a few outliers in the Old World.

*Cassia* contains about 400 species and is divided into three subgenera by Bentham<sup>12</sup> namely, *Senna*, *Fistula*, and *Lasiorhegma*. All these subgenera show the same combination of general characters in America, Asia, Africa, and Australia.

*Fistula* has above 20 species, about 8 in America, about 5 in Asia, 5 in Africa, and but 1 in Australia. These species are local, forming natural combinations into intermediate groups.

The great subgenus *Senna*, with more than 200 species, has a similar wide distribution, excepting the section *Psilorhegma*, which is confined to the Old World with its chief center in Australia, but, as Bentham remarks, these Australian species are truly Australian in type, namely, in their leaves being rigid, vertical, terete, or in having phyllodia developed, and with the pods straight or variously twisted.

*Lasiorhegma* is world-wide in distribution, but the three natural sections, *Apoucouita*, *Absus*, and *Chamæcrista*, into which it is divided, are distributed differently. *Apoucouita* consists of 3 or 4 American trees. *Absus* has 70 localized American species and 1 type an annual, abundant in Tropical Africa, Asia, and Australia, but not in America.

*Chamæcrista* has many herbs and undershrubs with 50 to 60 species in America and from 16 to 20 in the Old World.

*Vernonia*, a genus of about 500 species, and closely connected with many small genera, "has its chief centers in tropical America and tropical Africa, forming in both countries more or less divergent groups, but in different directions, the species more numerous in America, the forms more varied in Africa.

<sup>12</sup> Revision of the genus *Cassia*, Trans. Linn. Soc. London, vol. xxvii, pp. 503-513, 1869.

From tropical America it spreads more sparingly into North America and extratropical South America, and from tropical into Southern Africa, and eastward into tropical and subtropical Asia, forming in each of these outlying districts more or less local groups. More than three-fourths of the genus belong to the section *Lepidaploa*. . . . At least four-fifths of its species are tropical American, but it includes also the North American ones, a portion of those from Africa, and five or six Asiatic species."<sup>13</sup>

*Vernonia* itself is not indigenous in Australia, but *Pleurocarpaea*, close to *Vernonia*, is in Australia, and is a monotypic genus.

*Xanthoxylum*. (*Fagara*) Trees mainly of luxuriant type, about 150 species in all tropics and in 5 sections. The first section, with about 115 species, extends over all tropics, with a few outliers in North America, Paraguay, Argentina, the Andes, Japan, China, Korea, Manchuria, and other places. The second section is monotypic from Juan Fernandez. The third section with about 12 species is from the West Indies with the trees luxuriant in habit, while the fourth named *Blackburnia*, and at one time classed as a distinct genus, is confined to Australia and Hawaii. A fifth section, or, probably, a genus, consists of about 10 species in North America and temperate east Asia.

Around this great type are gathered many genera both tropical and temperate, but mainly tropical trees with large luxuriant and pinnate leaves.

Around the group or tribe of Xanthoxylæ, however, are gathered three large tribes, namely Boroniæ (xerophytes confined to Australia), Diosmeæ (xerophytes confined to South Africa and mostly shrubs), and Cuspariæ (confined to tropical America).

A study of *Psychotria* (700 species in the Benthamian sense) and its allies, *Hibiscus* (150 species approximately), *Ficus* (600 species), *Piper* (600 species), *Phyllanthus* (500 species approximately), *Peperomia* (500 species), *Solanum* (900 species), *Euphorbia* (700 species), *Bauhinia* (150 species), *Hedyotis* (in the Benthamian sense), and other vast tropical genera, show a very similar distribution to that here outlined for *Cassia*, *Vernonia*, *Xanthoxylum*, and *Acacia*, or better still, for *Mimosa*, in the Linnean sense.

This peculiar distribution suggests a connection of some

<sup>13</sup> G. Bentham, *Compositæ*, Jour. Linn. Soc. London, Botany, vol. xiii, p. 393, 1873.

decided description between the great tropical land blocks, and a connection, moreover, which appears upon first inspection to have ceased at the present time. Indeed, were one to consider only the evidence of one great family or order only, such as the Myrtaceæ, Leguminosæ, Solanaceæ, Rutaceæ, or Piperaceæ, it would seem impossible to escape the conclusion that the present tropical lands had been directly connected in the not very remote past. But the distribution of the mammals does not bear this out and, more important still, the facts of structural geology are directly opposed to the idea. In the Cretaceous, or Eocene, before the strong zoning of climate mentioned by Chamberlin, these genera most probably had a much wider distribution than they have at present, and at that time they may have moved along land bridges which existed much farther to the north than the present tropics, yet without leaving the mild and moist climate apparently so necessary to their existence. Such conclusion is indeed suggested by the existence of outposts of types such as *Solanum*, *Euphorbia*, *Sophora*, and *Hibiscus*, in the temperate regions.

The case of the oceanic islands should ever also be kept in mind in this connection. All the facts of geology go to prove the non-existence of direct land connection at any time between islands on the one hand such as St. Helena, the Azores, and the Hawaiian groups, and the neighboring continents, on the other hand. These appear to have derived their flowering plants from the great land blocks through the agency of sea-currents, birds, animals, and man.

For example, are we to conclude that the several species of *Commidendron* in St. Helena, the seven species of *Tetramolobium*, the 11 species of *Lipochæta*, the 12 of *Campylotheca*, 6 of *Dubautia*, 12 of *Raillardia*, 2 of *Hesperomannia* (all in Compositæ), 20 of *Pilea* (Rutaceæ), 16 of *Kadua* (Rubiaceæ), 11 of *Clermontia* (Lobeliaceæ), 29 of *Cyanea* (Lobeliaceæ), and so on, in Hawaii, all of endemic genera, were one and all wafted or carried to these islands, and yet exterminated on the main lands. Is it not rather an inescapable conclusion based upon the theory of probabilities that, since these lands must have been supplied by waifs and colonists from the great lands, inasmuch as the geology appears to disprove their former land connection with the continents, then they are the descendants of types brought to these islands in old times and which have since produced either endemic species or genera or both?

Among the numerous families which can be considered as illustrating the connection of the tropical lands and Australia



it is proposed to discuss the probable distribution of the *Leguminosæ*, *Myrtaceæ*, *Rutaceæ*, *Euphorbiaceæ*, *Verbenaceæ*, *Labiata*, *Sterculiaceæ*, *Sapindaceæ*, *Pittosporaceæ*, *Treman-draceæ*, *Malvaceæ*, *Apocynaceæ*, *Asclepiadaceæ*, and other large groups.

It would be beyond the scope of the present paper to deal with these great families in detail and the remarks herein will be confined, therefore, to the salient features of distribution in a few of the larger divisions of the families.

(2) *Leguminosæ*.

It seems safe to conjecture that<sup>14</sup> during the Cretaceous, or the Eocene, or both, the tribes of the *Mimosaceæ*, *Cæsalpiniaceæ*, and *Papilionaceæ*, now mainly confined to the tropics, were scattered over the greater part of the world, Australia being joined to Asia, and all the great land masses being connected directly within areas of mild and moist climate, although not at all necessarily, within the present tropical or subtropical regions.

The tribes which do not appear to have been in existence during the Cretaceous were the *Trifolieæ*, *Loteæ*, and *Vicieæ*.

It may be permissible, moreover, to infer that during this stage the great tribes such as *Sophoreæ*, *Cassieæ*, *Acacieæ*, *Galegeæ*, *Phaseoleæ*, and *Genistææ*, were abundantly represented mainly as trees of luxuriant habit, although the acacias and to a less extent the cassias suggest even in that remote period either the existence of a great climatic differentiation or of the existence of subarid, to arid, areas, or of waste open spaces. It may be mentioned in passing that similar evidence of the existence of xerophytes at this stage in flowering plant development is yielded by a study of many other great families, such as the *Campanulaceæ*, *Lobeliaceæ*, *Umbelliferæ*, and *Compositæ*. These tribes existed probably in all the great land blocks, Europe and Australia included.

The case of the *Sophoreæ* may be considered at this stage. During the zoning of climates, the regions of mild and moist climate gradually retreated from the higher latitudes toward the Equator, but as the change was accomplished very slowly, the plants had a long period in which to save themselves from extinction by the adoption of various devices against the increasing rigor of their environment. This factor of time as an ever-flowing quantity must ever be kept in view in the consideration of angiospermous development. The changes

<sup>14</sup> E. C. Andrews, The Distribution and Development of the *Leguminosæ*, Proc. Roy. Soc. N. S. Wales, vol. xlvi, 1914.



induced were not cataclysmic but gradual, the climate tending ever towards the dry and cold but with innumerable recurrences of mild and moist conditions temporarily, the ameliorating influences becoming less and less distinct as the Pleistocene, with its climatic rigors, was approached. In the earlier mild and moist period the luxuriant trees of the Sophoreæ would have been enabled to cross from the Old to the New World and from the New to the Old, in regions beyond the limits of the present tropics, and thus new genera might arise in the tribe which might be common to the New and Old World, and yet be unknown in Australia, which had become isolated before the great differentiation of climate ensued.

Thus would arise the idea that Australia was separated earlier than America and Africa. Moreover, great land blocks such as America and Western Africa might have effected an interchange of genera and species and thus present likenesses with each other, of a more modern character, than those of Australia with these great land blocks. This of course has reference only to the great tropical groups. With the increasing differentiation of climate, the Sophoreæ retreated more and more to the tropics, but certain hardy forms existed such as the old genus *Sophora* itself, or other hardy genera were formed, such as *Virgilia* and *Cladrastis*. These were the types in extratropical areas which could dispense with the old arborescent stage and the luxuriant foliage, and hence, as the extreme rigors of the Pleistocene arrived, it is noted that the majority of the noble trees of Sophoreæ vanish, and a herbaceous type is developed, namely, the Podalyriæ of the northern hemisphere.

The effect of the climate on the ancestors of the Sophoreæ and the Podalyriæ in the southern hemisphere is more instructive than in the northern hemisphere. In the north the tribe was almost exterminated owing to the excessive climatic rigor of the Pleistocene coupled with the ensuing competition of other and extremely hardy and vigorous types, begotten by the climatic revolution.

The Podalyriæ of the south mark a departure from the Sophoreæ during a great climatic differentiation preceding the separation of Australian from the tropical lands when the flowering plants began to feel the influence of the climatic changes. This land was relatively small and was confined to the tropical and warm temperate regions. It might, therefore, be expected that there would not, on the one hand, be such a great response in genera and species, in the numerical sense, as in the

vast Eurasian and American regions, and on the other hand, there would not be a development along the vigorous and aggressive lines such as might be expected in the great connected land blocks of the northern hemisphere.

In Australia there are vast expanses of coarse sandy soils which have been derived, ultimately, from the great sandy granites of East and West Australia—but derived, directly, in great measure, from the great exposures of Mesozoic sandstones, especially in Eastern Australia.

These soils are extremely loose and porous and contain moisture, almost permanent, at depths of a few yards from the surface, but they contain very little moisture near the surface except on the mountain sides, or in moist seasons. In dry seasons this sandy soil neither becomes caked nor hard, and the water level simply sinks at a very slow rate. On the dense heavy soils of the slates, andesites, basalts, and allied rock types, a long succession of moist and mild seasons would produce dense growths of luxuriant trees and vines to the exclusion of xerophytes generally, but if the region should be subject to great droughts and to long continued desiccating winds, and to great diurnal and annual changes of temperature, then this luxuriant growth would cease. In moist, mild seasons a luxuriant crop of herbage would arise, especially if the seeds of such herbage should be protected by special devices against excessive loss of moisture. In the long spells of dry weather this herbage would be burnt off, as it could not keep in touch with the underlying water supply, owing to the tough and non-porous nature of the dried upper clods of earth, while only trees such as were provided with very long and deep roots, and with special devices against excessive transpiration, could survive.

In the old moist and mild climate of Australia the heavier soils had a dense covering of luxuriant vegetation while the much greater areas of coarse, sandy soils (the central sea being then very large and the existing great central black and red soil plains being non-existent) were clad with mesophytic forest growths, much as may be seen to-day under similar conditions in New Zealand, northeast Queensland, and other countries, while on the open plains or low plateaus of such country there would be a tendency to form stunted forest growths of the mesophytes.

With the alteration of the Australian climate from mild and moist and uniform to fiercely-hot and dry summers, and to desolating dry winds during the winter, all this condition of

growth was changed. The plains of heavy soil were forsaken gradually by the luxuriant vegetation, except for hardy outliers which possessed deep roots and which were provided with special devices against excessive transpiration, and such plants as these even were in great danger of extermination. On the coarse, hungry, sandy soils, however, the old luxuriant vegetation found means whereby many of their kind might be preserved. If, for example, during the ages involved in the general and great alteration in the Australasian climate, it should be found that they could utilize, or modify, certain inheritances of structure or of chemical composition, so as to provide against excessive transpiration, then their ancient abode might still know them; if, for instance, they should secrete non-volatile oils or resins, or a latex; if the old luxuriant tree should be reduced to a shrub, or undershrub, or better still, to an annual herb; if the leaves should be provided with stony cells, stomata, and other devices, to conserve their contained moisture; or better still, if they should dispense entirely with their leaves or reduce them to linear, needle-like, spiny, pungent, horny, terete types, or if their seeds should be protected so that they could resist a drought extending over periods even of 50 or 100 years, then the safety of the family might be assured.

The *Sophoreæ*, or at least the ancestor of the tribes *Sophoreæ*, *Podalyriææ*, and *Genistææ*, found special facilities for survival on these hungry, sandy soils which were scorched by the summer sun and subjected always to the menace of long continued drought and desiccating atmosphere. The *Leguminosæ* indeed, as a whole are singularly liable to leaf alteration, they are also singularly fortunate as regards seed protection, and as regards ready fertilization. As the luxuriant arborescent forms of the *Sophoreæ* perished, one by one, on the open wastes of the heavy soil, so the porous soils of the sandstones were occupied by special types of the tribe, which could reduce their leaf surfaces; which could endure the gradual dwarfing process to shrubs and undershrubs; and whose heritage of long tree roots could be utilized in tapping the underlying moisture. The nutriment supplied to individual trees of the *Sophoreæ* was limited to the area which the roots could tap, and this, on barren, hungry soil, was sufficient only for small trees. The leaves also underwent wonderful transformations, pinnate types becoming simple, or being rolled into mere lines and points, or being discarded altogether. In this way a great number of individuals could live side by side on a given space, because the area covered at the surface was dependent on the

spread of root at the zone of moisture, and on the relative lack of nitrogenous, calcareous, and allied nutriment in the sands. The types thus evolved were exceedingly hardy and became vigorous and aggressive with the usual result, namely, the production of numerous genera and species. Hence during the double period of climatic differentiation the first of which occurred while all the great lands were in some close connection, the second after the isolation of the great tropical lands, the 19 or 20 genera and about 400 species of the Australian Podalyriæ appear to have been developed.

In South Africa, on the hungry Mesozoic sandstones, and in a climatic environment somewhat similar to that of Australia, the Podalyriæ of that region arose. In South America the conditions which obtained in South Africa and in Australia were not existent, and moreover, a more severe competition arose owing to the ingress of aggressive northern types, whereas South Africa, on the one hand, was protected by a barrier from northern competition, while Australia was protected by the ocean.

The story of the Genistæ is perhaps even more interesting. It is supposed by Bentham that Podalyriæ is related more closely to Genistæ than to Sophoræ, and this may, perhaps, be so,<sup>15</sup> owing to certain peculiarities of habit and foliage common to the tribes, nevertheless the bloom is nearer Sophoræ than Genistæ. In the tropics the Genistæ have almost vanished, with the exception of the great genus *Crotalaria* (300 species). In its early days, the Genistæ, like *Acacia*, were more given to populate open places than the jungle, hence their extinction, in part, in the dry tropics.

In the Northern Hemisphere, the Genistæ retained the traces of the old arborescent habit more than did the northern Podalyriæ and by reduction of size, and the rejection of foliage, in great part they held their own, and developed new and aggressive genera such as *Ulex*, *Genista*, *Spartium*, and *Lupinus*. In Australia the hungry, sandy soils gave them a chance, and new genera, such as the peculiar and vigorous tribe Bossiææ, were developed on the sandy and rocky wastes both as shrubs and undershrubs, with small leaves or with none. But the tribe never flourished in Australia as did the Podalyriæ. In South Africa, however, on the hungry, sandy soils, the tribe developed enormously with great aggressive genera such as *Aspalathus* (above 150 species).

<sup>15</sup> If this be so then Podalyriæ has had a parallel development with Sophoræ and with Genistæ.



The genera *Castanospermum* and *Podopetalum*, in Sphoreæ, were developed in the Australian jungles after the isolation of Australia, but these genera are monotypic and probably represent decadent genera, despite the fact that the individuals are luxuriant types. Sphoreæ, indeed, appears to be a decadent tribe which, however, possesses a powerful and vigorous offshoot, the Podalyriæ.

*Acacia* also is a magnificent example of the adaptation<sup>16</sup> of a tree with bi-pinnate leaves to a hungry sandstone setting by the rejection of its leaves and the development of phyllodes. The formation, later, of the great soil plains of the central areas, and of the plateaus of the eastern areas of Australia, gave the new vigorous subgenus a further field for its energies.

### (3) *Myrtaceæ*.

This is a family less elastic than the Leguminosæ in accommodating itself to a harsh and severe environment, and from the point of view of distribution it is to be compared with the Mimosaceæ or the Cæsalpiniaceæ rather than with the Papilionaceæ.

In the tropics the more primary types *Eugenia* (in the Benthamian sense) and *Myrtus* are widely spread and suggest former direct land connections between all the great land blocks, this older interchange of fertile types in regions of mild and moist climate, however, having ceased long since.

In tropical and subtropical America, after the zoning of the climate ensued, the Myrtaceæ were modified gradually with the development of the true Eugenias, *Myrcia*, *Calyptranthes*, *Marleria*, and other types. According to Berry<sup>17</sup> the genus *Myrcia* contains about 450 species, and represents one of the older, or primary, Myrtaceæ. But the type does not exist outside America, and, moreover, it is a vigorous, vast, and aggressive genus, which is confined to one compact area, hence it seems unlikely that it is as old as *Eugenia*, or *Myrtus*, which occur abundantly in all the large land blocks with the exception of Europe and America north of Mexico.

All of these American types belong to the tribe *Myrtæ*, no other tribe of the family having been developed in that country.

In Australia, however, the great areas of hungry, sandy soil,

<sup>16</sup> E. C. Andrews, The Distribution and Development of the Natural Order Leguminosæ, Proc. Roy. Soc. N. S. Wales, vol. xlviii, 1914.

<sup>17</sup> E. W. Berry, The Affinities and Distribution of the Lower Eocene Flora of South Eastern North America, Proc. Amer. Phil. Soc., vol. liii, pp. 222-227. 1914.



already mentioned on a previous page, furnished the Myrtaceæ with a chance for the development of xerophytic characters. During the earlier zoning of the climate it is possible that the important subtribe *Metrosidereæ* has been developed in the areas of good soils. At a period somewhat later the subtribe *Eucalypteæ* appears to have been developed, probably from the *Metrosidereæ*. *Eucalyptus* represents the adaptation of a luxuriant type to hungry, sandy soils in a warm climate.<sup>18</sup>

"The obstinate persistence of juvenile, opposite, cordate, sessile, and horizontal leaves in the genus, indicates that such leaf-types had been thoroughly well-established for a very long period in the family, before the evolution of the genus *Eucalyptus*; and that the later typical *Eucalyptus* leaf with twisted stalk is an adaptation to a harsher climate, and one which would tend to become extinct, in part, in favor to the old persistent type, under certain favorable climatic conditions."<sup>19</sup> Moreover, the great size of the trees of the genus, and their general appearance, proclaim the subtribe *Eucalypteæ* as a remove of no very great degree, from *Myrteæ*, although it must be borne in mind that the fruit is a capsule and not a drupe.

Like the phyllodineous acacias, *Eucalyptus* flourished first on the moist, hungry, sandy soils. At a later date, when the high plateaus were formed in the east, and when the great inland plains were formed, *Eucalyptus* developed numerous new species<sup>20</sup> to populate the fresh territory. This, however, it was enabled to do only after becoming a vigorous and aggressive type. All around Australasia it may be seen reaching out arms, as it were, for new lands to conquer. The eastern species offer never-ending puzzles to the systematists, many types apparently being in a state of saltation, the species overlapping in the eastern plateaus, no intermediate areas being unoccupied by the genus, it being prevented only from spreading beyond Australia by reason of the wide ocean barrier and the inability of the genus to grow in the jungle areas of the neighboring islands.

Meanwhile in Southern Australia, while the zoning of the climate became more pronounced, other subtribes and even another tribe of Myrtaceæ sprang into existence in the hungry, sandy areas. These fresh types, as time progressed, became

<sup>18</sup> R. H. Cambage, The Distribution and Development of the Genus *Eucalyptus*, Presidential Address, Proc. Roy. Soc. N. S. Wales, 1913.

<sup>19</sup> E. C. Andrews, The Distribution and Development of the Myrtaceæ, Proc. Linn. Soc. N. S. Wales, vol. xxxviii, p. 555, 1913.

<sup>20</sup> E. C. Andrews, *ibid.*, pp. 554-565.

smaller in size as individuals, the individuals became more depauperate, and more specialized, by far morphologically, than the earlier *Metrosidereæ* and the *Eucalyptus* of which the latter had not succeeded in reducing itself to a shrub or undershrub. Nevertheless the myrtle plants never succeeded in adopting the herbaceous habit. They always remained either as trees, shrubs, or undershrubs. The later, more depauperate and more specialized types were the subtribe *Bæckeæ* and the whole tribe *Chamælaucieæ* containing many genera vigorous in character.

The genera *Melaleuca*, *Callistemon*, and *Leptospermum*, occupy a peculiar position, in that they are not so close to *Myrtæ* as are *Eucalyptus* and *Angophora*, but their foliage suggests some relation with the allied family *Melastomaceæ*. These types *may* belong to the first great zoning of climate, which is conjectured to be late Cretaceous in age.

The essential oil in the leaves of this great family appears to have been of great assistance in enabling them to adopt the xerophytic habit and to populate the hungry sandy soils of Australia.

It is remarkable that nowhere else in the world do the members of the *Myrtaceæ* appear to have been enabled to adapt themselves well to a hot, dry, and sandy environment. In South Africa they are singularly lacking, owing to the inability of the old luxuriant type of the Cretaceous to produce a local secondary and xerophytic type of aggressive nature as it had in Australia. Similarly for the case of South America. The New Zealand myrtle members, outside of the tribe *Myrtæ*, and possibly of the subtribe *Metrosidereæ*, appear to have been derived from Australia, or from Australian and Malayasian waifs. It is quite conceivable that the *Metrosidereæ* may have developed in the north and entered the New Zealand during its connection with Australia by way of New Guinea or North Queensland.

The *Myrtæ*, like their allies, the *Combretaceæ*, *Melastomaceæ*, and *Rhizophoraceæ*, are essentially lovers of shelter, moisture, and heat, and were specially unfitted, as were also the *Myrtæ* proper, to withstand the great cold of the Glacial Period in Eurasia and North America.

#### (4) *Rutaceæ*.

The *Rutaceæ* are essentially magnificent and luxuriant arborescent forms, which as the genera *Xanthoxylum* and allied forms, are widespread over the fertile tropics as primary types,

with local secondary developments in America, South Africa, Australia, and the Northern Hemisphere. The endemic secondary forms in South Africa and Australia are xerophytes. The primary type is characteristically a tree with a beautiful appearance, possessing pinnate leaves, and a lover of mild and moist climatic conditions.

After the isolation of Australia from the great tropical lands, and the zoning of climates, the luxuriant Rutaceæ in that country found themselves faced with the great problem which had confronted the megathermic Leguminosæ and Myrtaceæ, namely, the possibility of being forced to retreat, defeated, to the narrow belt of coastal area possessing mild and moist conditions, or of accommodating themselves to the new conditions.

They had the hungry, sandy soils upon which to make experiments and they possessed a stock of essential oil glands in the leaves, and other parts of the plants, wherewith to check excessive transpiration during the slow desiccation of Australia. Like the Leguminosæ and the Myrtaceæ, they made use of the great areas of hungry, sandy soils, and by a gradual process of reduction in size of the individual from trees to shrubs, to undershrubs and herbs, they produced the large endemic tribe Boroniæ with 18 genera and about 180 species. The leaf surface was also much reduced, and the primitive luxuriant pinnate leaf has been changed in Boroniæ to small, simple, trifoliolate, or rarely pinnate types.

The sandy wastes and the sandstone areas contain nearly the whole of this large endemic tribe.

In South Africa, a similar development took place, where the old luxuriant Xanthoxyleæ produced the large endemic tribe Diosmeæ in 3 subtribes, the number of genera being 11 with from 185 to 200 species. As in Australia the development took place mainly on the hungry, sandy tracts of land lying within the temperate region and the resulting endemic tribe is markedly xerophytic. Each country presents a remarkable example of the local development of secondary types from the primitive Xanthoxyleæ in hungry, sandy soils in dry hot summer regions, the areas being isolated, however, during the parallel evolution. As in Australia also the secondary types were shrubs, undershrubs, and rarely herbs.

In tropical America, another endemic tribe, namely Cuspariæ, was developed, with about 16 genera and with 85 to 90 species.

In the fertile and warm areas of Eastern Australia the primary Xanthoxyleæ developed about 5 endemic genera, but

with the exception of the oligotypic *Melicope*, these genera are practically monotypic and quite unlike the aggressive and vigorous *Boroniae*.

In the northern hemisphere another tribe, the *Ruteæ*, was developed, but whether these were hardy secondary types of *Xanthoxyleæ* or a northern modification of another tribe, allied to *Xanthoxyleæ*, the writer is unable to say, owing to non-acquaintance with the tribe *Ruteæ*.

The *Toddaliæ* and the *Aurantiacæ* might, perhaps, for the purpose of geographical distribution, better be considered as separate families, much as *Stellatæ*, in *Rubiaceæ*, would be considered better as a family distinct from *Rubiaceæ*.

The *Malpighiacæ*, *Meliacæ*, *Burseracæ*, and *Simarubacæ*, are all close allies of *Rutaceæ* and their distribution is similar to that of *Rutaceæ*, except that the *Rutaceæ* with their essential oil content have been more elastic in accommodating themselves to harsh extratropical conditions.

Similar evidence is supplied by a study of the *Euphorbiacæ*, *Labiataæ*, *Verbenacæ*, *Sterculiacæ*, *Sapindacæ*, *Apocynacæ*, *Asclepiadacæ*, *Pittosporacæ*, *Tremandræcæ*, *Liliacæ*, *Orchidacæ*, and other families. The remarkable cases of the *Proteacæ* and the *Epacridacæ* are considered subsequently under other heads.

In nearly every case it has been the hungry, sandy soils which have formed the areas on which the distinctive developments have been conducted during the climatic zoning after the isolation of Australia. In every case the primary types are luxuriant and cosmopolitan in the tropics; in almost every case the endemic tribe, genus, or species, has been dependent for its existence, or its development, on the hungry, sandy soils. In nearly every case the development has been markedly extratropical, and in every case the new groups, whether myrtaceous, leguminous, rutaceous, euphorbiaceous, verbena-ceous, lamiaceous, or other angiospermous form, is xerophytic. In every case the tropical family from which the xerophytes have sprung has possessed some peculiar virtue, or principle, by which the family has been enabled to survive during the gradual process of desiccation, and during the interval necessary to reduce the tree size, the form, the leaf area, and so on. In the *Legumes* it was the ability to dispense with leaves, the ability to develop gums, and so on; in *Myrtaceæ* it was the presence of much essential oil, the development of capsular fruits and the reduction of leaf and of plant size; in *Rutaceæ*, it was the presence of abundant essential oil; in *Euphorbiacæ*, it was



the presence of a latex and the ability to modify the leaves and stems; this is also apparent in the Apocynaceæ and the Asclepiadaceæ; in Verbenaceæ and Labiatae, it was the presence of essential oils and the special provisions in the leaves against excessive transpiration. In Sapindaceæ and Sterculiaceæ it was the presence of viscid substances as also special provisions in the leaf and the root. In Liliaceæ and Orchidaceæ it was the bulb, the peculiar leaves, and the development of the herbaceous habit which helped so materially in the growth of the great endemic genera. In the Apocynaceæ and Aselepiadaceæ, however, the plants were not equipped so well to face the cold, and as with Myoporinaceæ, they are not so much to be found on the extratropical sandy soils as on the more tropical subarid areas.

In each case they are the vigorous, numerous, aggressive, and many-specied genera of Australia, which appear to chafe at the limits which the Australian island continent has placed upon them and which appear to demand new territory in which to develop still further; in other words, they act as though they were new and aggressive types, born of a common necessity.

With the rare exceptions mentioned above these great genera occur together in any of the large sandy areas of temperate Australia and those types, in the genera *Eucalyptus* and *Acacia*, which are to be found on the rich heavy soils may be seen, by their morphology, to be more highly specialized, and to be more recent in their origin, than the great mass of the sandstone flora types. In no case has any large genus, any subtribe, or any tribe, of Australia been produced away from the barren sandy wastes!

(5) *Euphorbiaceæ, Labiatae, Verbenaceæ, Pittosporaceæ, Treman-*  
*draceæ, Liliaceæ.*

*Euphorbiaceæ.* In this great family, the sandstones produced the endemic tribe *Stenolobeæ* with 11 genera, and about 80 species, and as with all the other great families in Australia, no other endemic tribe, subtribe, or large genus of this family, was developed except on the peculiar hungry sandstone areas of Australia.

*Labiatae.* In this great family the hungry sandstone areas practically possess the whole of the endemic tribe *Prostanthereæ* with 5 genera and about 100 species.

*Verbenaceæ.* The tribe *Chloanthereæ* here included is endemic with 10 genera and about 40 species, all being practically limited to the sandy soils and as with the Labiates and other



families here described almost all are small shrubby xerophytes with special devices for conserving moisture.

*Sterculiaceæ.* Here the tribe Lasiopetalæ with 7 genera and about 70 species, almost entirely endemic and markedly xerophytic and mostly on the poor lands of Western Australia. A monotypic genus and one or two doubtful species in this tribe are said to occur in Madagascar. Other large xerophytic and endemic genera belonging to this family also occur in Australia.

*Pittosporaceæ.* This family has 9 genera, and about 110 species. Of these *Pittosporum* is a large luxuriant type with about 70 species spread over the old world tropics and the mild and moist extratropical areas in Australia and New Zealand (an exception in the xerophyte *P. phillyræoides*), the other 8 genera are endemic in Australia and are mainly xerophytes on waste or open spaces or on hungry sandy areas.

*Tremandraceæ.* This is a small family endemic in Australia allied to the Pittosporaceæ, containing 3 genera and about 25 species. All are xerophytes and of depauperate type, almost confined to barren sandy wastes in extratropical Australia.

*Liliaceæ.* This large family possesses many tribes and subtribes endemic in Australia, all as depauperate and xerophytic types and confined almost entirely to the extratropical barren sandy wastes.

The complete Tribes Endemic	{	Tribe Xeroteæ, 3 genera. Between 30 and 40 species.
		“ Xanthorrhææ, 2 genera. About 15 species.
		“ Calectasiæ, 3 genera. About 3 or 4 species.
		“ Flagellariæ, 1 genus (monotypic).
		“ Drymophileæ, 1 genus (monotypic).
		“ Hemerocallideæ, 1 genus (oligotypic).

The tribe Johnsoniæ is endemic with 5 genera and about 20 species. 2 subtribes are endemic in the tribe Melanthaceæ with 3 genera and 6 species. 1 subtribe is endemic in the tribe Anthericæ with 5 genera and 40 species.

#### (6) *Orchidaceæ.*

In this vast family about 48 genera are found in Australia. Of these about 20 genera are practically Australian with about 160 species. In many of the genera, however, outliers occur in New Zealand. These remarkable genera, mainly peculiar to Australia, are not epiphytes but occur as very small plants with bulbs deeply set in the barren sandy soils, especially of extratropical Australia. It would appear that the older luxuriant

epiphytes had become terrestrial owing to the severe and harsh climatic conditions existing in the extratropical sandy wastes of eastern Australia. In short the trees no longer afforded them the necessary protection, whereupon they descended and were preserved in the sandy wastes by the development there of new xerophytic genera.

Of the 48 genera in Australia, 28 genera, comprising one-third of the total number of species, including the whole of the tribes Malaxideæ, Vandææ, Bletideæ, Arethuseæ, the first group of Neottideæ, and the Ophrydeæ, belong to the tropical Asiatic Flora represented in Australia by endemic or, frequently, by identical species. These are all tropical or eastern, some extending down to Tasmania, but none found in West Australia; five of these genera are also in New Zealand. The remaining 20 genera, comprising two-thirds of the species, are essentially Australian, belonging to three Australian groups of Neottideæ; four of these genera are, however, represented by single or very few species in the Indian Archipelago and eleven have New Zealand congeners, sometimes identical in species.<sup>21</sup>

This closes the case for the Tropical Problem. When the South African Problem shall have been discussed in connection with the distribution of the families Proteaceæ, Epacridaceæ, Compositæ, Campanulaceæ, Lobeliaceæ, Goodeniaceæ, and Candolleaceæ, it will be evident that the general position in the plant world of the endemic Australian vegetation will be even more apparent than it is already from the present *brief* statement of the Tropical Problem. A careful consideration of the evidence here adduced, however, in which the widespread existence in the fertile tropics of luxuriant primary types, distributed among vast genera, is evident, with the great local developments of secondary xerophytic and depauperate forms in these families within the great sandy and barren wastes of countries, such as extratropical Australia and South Africa, the genera being endemic in each country with very few exceptions, the morphological relations between the local, secondary types in the several countries being less than between each secondary type, the cosmopolitan primary types moreover of the tropics and these endemic genera constituting the *whole*<sup>22</sup> of the great genera of Australia, the same genera being also extremely hardy, vigorous, and aggressive, leads to the inevitable conclusion that the vast genera of the tropics have developed their existing species *in situ* after the isolation from each other of the old mild and moist

<sup>21</sup> G. Bentham, *Flora Australiensis*, vol. vi, pp. 268-269, 1873.

<sup>22</sup> Excepting the Proteaceæ, Epacridaceæ, Goodeniaceæ and Candolleaceæ, about to be described.

regions in America, Australia and Africa and Asia, and that the great endemic genera of Australia such as *Eucalyptus*, *Hibbertia*, *Backea*, *Pultenaea*, *Darlesia*, and the Australian phyllocladous development of *Acacia*, are local secondary types of the great primary cosmopolitan tropical types, which secondary types have been developed as xerophytes on the vast areas of sandy wastes in Australia, and have never migrated far from the old home, by reason of their isolation, and because, despite the vigorous and aggressive nature of these local types, they are xerophytes and could not find a suitable environment on the outlying islands which are possessed of mild and moist climates and clad with jungle growths.

(b) THE SOUTH-AFRICAN PROBLEM.

(1) *General Remarks on Supposed Land Connections of South Africa and Australia.*

This problem has been considered already in some measure under the previous heading. In the present part the special case of the peculiar relations of the South African and Australian vegetation is considered.

It has been thought by some biologists that South Africa and Southwest Australia must have been directly connected long after the development both of the Monocotyledons and of the most complex families of the Dicotyledons, to wit, the Compositæ, say at the close of the Cretaceous Period, because the genera *Helichrysum*, *Helipterum* and *Cassinia*, in Compositæ, the genera *Restio*, *Hypolena* and *Leptocarpus*, in Restiaceæ, the genera *Cæsia*, *Wurmbea* and *Bulbine*, in Liliaceæ, the tribes Proteæ and Persooniæ in Proteaceæ, occur in both countries, while the family Ericaceæ is abundantly represented in South Africa, and the allied family Epacridaceæ occurs mainly in extratropical Australia.

But before proceeding with the main discussion it would seem advisable to confront this slender evidence of possible former direct connection of South Africa and Australia with the evidence of much greater weight on the other side.

Thus the great family of the Myrtaceæ is almost absent from South Africa although it possesses very many genera and species in Australia, and although the Australian Myrtaceæ are exactly the types which might be expected to occur on the poor sandy soils of South Africa on the assumption of the existence of a land bridge directly connecting the latter country with Australia.

It may not be out of place at this stage to mention that there is at least a double expectation of types such as *Eucalyptus*, *Hakea*, *Persoonia*, and *Banksia*, in both South Africa and Australia, on the assumptions made by various biologists, firstly, that *Eucalyptus* forests and other growths now peculiarly Australian, were common in Cretaceous and Tertiary time in the north temperate regions, and that under the pressure of more aggressive types they were driven to Australia, and secondly on the assumption made by certain biologists that a land bridge directly connected South Africa and Western Australia. For, firstly, on the assumption that *Eucalyptus* originated in the Holartic region, as so many mammalian groups appear to have done,<sup>23</sup> it should have retreated towards South Africa during the general expulsion from the north, of types unfitted to survive such as *Hakea*, *Grevillea*, *Erica*, and *Eucalyptus* itself, much in the same way as we may imagine the Restiaceæ, Proteaceæ, and Podalyriæ (Papilionaceæ), to have done. *Eucalyptus* belongs to a tribe which contains 28 genera, with about 700 species, many of the genera being large and aggressive (*Eucalyptus* 300 species, *Malaleuca* 112, *Bæckea* about 70). Another large tribe, namely the Chamælaucieæ, is found growing side by side with the *Eucalyptus* tribe. Both are practically endemic in Australia, with the exception of a few specialized waifs in outlying islands. Were the genera of these tribes to be very few in number and were these rare genera in turn to be monotypic or oligotypic and specialized or archaic, with huge gaps in the continuity of their distribution, these assumptions of land bridges directly connecting Southwest Africa and Southwest Australia might pass unchallenged, but when both the tribes and the genera are so vigorous, so admirably adapted to the soils and climate of the South African sand wastes, it is incredible that Myrtaceæ such as these should not have made use of one of the assumed land bridges constructed by biologists apparently for the special benefit of the Proteaceæ and Resticeæ, whose greatest desire, if one may adopt this teleological form of speech, would appear to be to dwell side by side with the myrtle group in their stronghold, namely Australia. But neither the genus *Eucalyptus*, nor any members *whatever* of the great and aggressive tribes Lep-tospermeæ and Chamælaucieæ, occur in South Africa! When, in addition, it is found that the fossil leaf determinations of the northern hemisphere cannot bear the searchlight of im-

<sup>23</sup> W. D. Matthew, Climate and Evolution, Annals New York Acad. Sci. ence, vol. xxiv, pp. 171-318, 1915.



partial botanical criticism, the necessity for the deletion of the genus *Eucalyptus* from the lists of Cretaceous and Tertiary flowering plants in the northern hemisphere must at once be evident.

On the assumption also of a great land bridge which carried the Proteaceæ, Restiaceæ and the Gnaphaliciæ (Compositæ) from Southwest Africa it is strange that the Epacridaceæ, which is a large family in Australia, could not use this bridge. This is especially strange, seeing that the Epacrids contain large and aggressive genera, which are inseparably associated with the Proteaceæ on the hungry sandy wastes of extratropical Australia. Moreover, the Epacrids are not decadent types, but on the other hand, they are vigorous and full of life. So also the very numerous Ericaceæ, with *Erica* alone containing about 470 endemic species in South Africa, should have got across to Australia if the sandy land bridge existed which is assumed to have allowed the Proteaceæ, Restiaceæ and Gnaphaliciæ to cross. But Australia possesses not a single member of the vast South African tribe Ericæ nor does it possess any member even of the family Ericaceæ save a very few types in the southeast which, moreover, do not occur in any form in South Africa and which are best explained in Australia as waifs from South America and a couple of species in North Queensland which are specialized outposts of northern hemisphere types.

The Compositæ also in South Africa on the poor soils possess two tribes, practically endemic, which might well be expected to have used the land bridge assumed for the Proteaceæ because the sandy soils of Australia are excellently adapted to support such forms as *Cryptostemma*. Yet only one species of the tribe Arctotideæ occurs in Australia, namely *Cymbonotus*, and, according to a personal communication from Mr. E. Cheel of the National Herbarium, *Cymbonotus* is not strictly a native of Australia and cannot in any way be separated from *Arctotis*. The Goodeniaceæ, the Candolleaceæ, the Casuarinaceæ and the Tremandraceæ, are also families with large, vigorous and aggressive genera all confined mainly to the sandy wastes of Australia, but without representatives in South Africa, excepting a waif of *Scævola*. Yet these are just the types which should have used the sandy land bridge had it really existed.

The Rubiaceæ of the two countries also are not alike. Scarcely a family of flowering plants, outside those already mentioned, and the ubiquitous Cyperaceæ and Graminaceæ, show any close resemblance to each other in the two countries

excepting indirectly through the primary types of the cosmopolitan tropics.

The nature of this assumed land bridge has been emphasized purposely here, because it seems that such bridge has been postulated without sufficient attention being paid as to its nature. The Proteaceæ of South Africa and Australia both flourish on the barren sandy wastes of these two countries in extratropical areas, and the few luxuriant types of this family which occur in the Australian brushes (jungle) belong to the suborder Folliculares, and have no counterpart whatever in South Africa. If then there did exist a land bridge which was used by the types of Proteaceæ *common* to South Africa and Australia, then it must have been a sandy waste, and one therefore which would have allowed a ready passage for the South African Compositæ, the Liliaceæ, the Ericaceæ (Ericææ), and the Australian family Epacridaceæ, and the tribes Leptospermeæ and Chamælaucieæ in Myrtaceæ. And, again, in addition to this overwhelming evidence against the assumed existence of the land bridge after the development of the most complex types of flowering plants, there are the wonderful differences existent among the mammals of the two countries which must also be taken into account. South Africa possesses no marsupials, whereas Australia has no placentals. The answer to this may be made that marsupials *did* migrate from Australia to South Africa along the old sandy bridge used by the Proteaceæ, Restiaceæ, Compositæ, and a few small genera in Liliaceæ, while other flowering plants which loved such sandy soils could only look, as it were, towards the promised land from the bridge without entering. It may be assumed also that the waiting carnivora ate the unsuspecting marsupials as they arrived in South Africa by way of the land bridge. The wonder, in a case such as this, is that the lions, tigers, hyænas and other carnivores, which may be supposed to have annihilated the marsupials in South Africa, did not follow such good food along the bridge to Australia and there in turn feast upon the defenceless wallaby, kangaroo, wallaroo, paddymelon, beilby, kangaroo rat, opossum, and allied types.<sup>24</sup>

The evidence on the other hand suggests that the Proteaceæ, like the marsupials, flourished in the northern hemisphere and were driven to "dead ends" in South Africa and Australia, and there, in each country, on the sandy soils and under very

<sup>24</sup> See also in this connection an admirable paper by Mr. J. H. Maiden, entitled "Australian Vegetation," Federal Handbook on Australia, B. A. A. S., Australian Meeting, 1914, by authority.

similar climatic conditions, and protected in each case by barriers from severe outside competition, they rapidly deployed into fresh tribes, and subtribes, with the production of great vigorous and aggressive endemic genera, genera also which have always been endemic. The absence of the placentals in Australia affords some measure of the duration of the period of isolation of Australia, while New Zealand was isolated much earlier.

The cases of the Proteaceæ, Compositæ, Ericaceæ, Epacridaceæ, Campanulaceæ (with Lobeliaceæ), Restiaceæ, and Liliaceæ, may now be discussed briefly.

(2) *Proteaceæ.*

This family is divided into 2 suborders and 7 tribes, containing 50 genera and about 1,100 species.

Of these, Australia has about 700 species, in more than 30 genera in 7 tribes, in 2 suborders. New Zealand has 2 species in 2 genera in 2 tribes. New Caledonia has about 30 species in about 6 or 7 genera and several tribes. South Africa has about 275 species in 10 genera in 2 tribes, in 1 suborder. Tropical Asia has about 30 species in 1 genus in 1 tribe, and South America, mainly Tropical America and Chili, has about 65 species in about 7 genera in a couple of tribes, in one suborder. Although the suborders Nucumentaceæ and Folliculares are both abundant in Australia, the African species all belong to Nucumentaceæ and the Asiatic and American types all belong to Folliculares.

Berry, in an important and comprehensive paper,<sup>25</sup> supplies convincing evidence for the great radiation of the Proteaceæ in the mild and moist climate of the Cretaceous, with survivals of the family to-day mainly in the southern hemisphere. Bentham<sup>26</sup> was inclined to deny the existence of Proteaceæ as fossils upon general botanical principles and Engler<sup>27</sup> wrote "Die fossilien, geflügelten Früchte, wer für Samen der Proteaceen gehalten wurden, können sich zu den Coniferæ, Meliaceæ, Sapindaceæ, gehören." The fossil fruits and leaves referred to by the various writers mentioned in the previous paragraph<sup>28</sup>

<sup>25</sup> E. W. Berry, The Affinities and Distribution of the Lower Eocene Flora of South Eastern North America. Proc. Amer. Phil. Soc., vol. liii, no. 214, pp. 157-164, 1914.

<sup>26</sup> G. Bentham, Presidential address, Linn. Soc. London, 1870.

<sup>27</sup> Engler and Prantl, Pflanzenfamilien, III Teil, 1 Hälfte.

<sup>28</sup> Ettingshausen, Die Proteaceen der Vorwelt, Jahrbuch der K. K. geologische Reichsanstalt, vol. i, Vienna, 1881. Ibid., Wiener Zeitung, 21 March, 1880. Entdeckung des neuholländischen Charakters der Eocenflora Europas, Vienna, 1862. Unger, Neuholland in Europe, Vienna, 1861. Saporta (Marquis de), Flore fossile du Portugal, Lisbon, 1894. Newberry, J. S., Fossil Flora of the Amboy Clays, United States Geol. Survey, Washington, 1894. Berry, E. W., op. cit., pp. 157-164.

have been considered by some botanists as belonging to *Hakea*, *Grevillea*, *Persoonia*, *Banksia*, *Dryandra*, and allied types.

Although agreeing with Berry in his contention that the Proteaceæ were at one time luxuriant types in the northern hemisphere which were driven south at a later period, it is impossible to review the evidence past and present without coming to the conclusion that *Hakea*, *Persoonia*, *Grevillea*, *Banksia*, *Dryandra*, *Protea*, *Leucondendron*, and other allied types, never did exist in the northern hemisphere, but that they arose in the south as xerophytic developments of older widespread Cretaceous types. In Australia and Africa such genera as are enumerated here are all vigorous, hardy, specialized, aggressive, and xerophytic. They avoid the Australian and African jungles; they avoid all mild, moist, and sheltered positions; and they occur as highly specialized forms on the sandy barren waste of the two countries under consideration. Xerophytic Myrtaceæ, Compositæ, Leguminosæ, Ericaceæ, Epacridaceæ, and Lilaceæ, are their special associates, nevertheless like *Eucalyptus*, *Melaleuca*, *Erica*, *Leucopogon*, *Goodenia*, *Candollea*, *Hibbertia*, and *Pimelea*, they appear to strain at a leash as though eager to people new lands if only their large island home should be connected by large barren sandy wastes with other countries.

It seems permissible to infer that the development of the Proteaceæ appears to have begun in the great northern lands,—but it is difficult to decide upon which suborder was the earlier. The Nucamentaceæ have the more regular perianth, but the Folliculares also have many genera with regular perianths. The high specialization, however, of certain genera such as *Hakea*, *Grevillea*, *Banksia*, and *Dryandra*, in Folliculares, especially with respect to their anthers, which are sessile upon the perianth segments above the tube, together with the irregular perianths of *Grevillea* and *Hakea* suggests the relative recency of such highly specialized genera and, moreover, it would appear that they are vigorous and aggressive genera because of such specialization.

The primitive type appears to have been a large tree of luxuriant habit, with regular perianth, free stamens unattached to the perianth tube, and with large pinnate, compound, or lobed leaves.

With the zoning of the climate, and the development of aggressive plant types in the northern hemisphere, these Proteaceæ were gradually driven south, while the tropical types became more and more superseded by the more complex Symptalæ, Dialypetalæ and the Monocotyledons. The sandy wastes



of extratropical Australia and South Africa offered a home to these trees, and, thus, during the long gradual differentiation of the climate, the trees became smaller, and they developed marked xerophilous characters; and in proportion as the types became specialized and reduced in size or dwarfed, so did such types become vigorous and aggressive as *Grevillea*, *Hakea*, *Petrophila*, *Isopogon*, and *Persoonia*.

(3) *Compositæ*.

The problem of the development of the *Compositæ* as also of the *Ericaceæ*, *Epacridaceæ*, *Campanulaceæ*, *Lobeliaceæ* and allied types, might be considered equally well under the heading "The South African Problem" or the "Northern-Hemisphere Problem."

In South Africa and Australia the following genera are common:

<i>Australian Species.</i>	<i>South African Species.</i>
<i>Senecio</i> 30	200
<i>Gnaphalium</i> 7	8 to 10
<i>Helichrysum</i> 70	140 to 150
<i>Helipterum</i> 53	12
<i>Cassinia</i> 13	1
<i>Athrixia</i> 7	6
<i>Cotula</i> 8	22

Of these *Senecio* and *Gnaphalium* are cosmopolitan, *Helichrysum* has 26 species in Tropical Africa, 40 species in Madagascar, and the genus also extends into North Africa, Europe and Central Asia. *Helipterum* may be considered as a subgenus of *Helichrysum* for the purpose of distribution. *Cassinia* may be discarded as doubtful or as a waif, while *Cotula* has also six species in Europe and Asia. As against this resemblance with *Helichrysum*, *Helipterum* and *Athrixia*, the absence from Australia of the whole of the two South African tribes, *Calendulaceæ* and *Aretotideæ*, may be cited.

It would perhaps be advisable to preface the accompanying brief notes of the probable origin of the *Compositæ* in Australia and South Africa, by mentioning the distribution of the asters, the daisies, and the groundsels, as set out by Bentham in his monograph on the *Compositæ*.

*Aster* in the broader sense comprises the true asters of the northern hemisphere and a few genera almost inseparable from it except in habit which occur in the southern hemisphere and in Hawaii.

The true asters number 300 species and are herbaceous, loving cold countries, crossing the Equator only as one species on the high plateaus of Africa. Closely allied to the asters is *Olearia* (110 species) in Australia and New Zealand, not herbs, but generally shrubs or undershrubs with a few trees of moderate size. The shrubby South African *Felicia*, with about 50 species, is exceedingly close also to *Olearia* and *Aster* while the arborescent *Chiliotrichium* of 3 or 4 species in Chili and the arborescent to shrubby *Diplostephium* of about 20 species in the Andes, are also very close to *Olearia* and *Felicia*. The arborescent genera *Commidendron* (3 species) and *Melanodendron* (1 species) also in St. Helena are scarcely separable from *Diplostephium* in South America. The aster type is absent from the tropics except on the high plateaus.

*Erigeron*, *Celmisia*, *Tetramolopium*, *Vittadinia*, and *Teranea*, form a group very similar in distribution to the asters.

The daisies also have a peculiar geographical distribution. *Bellis* with about 5 species, in Europe and North Africa, *Astranthium* 1 or 2 species in America, *Seubertia*, 1 species in the Azores, *Steirodiscus* with 2 species in South Africa, are all practically identical as genera with *Brachycome* which possesses 40-45 species in Australia, the tropics having no member.

*Calotis* (17 species in Australia), *Bellium* (3 species in Europe), *Keerlia* (2 species in Mexico), *Garuleum* (3 species in South Africa), and *Minuria* in Australia are exceedingly close both to each other and they are close also to *Bellis*.

The *Groundsels*. *Senecio* contains 1,200 species and is "cosmopolitan and ubiquitous" (Bentham). It abounds "in local species in almost every region of the globe, in the Old and in the New World, from the Equator to the arctic regions and the extreme south, on Alpine summits, in stony wastes or sandy deserts, in swamps, on sea coasts, on the borders of streams . . . yet individually the species have not wide areas. No species is common to the New and the Old World, except in the far north no one has . . . its range interrupted by any considerable interval."<sup>29</sup>

Although the majority of the northern hemisphere *Compositæ* are herbaceous, as are those also of the deserts and subarid wastes, nevertheless the southern hemisphere and the oceanic islands preserve many arborescent forms representing all the larger tribes such as *Asteroideæ*, *Senecionideæ*, and *Helianthoideæ*.

<sup>29</sup> G. Bentham, *The Compositæ*, Journ. Linn. Soc. London, Botany, vol. xiii, p. 456, 1873.

The Compositæ favor the open spaces and rocky wastes of the world and avoid the dense jungle and thicket growths.

It seems permissible to infer that the ancestor of the composites was a tree which possessed opposite leaves, pinnate or compound, a compacted flower head possessing only disc florets with free anthers, flowers regular, but the plant possessing a tendency early to xerophytism somewhat similar in point of time to that exhibited by the primary type of *Acacia*. These plants flourished in the open places of the world, during the Cretaceous. As the seas were drained off the lands, and as the climate became differentiated the ancestral types forsook the low tropical lands, because in the first place they were not adapted to compete with the dense growths of the tropics, and because the deserts in the tropics were too dry and hot for the old lover of the well-watered but open spaces. As the lands became isolated one from the other local differentiation ensued, the old trees were weeded out in the north as the severe climatic conditions of the late and post-Tertiary approached and vigorous aggressive herbs were produced, which commenced to work their way south along the mountains and high plateaus.

The old tree *Aster* was among this group. In Australia the arborescent form was reduced in size and a shrubby habit was developed. From this the genus *Olearia* with 110 species in Australia and New Zealand was derived. In South Africa as in Australia, the old *Aster* had to face a gradual desiccation of climate during the isolation of South Africa, and the shrubby *Felicia* of 50 species was developed. In Chili, the old form was modified to the arborescent *Chiliotrichium*, so also in the Andes the arborescent genus *Diplostephium* was formed, while in St. Helena, the arborescent *Commidendron* and *Melanodendron* are closely related to the old widely-diffused tree-*Aster*. In the northern hemisphere the arborescent form was destroyed and a vigorous aggressive and cold loving herb was produced which worked its way south to the Equator in Africa. The evolution of *Bellis*, *Brachycome*, *Astranthium*, *Seubertia*, *Garuleum*, *Keerlia*, *Bellium*, *Calotis*, *Minuria*, and *Vittadinia*, was somewhat similar to that of the asters, except that the plants were herbs at an early stage during some differentiation earlier than the Eocene, and that they are a decadent race, except in Australia and the Mediterranean and, moreover, they were not adapted to cold conditions so much as to barren, sandy, and open conditions in climates not really cold.

*Senecio*, like the *Aster*, appears to have its primary form as a tree, but it is a form which, like all other of the Compositæ,

has become more and more herbaceous and correspondingly aggressive with the progress of time, and it appears to have adapted itself to stony and mountainous, as also to cold conditions.

The more the flowering plants are studied the more is the conclusion forced upon the student that many types have passed through two periods of climatic differentiation, the one prior to the great isolation of Australia, the other after the Eocene, or after the great isolation. The first differentiation appears not to have become so marked as the second. It has been pointed out, however, that the xerophytic angiosperms just discussed could be explained on the assumption of deserts throughout Cretaceous and Tertiary time with a great zoning of climate in past Eocene time.

It seems permissible to regard the earlier *Senecios* as trees, which frequented the open places and which loved moisture. These arborescent forms appear to have populated all the great land blocks before the isolation of Australia from Southern Asia, and the herbaceous habit also appears to have been developed among some of the species even before the isolation was complete. After the great isolation and the gradual differentiation of climate the *Senecios* were unable to make much headway in Australia owing to their greater preference for moist, cool places and their inability to flourish well within hot arid regions. In New Zealand they flourished in the moist, cool climate and the old arborescent habit is preserved in some species. Hawaii, and Juan Fernandez, illustrate in some measure the primary tree type.

It was in the northern hemisphere, however, that *Senecio* made its great and aggressive response to the cold changes both towards, and during, the Glacial Period. Over Eurasia and North America the new race spread rapidly, nor did it cease to travel until it reached the Magellan Straits where its progress farther was stayed. In the cold climate of the Chilean heights and of the country about Magellan Straits, however, it became strongly developed, about 260 species having been recorded thence. (Carl Reiche, *Flore de Chili*.)

In South Africa on the poor plateau soils *Senecio* made a magnificent response (200 species) to its environment.

*The Everlastings.* The case of *Helichrysum* and its allies may now be considered. These all belong to Inuloideæ, a tribe with many genera and species but decadent in great measure, although possessing a large and vigorous offshoot from the old



more or less withered stock of the tribe, namely, the great sub-tribe, Gnaphalieæ.

*Gnaphalium*, close to *Helichrysum*, is a cosmopolitan, and favors the tropics. The *Helichrysum*, or everlasting, group favors waste stony and sandy localities outside the cold regions. A study of the Australian types such as *Helichrysum* and *Cassinia* suggests that the early forms were trees favoring open places. A study also of the distribution of the Helichryseæ suggests that they are a branch of Gnaphalieæ which arose as warmth-loving types during the first great differentiation of climate and which spread thence to Australia, Africa, and New Zealand. As time progressed, and as the severe conditions of the middle, later, and post-Tertiary approached, they took refuge, in great measure, on the sandy barren wastes of Australia and South Africa, soils which had also been the salvation of the Proteaceæ, the Ericaceæ, Epacridaceæ, Leguminosæ, Myrtaceæ, and many other families. In proportion as the arborescent form was discarded, and the herbaceous habit adopted, so did the types succeed in life. In the northern hemisphere they were not as successful as in the southern because, unlike *Senecio* and *Aster*, they were not adapted to the cold climate so much as to the drier, sandy and stony wastes in warmer climates. The great display of *Helichrysum* and *Helipterum* both in South Africa and temperate Australia does not, therefore, demand the existence of a *direct* land connection between the two so much as it demands an old land connection between them by way of the tropical regions, the sandy barren wastes in each of the southern areas acting as a place of refuge to these types.

(4) *The Ericaceæ and the Epacridaceæ.*

These related families appear to have had two, if not more, distinct periods of revival, the one before the great isolation of the larger land blocks, the other during the great differentiation of climate culminating in the Glacial Period.

Both belong to the Sympetalæ. The Ericaceæ possess 8 or 10 stamens, all free, the anthers generally opening in pores and possessing appendages in many instances, while the Epacridaceæ have 5 stamens generally attached to the corolla tube, the anthers are only 1 celled, and they open in longitudinal slits, although a more primitive type (*Prionotes*), has its anthers two-celled. The venation is very peculiar, consisting of parallel nerves, very suggestive of monocotyledonous forms, while the Ericaceæ possess penniveined leaves.

The Epacridaceæ are peculiarly xerophytic, having leaves either small terete, acicular, pungent, grooved, thick or hard, and they are trees, shrubs, or undershrubs, which are confined principally to moist situations on the barren sandstones of extra-tropical Australia. They are as much an integral part of the indigenous, endemic, xerophilous, flora of Australia as are the Proteaceæ, and the Myrtaceæ.

Ericææ, in Ericaceæ, has its stronghold on the sandy barren wastes of Southwest Africa. *Erica* is only one of the many allied genera in that country, *Erica* itself, however, possessing there nearly 500 endemic species. This genus, however, does not favor wet situations as much as the Epacrids do. From a consideration of the distribution and the morphology of the families, it would appear that both families sprung from common ancestral types which were luxuriant trees, especially in the great northern lands, and in the tropics possessing leaves either nerved or penniveined, stamens free, anthers 5 to 10, with two cells opening longitudinally in slits and without appendages.

In the first great radiation these types reached Australia and South Africa. After the isolation of Australia and South Africa they retreated to the sandy wastes of the two countries. In Australia they became the Epacrids, in South Africa the Ericas. In each country they developed a great crop of vigorous and aggressive genera. During the second great differentiation of climate in the northern hemisphere, the other large tribes of Ericaceæ became strongly developed in the cold countries contemporaneously with *Senecio*, *Aster*, and other types, in Compositæ.

The newer cold types of the north, as *Gaultheria*, travelled south during the Glacial Period to the extreme south of America. Waifs thence were carried by the great westerly drift or by other means to Australia and New Zealand, developing in those countries a very few individuals belonging to two or three genera. (*Gaultheria*, 3 species, *Pernettya*, 2 species.) The genus *Wittsteinia*, one species only and belonging to the tribe Arbutææ, may be a waif, or it may be a relic of the old Cretaceous radiation.

(5) *Campanulaceæ (with Lobeliaceæ, and allied families).*

The Campanulaceæ and its allies are good examples of the two-period differentiation of climate. From an examination of Campanulaceæ, Lobeliaceæ, Goodeniaceæ, and Candolleaceæ generally, and of the peculiar arborescent Lobeliaceæ of Hawaii

(*Clermontia* 11 species, *Rollandia* 6 species, *Delissea* 7 species, *Cyanea* 28 species), the arborescent *Scelerotheca* of Tahiti and Raratonga, *Apethia* of Raiatea, the remarkable tree *Lobelias* of Hawaii, Abyssinia, and Central Africa, and the arborescent forms in America, it would appear that the early forms were trees which loved moist open spaces, the trees possibly without milky juice.

In the Cretaceous Period the primary types found their way into Australia, and during the first differentiation of climate, probably during the Cretaceous Period, the arborescent types became more and more herbaceous and found their way into Australia, South Africa, and other countries, as the genus *Lobelia*, and allied forms. The ancestor of *Campanula* and *Wahlenbergia* also found its way round the world about this period.

The oldest forms have produced the remarkable and specialized Goodeniaceæ and Candolleaceæ which arose in Australia on the barren, sandy wastes, after the great isolation of Australia and after great modifications had taken place in the stigma and filaments of the primitive type in Australia. In the northern hemisphere the ancestral types were driven out and all that we know of the middle era of the race after the differentiations into Campanulaceæ and Lobeliaceæ with milky juice, are the peculiar arborescent genera above mentioned, which are not actually perpetuations of old time genera, so much as they are newer genera allied to the older Lobeliaceæ and which have been evolved locally in response to their later environment of sandy waste in the peculiar climate of Australia.

After the isolation of the northern hemisphere and the climatic differentiation of post-Eocene time, *Campanula* appears to have been developed in the north, and *Wahlenbergia* in the south. The latter became aggressive and penetrated the north at a later date much in the same way as *Erica* had done among the heaths.

The Goodeniaceæ with an indusium to the stigma and the Candolleaceæ with filaments and pistil united into a column appear to be magnificent examples of ancestral types which, after retreating as arborescent forms from more favored surroundings in the north to a "dead end" in Australia, gradually developed the herbaceous habit on sandy and stony wastes which were subject to long, dry, hot spells. In the fullness of time these became hardy, vigorous, and aggressive types which, like *Wahlenbergia* and *Lobelia* of older and more northern

origin, are ready now to overrun the world, but which are limited in their range because of the ocean encircling Australia. Waifs, however, have survived the sea voyage in certain cases, for example—*Goodenia* with about 115 species, *Candollea* about 115 species, *Scævola* about 70, and *Dampiera* 35-40 species, and the individuals are exceedingly abundant on the sandy wastes of Australia.

The history of the Campanulaceæ, in the broader sense, is somewhat analogous to the history of the human races which reached East and South England as conquerors, and which after a time became less vigorous and were in turn thrust northward and west by the indriving of new wedges of invasion. In the barren wastes to which they were driven, and the consequent enforcement of laborious days, together with the elimination of luxury and pleasure, magnificent revivals were brought about and later days of courage and ability among the old exiles who, although beaten and discouraged awhile, now take their place again in the front of the world's progress.

(c) THE SOUTH AMERICAN PROBLEM.

(1) *General Remarks on Supposed Land Connections.*

The question of the possible land connection, or connections, between South America, New Zealand, Australia and Tasmania, has formed one of the most difficult but fascinating problems ever faced by students of geographical distribution from the time of Hooker<sup>30</sup> and Bentham<sup>31</sup> in England to that of Hedley<sup>32</sup> of Australia.

Hedley, one of the foremost of the present advocates for the Tertiary, or post-Tertiary, land connection of the areas under consideration with Antarctica, has stated his case simply and forcibly in the two papers cited above.

There are about 88 genera and 68 species of flowering plants, confined, almost entirely, to South America, the Antarctic Islands, Australia, Tasmania, New Zealand, and the neighboring islands. The Beeches (*Nothofagus*), the fuchsias (*Fuchsia*), the Araucarias (*Araucaria*), *Discaria*, the section *Psycrophila* of *Caltha*, *Oreobolus*, *Uncinia*, *Colobanthus*, *Ourisia*, *Azorella*, *Epilobium*, *Acæna*, *Aristotelia*, as also the species *Geranium sessiliflorum*, *Oxalis magellanica*, *Tillæa moschata*, *Tillæa verticillata*, *Juncus planifolius*, *Gentiana saxosa*,

<sup>30</sup> J. D. Hooker, *Journal Botany*, London, vol. iv, p. 137, 1845.

<sup>31</sup> G. Bentham, *Flora Australiensis*. Concluding Preface, vol. vii, 1878.

<sup>32</sup> C. Hedley, *Surviving Refugees in Austral Lands*. *Proc. Roy. Soc. N. S. Wales*, vol. xxix, pp. 278-286, 1895. *The Palæogeographical Relations of Antarctica*, *Proc. Linn. Soc. London*, Oct., 1912, pp. 80-90.



*Sophora tetraptera*, and *Euphrasia antarctica*, are amongst the most noted in this connection. The struthious birds, as the Rhea (S. America), the Ostrich (Africa and Asia), the Cassowary (North Australia), the Emu (Australia), the Moa (New Zealand), and the Epyornis (Madagascar), are also cited as evidence of former land connections between these regions. *Placostylus*, among land shells, the earth-worms, the reptiles, the marsupials, and other animals, are also cited as proof of former land connections.

It has been found difficult to discuss this most interesting and complex problem with justice from the point of view of the distribution of the animals, nevertheless it is just from the animal distribution that the strongest case is said to have been deduced for a former direct land connection between the various areas under consideration. The construction of the hypothetical continent Antarctica reaching arms of land to the southern land masses of South America, South Africa, Australia and New Zealand, and acting as a developing ground for the life forms common to the areas under consideration, is undoubtedly a most suggestive conception, and one which especially in the form in which Hedley has stated it, appears to be quite convincing from so many points of view. On the other hand it would be advisable to indicate some of the difficulties in the way of accepting this idea which have been suggested to the writer by a study of geology and botany.

As a preparatory step, however, it might be advisable to dispose of some of the general objections raised against this doctrine, which has been so suggestive and so full of promise to the investigator. It is considered by certain biologists that the plants and animals said to be common to South America, South-eastern Australia, South Africa, and New Zealand, need no direct land connections to explain their peculiar distribution but that they are to be explained rather as similar biological responses to similar environments. That is to say, the marsupials, the struthious birds, the pine trees, the beech trees, and the other forms common to these regions arose independently in each country as a response to a similar geographical environment.

Let us, in this connection, consider the case of the families, genera, and species, identical in South America, Australia, and New Zealand. The number of families of flowering plants is about 250, nevertheless the possible number, probably, is legion. Let us assume, however, that 250 is the limiting number. The possible number of genera in a family is immense, as is at

once apparent from a consideration of the doctrine of permutations and combinations. Let it be assumed, however, that a family may have only 1,000 genera, and furthermore let it be assumed that each genus may have only 2,000 species. Then because the South American and Australian continents have few points in common beyond the fact that each is in the southern hemisphere, the chance that a particular family of flowering plants should arise independently in each country is somewhat similar to the chance that a die with 250 faces and thrown fairly into the air, should fall down with any particular face uppermost. But there are 250 ways in which this may be done, therefore the chance is only 1 in 250. Similarly the chance that a particular genus should arise independently in each country in such a particular family would be similar to the chance of two particular faces on two dice falling uppermost if the dice were thrown fairly, the one with 250, the other with 1,000 faces. But the odds are 250 to 1 against one particular face turning up on the one die if thrown by itself and the odds are 1,000 to 1 against a particular face turning up on the other die, therefore the odds against both of these particular faces falling uppermost when the two dice are thrown together is 250,000 to 1. Similarly the chance that a particular species should arise in two countries independently, all other things being equal, is somewhat similar to the chance that a particular face on each of three dice, one of 250 faces, one of 1,000 faces, and one of 2,000 faces, should fall uppermost if thrown fairly into the air. But the odds against this are  $250 \times 1,000 \times 2,000$  or 500,000,000 to 1, and the chance that two identical species should be evolved independently in each of two isolated countries would be only 1 in 250,000 billions. And the chance that 80 genera and 60 species should be evolved independently would be infinitely more remote than the vanishing chance already mentioned.

On the other hand, it is well known that plants are continually being transported by winds, sea currents, by birds, and by man, from various lands to other lands, and, moreover, geology teaches us that, in the past, various land masses have been directly connected to each other. Identity of families, genera, or species, therefore, are more simply explained by consanguinity of origin than by the assumption of multiple origins. The present distribution of the plants and animals in Australasia, New Zealand, South Africa, South America, and the Antarctic Islands, is, therefore, concerned rather with the relative merit of certain hypotheses of transport or of migration,

consanguinity of origin being admitted as the simplest explanation of the presence of identical families, genera, and species, in land blocks now not in direct communication with each other by land.

(2) *On Certain Unexplained Peculiarities of Angiospermous Distribution in these Southern Lands.*

The angiosperms, as a whole, which are common to the lands under consideration are not very cold types such as exist in many parts of the northern hemisphere. There are, indeed, identical species in the areas under discussion which love the cold. These, however, such as *Geranium sessiliflorum*, *Geranium dissectum*, *Oxalis magellanica*, *Tillæa moschata*, *Euphrasia antarctica*, *Gentiana saxosa*, and *Juncus planifolius*, may be explained as being due to the action of winds, sea rafts, sea currents, birds, or of man, much in the same way as, in latitudes slightly warmer, plants such as *Entada scandens*, *Sophora tetraptera*, *Mimosa pudica*, *Convolvulus soldanella*, *Ipomea pes capræ*, *Senecio lautus*, and others, are known to be distributed by these and similar agencies.

On the other hand, many cold types in South America have not a single representative (excepting one or two species of *Oxalis*) in New Zealand, Tasmania, or Australia. For example, *Patagonium* with 150 species in Chili, especially the Andean heights, *Astragalus*, one of the most vigorous and aggressive of cold country plants, has 75 to 80 species in Chili and Antarctic South America, *Lupinus* (2 species), *Vicia* (30 species), *Lathyrus* (20 species), *Haplopappus* (100 species), *Oxalis* (90 species), *Escallonia* (25-30 species), *Valeriana* above 50 species in Chili and Antarctic South America, *Alnus*, *Agrimonia*, *Saxifraga*, *Ribes*, *Hieracium*, and other forms which frequent cold countries, and are found in Chili and the Andean heights, have no representatives in Australia and New Zealand.

Moreover, there appears to be very meager evidence, either astronomical or geological, to justify the assumption as to the movement of the Poles even as much as 1 to 3 degrees since the Jurassic or Cretaceous. The Poles therefore may be considered as having been practically stationary both before and after the Pleistocene<sup>33</sup> glaciations, as far back in time indeed, in all probability, as the origin of the angiosperms. This being so, it is reasonable to expect, on the assumption of an Antarctic

<sup>33</sup> Joseph Barrell, "The Status of the Hypothesis of Polar Wanderings," *Science*, N. S., vol. xl, pp. 333-340, 1914.

origin for the plants common to South America and Australasia, that such plants must have made some provision for the many months of darkness which they must have experienced in their migrations across the South Pole region from South America to Australia. What provision, it may be asked, did these plants make for the long winter's night? Did they simply rest, and shed their leaves, from which the chlorophyll had departed, or did they dispense with their leaves entirely? As a matter of fact, instead of having structures or devices specially adapted for the polar darkness, they are just those types of plants which might be expected to have been developed in a temperate climate, with the exception of the cold species common to the various areas under consideration and already enumerated in part, and which may be found also on the islands lying between Cape Horn and New Zealand. *Epilobium*, *Senecio*, *Caltha*, *Ranunculus*, *Tillæa*, and other genera, are common to the areas considered, but they are cosmopolitan in temperate and cold regions. At the least one would expect such types to be deciduous, but this is exactly what they are not.

### (3) *The Catkin-bearing Plants.*

The possible distribution in time and space of the catkin-bearing plants may be considered in this connection. This deduced distribution is suggestive of the method of dispersal and development of *Librocedrus*, *Podocarpus*, *Dacrydium*, *Caltha*, *Ranunculus*, and *Epilobium*, in what may be called the southern "dead-ends" of the world.

From a comparison of the various types of plants which bear catkins, it may be conjectured that the earlier types were forest trees of luxuriant habit, many types possessing beautiful pinnate or compound leaves, and moreover trees which seem to have been lovers of mild and moist climates. They appear to have spread over the world during the Cretaceous, or at any rate, before the isolation of Australia and New Zealand from the greater land blocks. At a stage relatively early in the history of angiosperms these types appear to have been unfitted to cope with the severe competition of the entomophilous jungle-plants of the more tropical regions, inasmuch as the catkin-bearing plants were adapted to wind fertilization and were hampered in great measure by the suffocating and strangling action of the later plant types of the milder and moister climates. Not only so but the hard baked clays and waterless tracts of the dry torrid regions were also unfavorable to their



development. Owing to these and other causes they were forced north and south of the tropical and subtropical lands. This had been the history of the Coniferæ also about the same time, or perchance, at an earlier period.

In the southern lands *Fagus* appears to have established itself firmly, although there was a wholesale extinction of amental types there either at this or a later period. Casuarinaceæ, however, is one of the families which sprang from an early form, by adapting itself to the hungry and barren sandy soils in the warmer portions of Australia. One of the most serious handicaps which had been imposed upon the Coniferæ and the Amentales was the peculiarity of their constitution, whereby only with the greatest difficulty were they enabled to reduce their size as individuals. This inability to reduce the great size of their woody stems brought about the extinction of very many genera, and, perhaps, even families, during the great zoning of the climate. The Casuarinaceæ offset this inherent defect in the family constitution by reducing the leaf surface and by sending down long roots to tap the underground sources of moisture, and, moreover, this type succeeded also in life by following watercourses, swamps, and other supplies of moisture, such as occur on the sides of mountains formed of porous or well-jointed sediments or sandy rocks.

But during the second great differentiation in the northern hemisphere the Amentales became very vigorous especially as the Glacial Period was approached. During this post-Eocene Period, *Quercus*, *Salix*, and other types increased in numbers and began to advance south. Especially qualified were these grand types for the conquest of cold well-watered regions after their development of the deciduous habit, whereby they could rest in the winter. In the far south *Fagus* only succeeded in facing the cold by reducing the leaf surface, by the crowding together of individuals and by keeping in the shelter of mountains as much as possible. *Fagus moorei*, in the northern portion of New South Wales, has a large leaf suggestive of the earlier more luxuriant amental leaf. The Casuarines on the other hand, are striking examples of the extreme reduction of leaf surface. The one exhibits in a marked degree an adaptation to a cold, moist, but sheltered area, the other exhibits in an equally marked degree an adaptation to poor hungry soils and to a climate showing marked diurnal changes of climate.

*Alnus*. In South America *Alnus* is to be explained, probably, as a southern immigrant during the great Glacial Period, although it is possible that it migrated to South America and

to Australia during the earlier differentiation of climate and that it was killed off at a later period in Australia. *Quercus* also may have travelled south during the earlier period, but its distribution suggests that it belongs to the later period of development. So also *Salix* appears to belong to the second period. It seems permissible, however, to infer that *Alnus*, *Salix*, *Quercus*, and some allied types, are to be referred to the period of development of *Astragalus*, *Ulex*, *Lathyrus*, *Vicia*, *Lupinus*, and *Carduus*, namely, one after the isolation of Australia and New Zealand from the world proper.

The absence of these types from South Africa may be explained as being due to the lack there of cool, to cold, and well-watered country such as occurs in Southern Chili, South-east Australia and New Zealand. Before any family adapted to the xerophytic conditions within South Africa had opportunity to develop, the plants with catkins appear to have perished in that region.

These notes are inserted here merely with the intention of drawing attention to the hitherto unexplained botanical difficulties on the assumption of a Tertiary or post-Tertiary land connection between the southern lands and Antarctica. On the other hand the "Cretaceous and Eocene radiation" affords one explanation of this peculiar angiospermous distribution.

(d) THE NORTHERN HEMISPHERE PROBLEM.

This is bound up in the general problem of South America and South Africa, and the possible distribution of one family only, namely, Umbelliferæ, is discussed, inasmuch as it is typical of the distribution of families such as Cruciferæ, the Amentales, Ranunculaceæ, Gentianaceæ, Scrophulariaceæ, Boraginaceæ, and Stellatæ (Lindley).

(1) *The Umbelliferæ.*

A study of the distribution and nature of the umbelliferous plants suggests that there have been at least two great differentiations of climate in the world since the birth of the family. This is especially well seen by a comparison of the Australian and northern hemisphere types.

The Umbelliferæ belong to an order of specialized forms known as the Umbellifloræ containing three families, namely, the Araliaceæ, Umbelliferæ, and Cornaceæ. The Araliaceæ are large trees of luxuriant habit, which are found generally in the fertile tropics or subtropics. The Umbelliferæ are mainly herbs, with leaves usually highly compound. In a very

few Australian types, however, the shrubby habit is still retained and the leaves may be compound or simple. These herbs and dwarfed forms characterize the cool and cold temperate regions, but in Australia certain large and endemic genera are xerophytic and occur on the hungry sandy soils of warm and cool temperate Australia. The Cornaceæ are mainly trees and shrubs adapted to the cooler temperate regions and with leaves simple or compound.

From this it may be conjectured that the ancestral forms of the Umbelliferæ were trees of luxuriant habit, with compound leaves, and lovers of mild and moist climate, that upon an early differentiation of climate, probably in the Cretaceous, the Umbelliferæ were developed in open and well-watered regions after the wide dispersal of the ancestral forms and while these earlier Umbelliferæ were still trees or shrubs. These types reached Australia apparently during some portion of the Cretaceous and at a later date, after the great isolation of Australia from the rest of the world, while the Australian plants were faced with the gradually approaching but pronounced climatic differentiations, these early Umbellifers found a refuge on the large barren sandy tracts, which sandy wastes at the same time were causing new large and aggressive genera to spring up among the Myrtaceæ, Leguminosæ, Labiatæ, Euphorbiaceæ, Epacridaceæ, Goodeniaceæ, Candolleaceæ, Proteaceæ, Dilleniaceæ, and other families. In this favorable setting the large endemic genera *Xanthosia*, *Trachymene*, *Siebera*, and *Didiscus*, were developed, as also the strange and beautiful *Actinotus*. All these are strongly xerophytic and belong to the same great period of evolution in Australia which produced the *Eucalyptus*, *Goodenia*, *Leucopogon*, the *phyllodineous acacias*, and other types, which all flourished together on the waste sandy tracts of the island continent. A very few of these xerophytes bear distinct traces of their old shrubby or arborescent habit, such as *Trachymene Billardieri*, which is a low shrub. In the north these early types of the Umbelliferæ were subjected afterwards to the great late and post-Tertiary differentiation, and the forms which had already been expelled in great part from the mild and moist region during the first great differentiation, were reduced to herbs during this second stage, and others being converted to hardy, vigorous, and aggressive types in the northern hemisphere, they commenced their way southwards sending off shoots along the American mountains to Chili and Antarctic South America. Thence some of them appear to have been carried by sea currents, by birds, or

by men, to Australia and New Zealand. *Azorella* appears to have reached Australia and New Zealand from South America by one of these means. *Daucus* also appears to have been introduced into New Zealand and Australia from the north by winds, by sea currents or by ancient man.

From this it will be seen that the evidence favors the idea that Umbelliferæ is a family of great age which had its dwarfed and open-country habit determined during a period of climatic differentiation, antedating the isolation of Australia, and that its great herbaceous and cold-country development is only of relatively recent age. The origin of the order may be placed far back, perhaps before the upper Cretaceous.

A similar story is revealed by a study of the Ranunculaceæ, the Magnoliaceæ, the Anonaceæ, and allied types. *Caltha* and *Ranunculus* have had histories somewhat similar to that of the types *Aster-Olearia-Felicia*, of *Senecio*, of *Bellis-Brachycome-Astranthium*, of *Fagus-Nothofagus*, and of *Campanula-Wahlenbergia*. In each case, with the exception of *Fagus*, the old luxuriant and arborescent type of the mild moist regions of the world has been altered to dwarfed and specialized types which have spread north and south. These in turn have been modified considerably during the severe climatic changes of late and post-Tertiary time with a deciduous habit among the trees, or a herbaceous development in the north and a xerophilism adapted to subarid, icy, or sandy wastes in the south.

(e) THE NEW ZEALAND PROBLEM.

Both this and the problem of the relation between Eastern and Western Australia are too complicated to be discussed here in detail and the briefest mention only is made of the subject at this stage. The literature of New Zealand botany, however, is voluminous and valuable owing to the labors of Hooker, Kirk, Coekayne, Cheeseman, Thomson and others.

In the remote past, perhaps in some portion of the Cretaceous Period, there appears to have been a land connection between New Zealand and Northern Australia indirectly by way either of Malayasia or New Guinea. The case for this probable land connection has been stated ably by Hedley.<sup>34</sup>

Along this assumed land connection the earlier Araliaceæ, Leguminosæ, Rubiaceæ, Compositæ, Myrtaeæ, Cupuliferæ, Coniferæ, Scrophulariaceæ, and other families, may have passed. The isolation of New Zealand from the world was

<sup>34</sup> C. Hedley, A Zoögeographic Scheme for the Mid-Pacific, Proc. Linn. Soc. N. S. Wales, vol. xxv, pp. 391-417, 1899.



effected long before that of Australia, and forms such as *Coprosma* and *Celmisia* were developed and sent out here and there as waifs. *Veronica*, *Epilobium*, *Senecio*, *Celmisia*, *Raoulia*, *Cotula*, *Coprosma*, *Carmichaelia*, and *Ranunculus*, and some other types underwent saltation during the late and post-Tertiary revolutions in the topography while the great plateaus and gorges of New Zealand were being formed. Types such as *Persoonia*, *Leptospermum*, and others, may be considered as descendants from Australian waifs. *Azorella*, *Geranium*, *Crantzia*, and many other forms, appear to have reached New Zealand by way of cold or South America, through the agency of sea currents, rafts, birds, or by other means.

(f) THE DEVELOPMENT OF PLANTS WITHIN AUSTRALIA SUBSEQUENT TO THE ISOLATION OF THE ISLAND CONTINENT.

This is too large and important a subject to be discussed in detail at this stage and may be dismissed in the present report with the statement that Australia appears to have been stocked with plants, both as luxuriant trees, as xerophytes, and as dwarfed forms, during some distant period, which may be conjectured as the upper Cretaceous; that after the isolation of Australia from the world generally, many of both the old luxuriant types and the stunted forms were driven into the sandy wastes of *extratropical Australia* and there, in their new surroundings, they developed numerous xerophytic species, many very large genera, numerous subtribes, tribes, and even certain families, which from weak and modest beginnings, gradually became hardy, vigorous, and finally aggressive, and whose only real limits, indeed, in later days, were set by the peculiar insular position of Australia on the one hand, and the inability of the xerophytic growths to invade the jungle-laden areas, on the other hand. During the later and post-Tertiary Period, when the great plateaus and gorges of Eastern and Southeastern Australia appear to have been formed, certain of the endemic genera underwent saltation thus causing serious confusion among the systematists, much in the same way as *Veronica*, *Epilobium*, *Carmichaelia*, *Coprosma*, and other types had caused trouble among workers dealing with the remarkable New Zealand flora.

So complex and difficult did the problem appear that a botanist so eminent as Baron Von Mueller proposed to solve it by including numerous forms under one genus which hitherto had been described under various genera and many species under one species which previously had been described

as belonging to several species. Bentham also, in his *Flora Australiensis*, included many forms under one species in various genera and families. Cheeseman also appears to have experienced the same difficulty in the preparation of his "Hand Book of the New Zealand Flora." This solution is unsatisfactory, however, inasmuch as it simply suggests to the observer that there are many perplexing forms belonging to the one species or genus.

It is probable that the solution is to be found by a knowledge of the geographic and oedaphic, as well as of the morphological, and chemical, factors. Thus, when the botanist, who may be studying *Acacia*, learns that there has been a great revolution in the topography of Eastern Australia by the formation there of high plateaus in late and post-Tertiary time, with the consequent production of a threefold climate in the same region, namely, mild and moist along the coast, cold and bleak on the plateau heights, and relatively dry and hot on the western slopes, and he knows, moreover, that a variety of *Acacia longifolia* is recorded from the mountains, another from the coast and still another from the creek banks, then he may be courageous and separate all as species, recognizing each as undergoing transition or saltation during the present time. Or when *Acacia salicina* is seen as a handsome tree on the deep, loamy soils of the watercourses, and as a straggling plant on the dry barren sandstones of the interior, the two having very different appearances, then *A. salicina* of the loam may be considered as an adaptation of the sandy form to a more congenial habitat, and as one which either is, or soon will be, a species different from the old type of the barren hillsides. *Eucalyptus albens* and *E. hemiphloia* admit of similar treatment. Or again, if species of *Eucalyptus*, such as *E. amygdalina*, *E. coriacea*, and others, should show differences on the mainland of Australia from similar forms in Tasmania such that confusion should be caused among systematists as to their proper relations to each other, then it might be advisable to consider the allied types in the two regions as having been the one species in recent time when Tasmania was connected to the mainland by a narrow neck of land and that geographic isolation under different climatic environment in the two regions is now converting certain individual species into two.

Similarly *Veronica*, *Epilobium*, *Coprosma*, and other genera, in New Zealand might be treated advantageously in this manner. In other words, the geographical station of the plant, the peculiarities of that station with respect to other stations con-

taining species which are closely allied, whether, for instance, separated by long stretches of ocean, by wide lowlands unfitted to support the species now isolated, whether isolated for a long or a short period of time, or now growing under different climatic conditions or on different soils; all these points should be taken as the testimony of independent witnesses in the matter of the classification of the plants, much in the same way as the habit of the plant, its foliage, wood, corolla, calyx, andrœcium, gynœcium, oil contents, and other important chemical and morphological characters, are admitted at present.

After all it does not alter the position materially so long as the workers are consistent in their methods of classification as was pointed out in 1869 by the master mind of Bentham when describing the genus *Cassia*.

#### SUMMARY.

It seems permissible to infer from the evidence herewith supplied, partly as a result of the internal evidence of the recognized modern classification of flowering plants, and partly as the result of the independent testimony of the Australian, the South African, the tropical, the South American, and northern hemisphere, types of plants, that the isolation of Australia from the world generally in the later Mesozoic Period was preceded by a general condition of mild and moist climate over the greater portion of the world with the production of the various known orders of the flowering plants, and that this period was associated, in its later phases, with the development of families, and of genera, which showed either a tendency to frequent open spaces, as the Composites, or an actual tendency to become xerophytic or herbaceous, such as *Acacia* or *Campanula*. This condition may have arisen either as a development in poor soils and open exposed wastes, moving parallel with the great development of luxuriant types in the Cretaceous, or it may have marked a differentiation, or zoning of climate, after the development of the main orders. The study of the Australian plants favors the idea that desert and open waste places existed during the so-called cosmopolitan mild and moist climate of the Cretaceous and the Eocene, as exemplified by the perpetuation of xerophytes such as *Acacia*, *Campanula*, and *Helichrysum*, prior to the isolation of Australia.

Both before and after the isolation, that is, during the earlier and later great differentiations, or zonings, of climate, many

families of plants, which had been lovers of warmth and moisture to the north of Australia, had been driven, in part, at a later stage, to the south, under the stress of severe competition and, in part, by reason of their own facilities for migration. These, during the various differentiations of climate, accommodated themselves to the peculiar sandy soils of Australasia in the temperate regions. This accommodation consisted of reducing the size of the old luxuriant tree, of reducing the leaf surface, or by the rejection of leaves entirely, of the utilization and increase of the amount of latex, essential oils, kinos, or of wax, already well developed in the families considered; of the development of other special devices for checking excessive transpiration such as the development of stomata, of stony cells and of indumentum; of lengthening the root and otherwise enabling it to tap the underground supplies of water. These soils were particularly adapted for the support of this xerophytic vegetation inasmuch as they never became intensely hard in time of drought, and although they never contained a rich supply of nutriment even under conditions of heavy and continued rainfall, nevertheless they ensured a scanty, but sure, supply of moisture for trees or shrubby growths which could develop roots long enough to tap such supply. Small herbs with either thick roots, or with bulbs, such as the orchids, the lilies, or certain composites could grow in most seasons by storing moisture either in the thickened rootstock, or in bulbs. The most remarkable point about this wonderful Australian endemic flora is the focussing, segregating, or congregating, of all possible types of the flowering plants on to the barren, uninviting, sandy soils during the great climatic differentiations of the later and post-Cretaceous. Thus the Myrtaeae in great measure foresook the rich soils and the sheltered regions to commence afresh on these hungry wastes; the Proteaceae, the Rutaceae, the Stereuliaceae, and the Euphorbiaceae, all in part forsook the jungle for the unattractive setting of the sandstones; the orchids descended the trees to develop numerous large genera on the sandy expanses, and the epaerids, the verbenas, the labiates, and the umbellifers, became dwarfed so as to flourish on the barren soils. From weakness these peculiar plant assemblages became strong; they became numerous in species and individuals, they became finally aggressive, but only after new genera, new subtribes, new tribes, and even new families, in some cases, had been developed. For it must be remembered ever by the student of Australian botany, that no large genus of world-wide distribution has a great develop-



ment in Australia unless that genus has been modified to an extent that it is scarcely recognizable as the world-wide type until such time as it has flowered.

*Examples:* The *phyllodineous Acacias*, *Phyllanthus*, and a section of *Cassia*. And in such case the specialization of the forms has always taken place on the sandstone. This specialization it is which marks the Australian sandstone vegetation. The primary types are to be found mainly as luxuriant forms within the cosmopolitan tropics, whereas the *secondary*, specialized, xerophytic, and depauperate, types are to be found on the sandy soils of extratropical Australia. This specialized vegetation has an origin relatively recent.

The genera include *Eucalyptus* (300 sp.), *Grevillea* (200 sp.), *Hakea* (112-115 sp.), the *phyllodineous Acacias* (420 sp.), *Melaleuca* (115 sp.), *Goodenia* (115 sp.), *Candollea* (105 sp.), *Hibbertia* (105 sp.), *Persoonia* (65 sp.), *Banksia* (50 sp.), *Dryandra* (50 sp.), *Pultenaea* (100 sp.), *Casuarina* (25 sp.), and *Ptilotus* (76 sp.), and these originated on the sandy soils of Australasia and have never travelled far from their birthplace.

This Australian vegetation belongs to families which originated partly in the north temperate regions, and, partly, in the tropics. Under stress of circumstances the plants tended to migrate south from the tropics. One branch moved south into Australia and developed the secondary specialized forms enumerated in the preceding paragraph, another branch travelled to South Africa, and there under similar climatic influences, and upon similar sandstone areas, it developed a flora analogous to that of the specialized Australian types. Another moved down South America, but did not meet conditions similar to those of Africa and Australia. Another branch which had moved down all the great land connections between the northern and southern continents developed in the cool and moist regions of New Zealand, Southeast Australia and South America. This type perished in Africa during the great climatic differentiation.

ART. XXIV.—*Mineralogical Notes*; by B. K. EMERSON.1. *Limonite pseudomorph after diabantite, after anhydrite.*

Years ago I discovered anhydrite in large bluish-white masses in the trap at Larrabee's Quarry on the north line of Holyoke.\* It is in tabular aggregates resembling cleavelandite, slightly radiate, but sometimes radiating so rapidly that plates bend 90 degrees in one inch. The plates vary from one-eighth inch thick to extreme thinness. It shows three perfect cleavages, and striated crystal faces. Pyrite and calcite are in the same cavities suggesting its origin. In many cases regular prismatic and tabular cavities occur in the zeolite-calcite aggregates in the cavities of the trap, which I have been accustomed to refer with doubt to selenite.† Recently I have received specimens from the third Westfield quarry, counting from the south, on hillock 380 feet above sea, and 1/2 mile north of the railroad, which show such cavities reaching 2 inches in length and width and 1/4 inch in thickness, but generally much thinner down to 1/32 of an inch. In several cases the enclosing mineral has penetrated the two perfect cleavages of the original mineral which are rectangular; the one parallel to the broadest surface, *c*, and the other at right angles thereto and parallel to the greatest length of the crystal, *b*. At times the exterior of this broadest face is preserved in a perfect cast which is striated like the *b* face of anhydrite and at other times it has been etched during enclosure so that the tracing of the two rectangular perfect cleavages parallel to *b* and *c* are well shown on *a*. The crystals were flat rectangular plates sometimes cut by a brachydome.

These cavities have been filled by diabantite which appears first in small tufts and then fills the space entirely, showing a central suture where the two growths have come together. These tufts are often altered to bright gold-yellow forms which I have described as diabantite-vermiculite,‡ and the complete fillings also show every stage of the change from fine fibrous green diabantite to a porous impure limonite, which latter is thus a pseudomorph by replacement of anhydrite, and by chemical alteration of diabantite.

The same negative forms have been found at the Cheapside quarry south of Greenfield in thinnest plates and in long stout prisms coated with datolite, or enclosed in the same. The blades are often over three inches long. The blades have also been inclosed in quartz and sometimes several quartz crystals

\* Mineral Lex. Old Hampshire Co., Bull. 126, U. S. G. S., p. 26, 1896.

† Loc. cit., p. 90.

‡ This Journal, xxiv, 198, 1882.

have grown directly against the flat surface of a plate producing basal faces on the quartz which replace the pyramid entirely and take a sharp cast of the striated crystal face of the anhydrite.

2. *Paragenesis of minerals in diabase.*

A Quarry No. 1, Westfield.

1. Anhydrite in blades 2 inches long and 1 inch wide.
2. Massive transparent calcite.
3. Datolite massive and in one inch crystal.
4. Solution of anhydrite.
5. Diabantite replacing anhydrite.
6. Coarse wine-yellow dog-tooth spar.  $R^3$  sometimes truncated at apex by R.
7. White coating of chalcedony.
8. Fine-grained white dog-tooth spar,  $R^2$ ,  $\alpha R$ .
9. Change of diabautite to limonite.

B Cheapside Quarry, Greenfield.

1. Anhydrite in blades.
2. Quartz.
3. Solution of anhydrite.

C

1. Anhydrite.
2. Datolite and calcite.
3. Calcite.
4. Solution of anhydrite.

Amherst, Mass.

ART. XXV.—*A New Tortoise and a Supplementary Note on the Gavial, Tomistoma americana*; by E. H. SELLARDS.

IN connection with a paper on pebble phosphates the writer, in 1915, mentioned and illustrated a large land tortoise from the Tertiary of Florida.\* Additional specimens of this tortoise have now been obtained indicating that it is a characteristic and not uncommon fossil of the Florida land pebble phosphate deposits. The species apparently is new and may be known as *Testudo hayi* in recognition of the studies of Testudinata by Dr. O. P. Hay. The type specimen of this species, which includes a part of the carapace and plastron of a single individual, was contributed by the Phosphate Mining Company, Nichols, Florida. A second specimen including a considerable part of the carapace has been obtained from the Amalgamated Phosphate Company, Brewster, Florida. Both specimens are from the Bone Valley formation which is either of late Miocene or of early Pliocene age. The origin of this formation has been discussed and a number of the vertebrate fossils illustrated in the paper to which reference has been made.

*Testudo hayi, sp. nov.*—This species includes large tortoises which reach a size of approximately four feet in width by five feet in length. The height of the carapace is estimated at twenty-seven inches. Of the neurals the second is octagonal or nearly so. The remaining neurals four to eight are hexagonal. The proximal end of the second costal is slightly reduced in width and comes in contact with the second neural only, while the third costal touches the second, third and fourth neurals. The first or penultimate supra-pygial is large and rests upon the eleventh marginals and the pygal. The second or ultimate supra-pygial, on the contrary, is much reduced. The length of the xiphiplastron from the bottom of the xiphiplastral notch to the outer margin at the suture with the hypoplastron is 300<sup>mm</sup>.

Under the name *Testudo crassiscutata*, Leidy in 1889 described a tortoise obtained on Peace Creek, Florida. The type of Leidy's species includes portions of the anterior and posterior lobes of the plastron, a femur and a tibia and fragments of the carapace. By comparing the posterior part of the plastron it is seen that the median notch of *T. hayi* is deeper and more acute than is that of *T. crassiscutata*. The exterior wall of the hypoplastron of *T. hayi* is vertical while in *T. crassiscutata* the exterior wall of this bone slopes inward. Although representing a larger individual the carapace of *T. hayi* is thinner than that referred to *T. crassiscutata*.

\* Fla. Geol. Surv., Seventh Annual Report, pp. 70, 75, figs. 7 and 9, 1915.



FIG. 1.

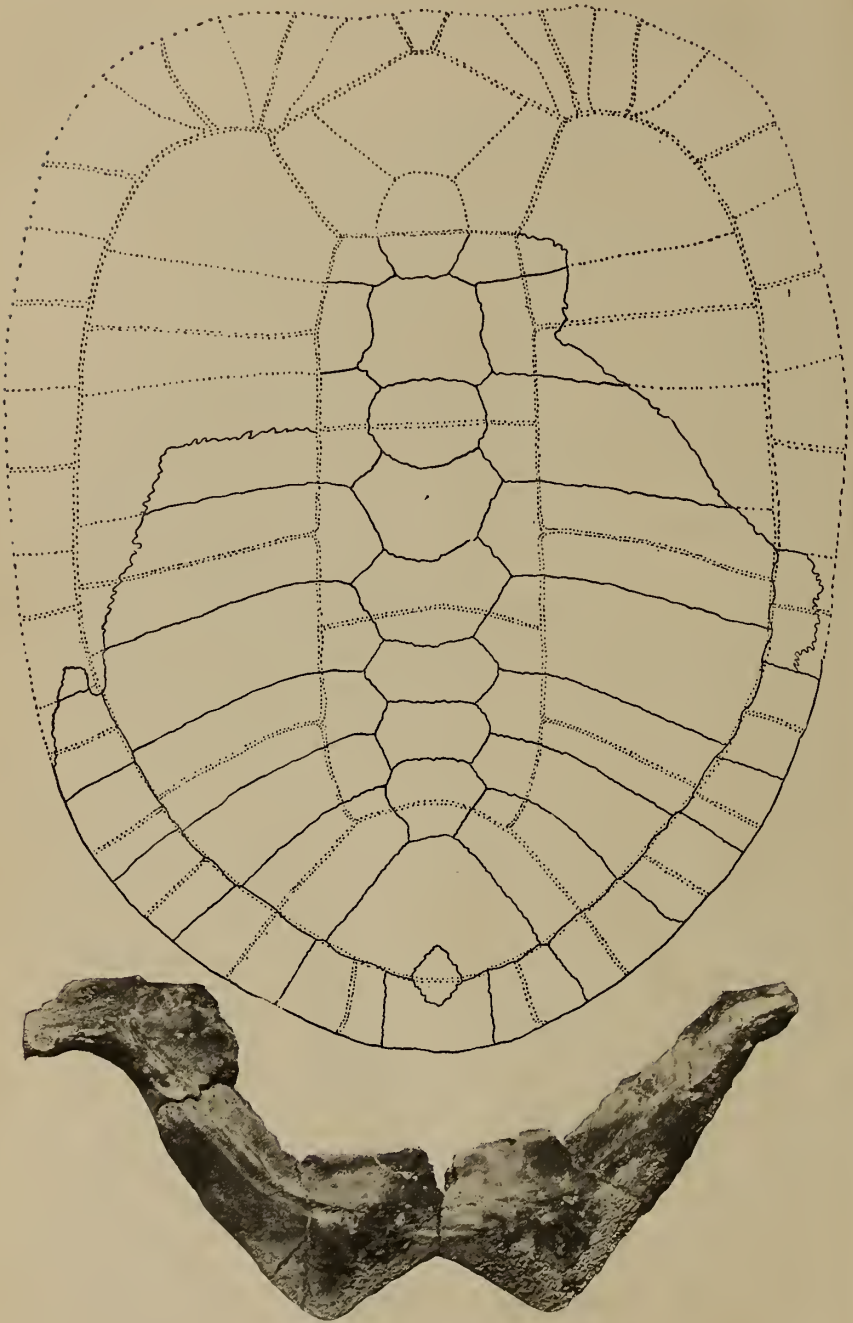


FIG. 1. *Testudo hayi*. Type. Carapace and posterior lobe of plastron. One-twelfth natural size. Fla. Surv. coll. No. 5001. The front part of the carapace which is lacking in the specimen is restored.

*Supplementary Note on the Gavial, Tomistoma americana.*

The gavial, *Tomistoma americana*, described by the writer in 1915, is of special interest from the fact that it is at present the only known member of this group from the American Cenozoic. Of this form there has been known heretofore only the rostrum which served as the type of the species and a fragment of a lower jaw which was regarded as a paratype.\* Recently, however, there has been obtained from the same locality and from the same deposit as the type specimens, parts of the lower jaws of ten or twelve individuals, with which is associated a few pieces of upper jaws, dermal plates and a vertebra. From the specimens now at hand it is possible to add to the description of the lower jaw. The rostrum which originally served as the type of the species represents, as shown by the specimens now at hand, an individual by no means fully grown. As in the case of the specimens first described, the additional material representing this gavial has been obtained by the Amalgamated Phosphate Company at Brewster, Florida, and has been contributed to the Florida Geological Survey through the general manager of the company, Mr. Anton Selmeider.

The front part of the jaw of this gavial is represented by specimens Nos. 6158, 5871, 5875, 5876 and 5879 of the Florida Survey collection. The two front teeth of the lower jaw, as shown by this new material, incline upward, forward and outward, and thus pass between the first and second teeth of the premaxilla which is grooved to receive them. The second mandibular tooth is strongly developed and is separated by a considerable space from the first tooth, and passes between the third and fourth teeth of the upper jaw. The groove in the premaxilla which receives this tooth is more pronounced as shown by specimen No. 6158 in the large individuals of the species than on the specimen which served as the type of the species. Into the broad groove between the first and second lower teeth is received the second and third upper teeth. The space between the first and second lower teeth shows a proportionate increase with age, the teeth of the young specimen being about equally spaced. The third lower tooth is small and falls between the fourth and fifth teeth of the premaxilla, being there received in a pit at the outer side of the bone which in old individuals becomes quite pronounced. The fourth mandibular tooth is the largest of the lower jaw and passes into the notch or constriction of the rostrum and hence between the fifth and sixth upper teeth. From the second lower and third upper to the tenth lower and eleventh upper the teeth alternate and interlock, the side of the jaws being

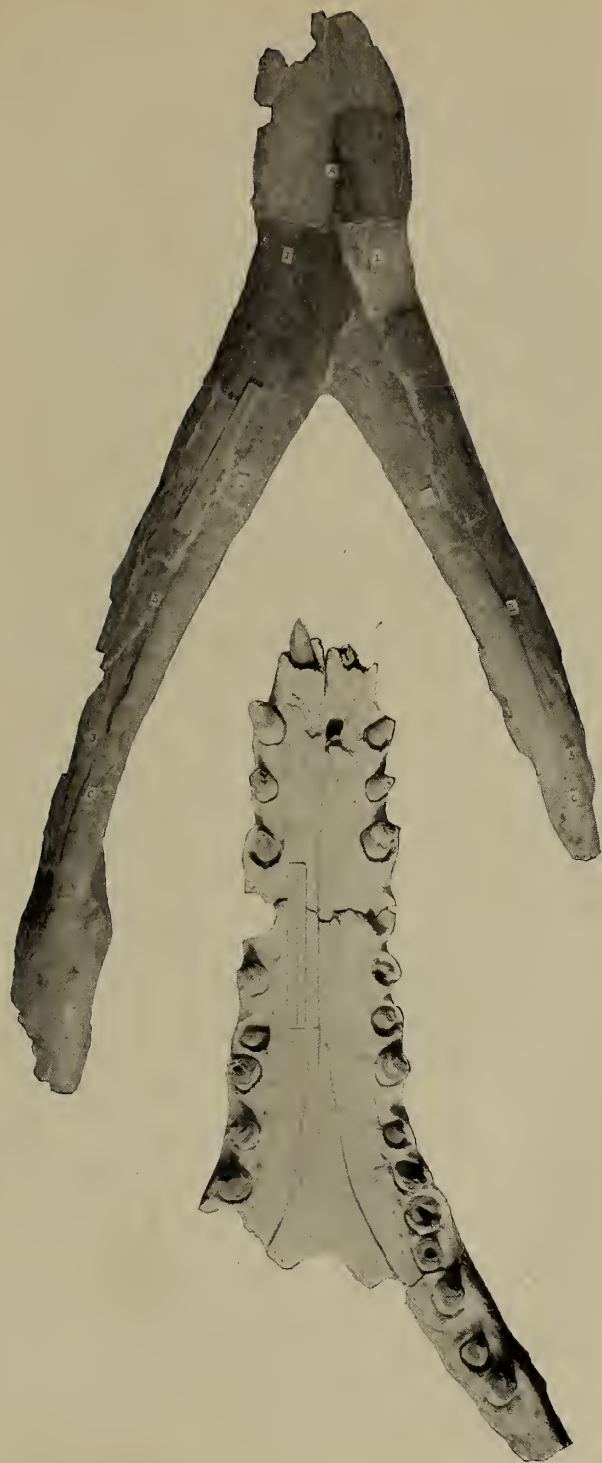
\* This Journal, vol. xl, pp. 135-138, 1915.

grooved between each tooth to receive the corresponding tooth from the opposite jaw. Back of the tenth lower and eleventh upper the teeth do not pass to the outer side of the jaw, but are received in pits in the jaw.

The symphysis of the jaw, as shown by specimens Nos. 6158 and 5879, begins opposite the eleventh or the twelfth mandibular tooth. In specimen No. 5880, the front part of which is wanting, may be seen sockets for seven teeth back of the symphysis, representing apparently the eleventh to the seventeenth or the twelfth to the eighteenth teeth inclusive, from which it appears that the full number of teeth in the lower jaw is seventeen or eighteen. The splenials, as noted in the writer's original description, take part in the symphysis and extend forward, as shown by the specimens now on hand, to a point opposite the seventh mandibular tooth. The under surface of the back part of the lower jaw is well shown by specimen No. 5891 which is illustrated in the accompanying text figure. The bones seen from the underside of the jaw are the dentaries, splenials and angulars. The termination of the dentaries is not definitely shown, but these bones may be seen to extend approximately one half the length of the ramus of the jaw. The limits of the splenials are very well shown and are seen to extend somewhat more than one half the length of the ramus. The angular is wedged in between the splenials and the dentaries and forms the lower margin of the jaw at the angle.

While no one jaw has been found complete, yet an approximate measurement of the lower jaw may be obtained by combining measurements from the two largest specimens of the collection. In the larger of these, No. 6158, the front part of the jaw as already noted is preserved, while in the other, No. 5891, which is but slightly smaller, the back part of the jaw is practically complete. The symphysis of the jaw of the large specimen measures 610<sup>mm</sup>, while on the slightly smaller specimen that part of the jaw back of the symphysis measures in a direct line following the axis of the jaw 725<sup>mm</sup>. The full length of the lower jaw of a large specimen of this gavia was, therefore, somewhat more than 1335<sup>mm</sup>, or about four feet and three or four inches. By way of comparison it may be noted that the splenial bones in this species take part in the formation of about four-elevenths of the symphysis; while the symphysis itself includes about four-ninths of the entire length of the jaw. The width of the jaw of the largest specimen, measured at the forward end of the splenial, is 170<sup>mm</sup>, the jaw being proportionately broader than that of the modern species of the genus.

A number of dermal plates of crocodillians are found at this locality which with little doubt are referable to this spe-



Figs. 2 and 3. *Tomistoma americana*, Fla. Surv. coll. Nos. 5891 and 6158. One-eighth natural size. The rule seen in the photograph has a total length of 60<sup>mm</sup>. In front of "A" the jaw consists of the dentaries alone; back of "A" the splenials intervene between the dentaries. Although not complete the dentaries (1) may be seen to extend to a point midway between "B" and "C," where they form the exterior of the jaw. The splenials (2) extend forward taking part in the symphysis of the jaw to "A." In the ramus they extend back to "C" forming the lower part of the inner margin. The angular (3) which is wedged in between the dentaries and the splenials, extends forward to "B." The length of the ramus of the jaw as shown by fig. 2 is 775<sup>mm</sup>, or measured along the axis of the jaw in a direct line, 725<sup>mm</sup>. The length of the jaw as shown by fig. 3 measures 610<sup>mm</sup>.



eies. These plates are heavy deeply pitted pieces of bone, the largest of which measure 100 by 130<sup>mm</sup> in size and are 16<sup>mm</sup> thick. A vertebra, the centrum of which is 70<sup>mm</sup> long by 50<sup>mm</sup> wide, has been obtained from this locality and presumably represents this species. This vertebra is probably the seventh of the series.

The skull of this extinct gavial is somewhat more massive than is that of the modern species. Thus a jaw of *T. schlegeli*, the symphysis of which measures 610<sup>mm</sup>, has a width at the forward end of the splenials of 170<sup>mm</sup>, the width being more than one-fourth the length. In the recent species the width of the jaw at the same place is contained in the length  $6\frac{1}{2}$  times, thus indicating a more narrow jaw and skull. The symphysis of the jaw of *T. schlegeli* begins opposite the fourteenth tooth, while in *T. americana* the symphysis as previously stated begins opposite the eleventh or twelfth tooth. In the proportionate length of the symphysis to the jaw as a whole, however, as well as in the extent to which the splenials enter into the symphysis, the two species do not differ to any great extent.

The body proportions of this gavial probably do not differ greatly from those of the existing species of the genus, and hence by comparative measurements it is possible to form a reasonably close estimate of the size of this extinct animal. Upon comparing the modern species, *Tomistoma schlegeli*, it is found that in an individual, the full length of the body of which is 9 feet and 7 inches, the lower jaw measures 2 feet and 2 inches.\* Assuming that a somewhat similar proportion holds between the length of the jaw and of the body of *T. americana*, and applying these measurements, the conclusion is reached that large individuals of the Florida gavial, the jaw of which exceeds 4 feet, attain a length of 18 or 19 feet, and hence were somewhat larger than the existing gavial of this genus which seldom exceeds 15 feet in length.

\* Measurements from the recent skeleton kindly supplied by Geo. M. Ward of the Ward Natural Science Establishment.

ART. XXVI.—A Fossil Nutmeg from the Tertiary of Texas ;  
by EDWARD WILBER BERRY.

THE Nutmegs, with somewhat less than 100 existing and widely distributed tropical forms, constitute the family Myristicaceæ of the order Ranales. Satisfactorily determined fossil forms are entirely unknown so that the remains which form the subject of the present paper are not without interest.

These are found in the Catahoula formation of Trinity County in eastern Texas from which I described the fruits of a date palm some years ago,\* and were collected by Charles Laurence Baker. The matrix of this material was the basis for a highly interesting study of the petrography of the Catahoula sandstone made by M. I. Goldman† and published in this Journal in 1915. The evidence of the flora and that furnished by the study of the sediments supplement one another in throwing considerable light on the physical conditions of Catahoula time which will be referred to on a subsequent page.

The fossil species of nutmeg, obviously new, is represented by characteristic remains of the pericarp and of the seeds. It may be described as follows :

*Myristica catahoulensis*, sp. nov.

Pericarp broadly ovate, slightly longer than wide, approximately circular in cross section, thick, two-valved, about 5<sup>cm</sup> in length and 3.75<sup>cm</sup> in diameter, enclosing a single large seed. The aril either decayed before fossilization or became separated from the seed and was not preserved in the same deposit and the perisperm is likewise missing. The seed is large, circular in cross section, evenly rounded proximad and shows a distinct hilum. It is slightly narrowed and bluntly pointed distad. The surface is ornamented by numerous irregular longitudinal corrugations marking the ruminating endosperm. These markings are in faint relief and much less prominent than the corresponding markings of the commercial nutmeg, due in a measure to the fact that fossils are all casts in a somewhat porous sandstone. Similar artificial casts of the strongly marked commercial nuts are scarcely to be distinguished from the fossil casts. The nuts, of which several have been found, are about 3<sup>cm</sup> in length by 1.7<sup>cm</sup> in maximum diameter, which is midway between the apex and the base.

This species is based on the single valve of the pericarp shown in figs. 4-6 and on the partial remains of several nuts,

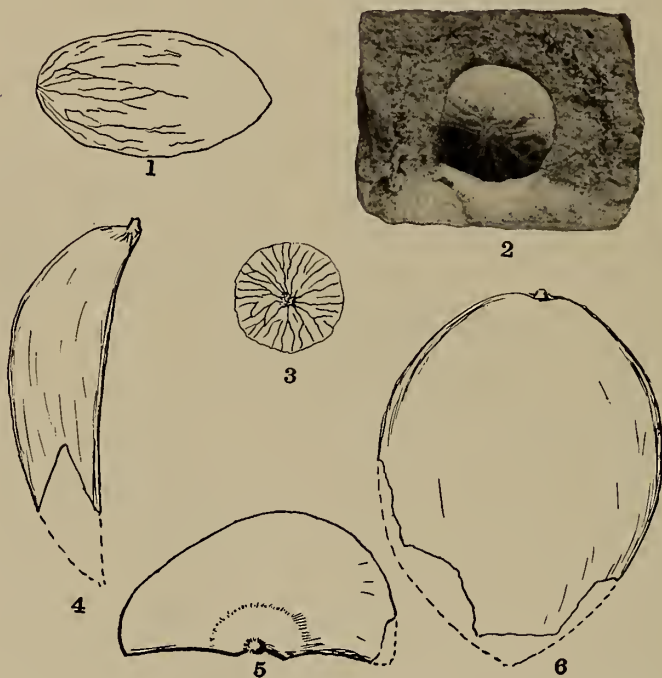
\* This Journal (4), xxxvii, pp. 403-406, 1914.

† Ibid., xxxix, pp. 261-287, 1915.

only one of which is perfect (fig. 1). The nuts were apparently relatively abundant, but since they were only discovered in the weathered sandstone there are few that are reasonably complete although there are several showing parts of the sides or ends, in some cases half complete as in fig. 2.

As I have mentioned, all the plant remains at this locality are in the form of casts and the nuts must have been buried by

FIG. 1.



FIGS. 1-6. *Myristica catahouleus* sp. nov. from the Tertiary of Texas.

1. Side view of seed.
- 2, 3. End views of same.
- 4-6. Side, top and front view of a valve of the pericarp.

wind-blown sand since they lie in the sand at all angles. The æolian character of the sandstone at this outcrop is of the greatest importance in explaining the absence of both aril and perisperm, and is, therefore, deserving of comment. The evidence for this conclusion is derived from several sources. Many of the leaf specimens are curled and not flat as they would almost invariably be if laid down in water. These and

other associated nuts are jumbled in a confused mass at all angles. Violent currents could form such a jumble, but the nuts would not be heavy enough to be deposited under such conditions but would be carried away by water action strong enough to stand them on end, nor would water-logging in more quiet waters explain their varying positions. Associated with nutmegs are much more numerous large-ribbed nuts as yet unidentified. These lie at all angles in the sandstone but occur elsewhere in clays, in which case they invariably lie on their sides. The conclusions of Dr. Goldman, based on a petrographic study of the matrix, i. e., the proportion of different sizes of grains present, their rounding, the ratio of feldspar to quartz, the degree of weathering, absence of clay, proportion of heavy minerals, etc., for a detailed discussion of which the reader is referred to the paper cited, point to strong æolian action in a hot arid climate.

The nuts are fully matured and evidently were shed naturally and at no great distance from the sand flats where they subsequently became entombed. The sediments do not, according to Dr. Goldman, show characters of dune sands, and I infer that the winds which rounded and sorted the sand grains were not constant enough in direction to form dunes of any size. Under such conditions of blowing about the arils would soon be lost, but the perisperm cannot be conceived of as being so readily dissipated although I know of no other method to account for its absence. It must be remembered that less than a dozen nuts are known, that much of the sand from near-by outcrops appears to have been blown into pools of standing water where the accompanying leaves were fossilized in a normal flat condition, and that the small percentage of nutmegs preserved in the wind-blown sands may thus be exceptional when the possibility is considered of large numbers fossilized in a normal way with perisperm intact.

That the fossils are unmistakably those of a species of *Myristica* I think no botanist will dispute. No leaves that I can identify as those of *Myristica* have as yet been determined, but the leaf material is scanty, and I have not enough recent material of this genus for intelligent comparison of the foliar organs.

The recent species of this family which number about 90 forms are variously treated. De Candolle\* referred them all to the single genus *Myristica* which he segregated into 13 sections, and this is the method followed by Prantl† in *Die Natürlichen Pflanzenfamilien*. Other authors raise a number of these sections to generic rank, quite rightly so it seems

\* Ann. Sci. Nat., 4th ser., Bot. tome iv, pp. 20-31.

† Teil III, Abth. 2, 1891.



to me. I have, however, preferred to refer the fossil to *Myristica* since comparative recent material for closer discrimination is lacking. The nutmeg of commerce belongs to the section *Eumyristica* with about 15 existing species of the Asiatic tropics. It is a small tree, endemic in the Moluccas and has long been under cultivation judging both from the numerous varieties extant and the historical records, since Europe has been receiving nutmegs from this region, beginning with the trade through the Arabs in the 6th century. The nutmeg has been introduced into other East Indian islands as well as on Bourbon, Mauritius, Madagascar and in tropical America, usually with indifferent success.

While the Texas fossil is much like the commercial nutmeg in size and characters it is also similar to existing American species, of which there are about 25. These are mainly South American, but the sections or genera *Virola* Aublet and *Compsonaura* De Candolle both occur also in Central America. The fossil nuts are remarkably like those of *Myristica* (*Compsonaura*) *costaricensis* Warburg, but the pericarp is much larger and more massive.

Beyond the fact that they are tropical I know little regarding the habitat of the recent species. Many are certainly insular and coastal forms, their range in the Pacific extending eastward to the Fiji, Tonga and Samoan islands, the former having 4 or 5 species. Schimper records 4 species in his Indomalayan strand flora. *Myristica subcordata* Blume of New Guinea and *Myristica littoralis* Miquel of Java are both members of Barringtonia or beach-jungle association. Both Gaudichand and Guppy record unopened *Myristica* fruits in the Pacific sea-drift although their floating powers are not great and they are normally dispersed by fruit pigeons (Moseley, Hemsley, Guppy).

Referring to the foliage it may be noted that contrary to the opinion of Hooker and Thomson (*Flora Indica*), DeCandolle found that the flowers and fruits were much alike throughout the family and that the leaves furnish the most useful characters for differentiation, especially in their venation, and this opinion was also shared by Miquel. It would seem that the lack of comparative material has hitherto prevented the recognition of fossil foliage of *Myristica*. Certainly no definite evidence of extinct species has heretofore been published although the distribution of the existing species in tropical Asia, Africa and America is convincing enough evidence that the group had an extensive, even if unknown, Tertiary history. The only previously known fossil records are based on a very few and indifferently characterized leaf impressions from the Miocene of Labuan (Borneo) described by Geyler\* as *Myristicophyl-*

\* Geyler, Vega Exped., vol. iv, p. 498, pl. 33, figs. 3-6, 1887.

*lum majus* and *minus*, and by equally unconvincing leaf fragments described by Engelhardt as *Myristica fossilis*\* and coming from beds in Equador and Chile considered to be either Eocene or Oligocene in age.

On the other hand, the family Anonaceæ, which is closely related to the Myristicaceæ, is represented in the fossil record by over a score of species of *Anona*, *Asimina*, *Guatteria*, etc., ranging in age from the early Upper Cretaceous through the Tertiary. Both *Anona* and *Asimina* are represented in the Lower Eocene flora of the Mississippi embayment area.

*Myristica catahoulensis* comes from a cut on the International and Great Northern Railroad in southern Trinity County, where a spur to the Government lock leaves the main line, and the Catahoula formation in this area is either late Eocene or early Oligocene in age. The flora is a coastal one and strictly tropical in character.

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\* Abh. Senck. Naturf. Gesell., xvi, Heft 4, 1891, p. 663, pl. 6, f. 9, pl. 7, fig. 12, 1891. Ibid., xix, p. 13, pl. 1, f. 21, 1895.

ART. XXVII.—*Notes on Devonian Faunas of the MacKenzie River Valley*; by E. M. KINDLE.

THE Devonian rocks east of the MacKenzie valley are bordered for nearly a thousand miles by the Pre-Cambrian rocks of the Canadian shield.\* The geological map of North America, published through the coöperation of the geological surveys of the United States, Canada, and Mexico,† indicate the termination of the broad belt of the MacKenzie valley Devonian on the north by a western lobe of the Pre-Cambrian rocks which, in the region east of the delta of the MacKenzie, are bordered by the Cretaceous formations according to this map.

A coral collected by H. W. Jones and transmitted to me by Mr. Chas. Camsell furnishes evidence of the presence of Devonian Rocks, in this very northerly region east of the delta of the MacKenzie within 70 miles of the Arctic coast, where published data show only Cretaceous and Pre-Cambrian terraines. The specimen collected by Mr. Jones was obtained on the east side of Gull Lake from the limestone shown in fig. 1. The photograph shows a limestone section with a thickness of more than 100 feet in which the beds lie nearly horizontal. The Gull Lake district is one which does not appear to have been traversed by geologists. The geography of the district was described by A. H. Harrison in 1908.‡ Gull Lake is probably Long Lake of Harrison's map or one of the small lakes near Long Lake. Long Lake is the most westerly of a chain of lakes lying east of the delta and trending a little east of north through a region lying, according to Harrison's map, between 100 and 500 feet above the sea.

The corallites of the specimen on which the determination of this new occurrence of Devonian rocks is based are partially silicified and imbedded in an impure grey limestone. The coral belongs to the species *Acerularia davidsoni* E. & H. It represents the variety of this species described by Hall from the Iowa Devonian as *A. profunda*. The variable character of the size of the corallites ascribed to *A. profunda* is well illustrated by this specimen, the smaller ones having no more than half the diameter of the larger ones. Most of the cells have 40 or more radial denticulated lamellæ. In this identification I have followed Rominger in treating Hall's *A. profunda* as a synonym of *A. davidsoni*.

\* McConnell, R. G., Ann. Rept. Geol. Surv. Can., n. ser., vol. 4, 1890, p. 14D.

† U. S. Geol. Surv., Prof. Paper 71, 1911.

‡ A. H. Harrison, In Search of a Polar Continent, pp. 1-292, map (E. Arnold), London, 1908. Idem, In Search of an Arctic Continent, London Geog. Jour. vol. xxxi, pp. 277-287, map, 1909.

Although no other fossil was secured by the collector, the occurrence here of this species affords conclusive evidence of the presence at Gull Lake of a Devonian fauna. *A. davidsoni* is a characteristic species of the Middle and Upper Devonian of Iowa, Michigan and Wisconsin.

This coral has not been previously reported in western Canada. It will therefore be of interest to note here the pres-

FIG. 1.



FIG. 1. Devonian limestone at Gull Lake, east of MacKenzie River delta. Photograph by H. W. Jones.

ence of *A. davidsoni* in another collection from the MacKenzie valley obtained at a locality 30 miles Northwest of Hope, which is just inside the Arctic Circle. This collection, which was made by Mr. T. O. Bosworth and presented to the Canadian Geological Survey together with other collections from the MacKenzie valley, includes the following species:

*Acervularia davidsoni*  
*Camarotoechia* sp.  
*Atrypa reticularis*  
*Newberrya laevis* Meek  
*Cyrtina panda* Meek  
*Martinia meristoides*.

This faunule from Northwest of Hope shows an assemblage including several species listed by both Meek\* and Whiteaves† from the MacKenzie valley collections of Kennicott and McConnell. Each of these authors considered the MacKenzie

\* Trans. Chicago Academy of Sciences, vol. i, pt. 1, pp. 61-114, pls. 11-15.

† Can. Geol. Surv., Contr. to Can. Pal., vol. i, pt. III, pp. 197-253, pls. 27-32.



valley fauna to represent a Middle Devonian horizon. It represents in the writer's opinion both Middle and Upper Devonian horizons. In the faunule now under discussion from Northwest of Hope such distinctly Upper Devonian species as *Spirifer disjunctus*, which is conspicuous in the faunules listed by Whiteaves,\* are wanting and the species present appear to represent the Middle Devonian fauna of the MacKenzie valley.

The single species of coral which represents the Gull Lake Devonian fauna affords rather meagre evidence for its close correlation with other faunas, but the presence of the same species of *Acervularia* in the fauna just listed from Northwest of Hope suggests that they are both representatives of the same Middle Devonian horizon.

Another collection from the MacKenzie River Valley which has recently been studied by the writer shows in addition to the faunas with which we are familiar through the work of Meek, McConnell, and Whiteaves, a Devonian facies not previously recognized in that region. This collection was made by Mr. Charles Camsell at Pine Point, on the south shore of Great Slave Lake. The fossils from this station are from beds described in Mr. Camsell's notes as "very bituminous and full of fossils. They lie flat and are associated with beds of limestone in low cliffs 3 or 4 feet high at the water's edge."

The fauna occurs as flattened or crushed shells in a black calcareous and highly bituminous shale. Some specimens might be properly called limestone,—coal black in color. When freshly broken this rock gives a strong petroleum odor.

The species recognized in this black shale fauna are the following:

- Lingula* sp.
- Leiorhynchus* cf. *laura*
- Pterochaenia fragilis*
- Styliolina fissurella*
- Tentaculites gracilistriatus*.

The fauna of this black shale has not been previously recognized in the MacKenzie River Valley. This fauna contains nothing which will enable one to decide positively with which one of three or four Middle and early Upper Devonian black shale horizons it is most closely allied. The last three species might occur as early as the Marcellus shale or as late as the Ithaca shale of the New York Portage. The absence of species characteristic of the black shale horizons of the Portage, however, together with the closer resemblance of the *Leiorhynchus* to a form not common above the Marcellus, lead me to place the fauna, provisionally, in the Middle Devonian.

Geological Survey, Ottawa, Canada.

\* L. c., pp. 248-253.

ART. XXVIII.—*New Points on the Origin of Dolomite* :\* by  
FRANCIS M. VANTUYL.

*Historical Review.*

THE problem of the origin of dolomite has long occupied the attention of geologists and many theories have been advanced for its formation, but no one of these theories has been widely accepted. Von Buch (1)† was the first to seriously attempt to explain the formation of the rock. As early as 1822 in his writings on the dolomite of the Tyrol, he ascribed its origin to the action of volcanic vapors, rich in magnesia, on limestone, and there was some basis for this belief, for the rocks are there penetrated by augite-porphry. Frapolli (2) and Durocher (3) later expressed similar views upon the origin of the rock, and Favre (4), basing his supposition upon the conditions of the experimental production of dolomite by Marignac, concluded that the dolomite of the Tyrol was formed by the alteration of limestone beneath the sea at a temperature of 200° C. and at a pressure of 15 atmospheres, corresponding to a depth of 150 to 200 meters, by magnesium compounds furnished by the action of sulphurous and hydrochloric acids of volcanic origin on the lava of submarine melaphyr eruptions.

In 1834 Collegno (5) pointed out the frequent association of gypsum and dolomite in the St. Gothard region and regarded them both as transformation products resulting from the action of magnesium sulphate in surface waters or limestone. Morlot (6) also favored such a theory of origin.

As early as 1836 Beaumont (7) ascribed the origin of dolomite to the alteration of limestone by circulating solutions of magnesium bicarbonate and, assuming that the replacement was molecular, he calculated that the change should be accompanied by a decrease in volume of the original rock to the extent of about 12.1 per cent. Actual porosity determinations by Morlot (8) on a dolomite sample from the Alps later seemed to confirm this prediction.

In 1843, A. W. Jackson (9) suggested that ascending spring-water bearing magnesium bicarbonate might effect the change. Nauck, Hanssmann, Bischof, Zirkel and others, however, subscribed to the view that ordinary circulating ground water bearing magnesium bicarbonate had attacked the limestone.

\* The present article is based on a more extended paper which constitutes a portion of volume xxv of the Iowa Geological Survey. The reader is referred to this report for details.

† For numbered references to the literature, see the list at the end of this article.

Van Hise (10) also attaches much importance to dolomitization after the limestones emerge from the sea.

In 1846 Green (11) offered the suggestion that some dolomitic limestones might be formed by the decomposition of olivine sand incorporated in the original limestone and the recombination of the magnesia with the lime. He calls attention to the fact that olivine sand, derived from the action of the waves on lava, constitutes an important constituent of the coral-reef rock about the borders of the Hawaiian Islands and regards this as significant.

Dana (12) in 1843, attempting to account for the dolomite of the coral island of Metia, supposed that it had been formed by the action of magnesium salts of heated sea water on limestone. Twenty-nine years (13) later he expressed the view that the same dolomite had been formed in sea water at ordinary temperatures but perhaps in a contracting lagoon where magnesium and other salts were in a concentrated state. Sorby (14) likewise favored the theory of marine alteration and the same origin has been urged, either for dolomites in general or in special instances, by Von Richthofen, Doelter and Hoernes, Hoppe-Seyler, Mojsisovics, Murray, Skeats, and F. W. Pfaff. In support of this theory are also the observations of Weller (15) who, from a faunal study of the Galena and Niagara dolomites of the Upper Mississippi Valley, concludes that they were deposited originally as limestones and later metamorphosed. More recently, Blackwelder (16) has also advocated the replacement theory for the origin of the Big-horn dolomite of Wyoming, but owing to the very slight porosity of this rock he is led to suggest that the alteration proceeded contemporaneously with its deposition rather than subsequent to its consolidation.

F. W. Pfaff (17) believes that the alteration takes place at considerable depth and in concentrated seas, but Phillipi (18) vigorously controverts this view since he has good evidence that dolomitization may proceed in the open sea and at shallow depths. Skeats' (19) studies of the coral reefs of the Southern Pacific also seem to show that concentration and pressure are not important factors. On the other hand, both Nadson and Walther (20) have suggested that bacteria may play an important part in the alteration.

Still other geologists have supported the theory that dolomite represents a direct chemical precipitate from the ocean. Boué (21) as early as 1831 advocated this method of origin. Bertrand-Geslin (22) and Coquand (23) were also early supporters of this view. That dolomite can be formed as a chemical precipitate is pointed out by Zirkel (24) who shows that the occurrence of crystals of dolomite in veins and druses indi-

icates its possible chemical deposition on a larger scale in nature. Fournet (25) regarded the dolomitic beds interstratified with limestone in the Tyrol as original precipitates. His studies showed that the volcanic theory of Von Bueh was no longer tenable. Others who have advocated the primary precipitation theory in one form or another are Loretz, Forehammer, Hunt, Vogt, Daly, Linek, and Sness.

As to the nature and cause of the reactions which have been supposed to give rise to the chemical precipitation of dolomite, there have been differences of opinion. Forehammer (26) attributed the reaction to the action of calcium carbonate of spring water on the magnesium salts of the sea, while Hunt, (27) basing his views on experimental evidence, regarded dolomite as the product of the action of sodium bicarbonate on the magnesium chloride and magnesium sulphate of the sea. Linek (28) and Daly (29), on the other hand, emphasize the importance of ammonium carbonate furnished by decaying organisms on the sea bottom as the precipitating agent.

Still another primary theory is that introduced by Lesler (30) to account for certain dolomitic layers in the "Calciferous" limestone near Harrisburg, Pa. These he believed to represent ordinary mechanical sediments which were deposited at the time the limestone was laid down. The elastic theory has been adopted more recently by Phillipi (31), who regards certain impure dolomites of the Muschelkalk of Germany as mechanical deposits possibly derived from the residuum of limestones low in magnesia. Grabau (32) has concluded that certain impure dolomitic limestones and waterlines of the Salinan and Monroan series have had a similar origin.

An entirely different theory of origin is that which was introduced by Grandjean (33) in 1844, to explain the production of the dolomites of the Lahn district. He assumed that by the atmospheric leaching of the lime from an original limestone of low magnesia content, a true dolomite might in time result. Both Bischof and Hardman later demonstrated the plausibility of this theory experimentally, and Hardman (34) immediately accepted it to explain the origin of the Carboniferous dolomites of Ireland. In 1895 Hall and Sardeson (35) applied the same theory in interpreting the history of the Lower Magnessian series of the Upper Mississippi Valley.

Högbom (36) on the other hand, regards surface leaching as of minor importance and emphasizes the effect of marine leaching. He has proven the reality of this process, on a small scale at least, in the modern seas and concludes that some dolomites of former periods may have been formed in this manner. Judd (37) is of the opinion that the weakly dolomitic portions of the atoll of Funafuti may be explained upon the basis of



this theory but regards the magnesia content of the more highly dolomitic portions as having been enriched by reaction with the magnesia of sea water.

#### *Experimental Evidence.*

On the experimental production of dolomite there is a voluminous literature. This has been well summarized by F. W. Pfaff (38), and later by Steidtmann (39). Dolomite has been frequently prepared artificially under conditions of high temperature or high pressure, or both, but it has been produced in the laboratory at ordinary temperatures and pressures only in rare instances, and then in minute amounts and under conditions which doubtfully operate in nature, at least on a large scale. It must be conceded then that these experiments furnish little evidence as to the actual conditions obtaining when extensive beds of dolomite are formed naturally. For the purpose of obtaining more accurate data on this point, a series of experiments was begun at ordinary temperatures and pressures early in 1912. In this series it was attempted to simulate natural conditions as near as they could be estimated, and to obtain some quantitative measurement of the effect of time and of concentration in the production of dolomite. In one set of experiments it was attempted to reproduce the conditions which exist in nature when limestone is altered to dolomite beneath the sea by solutions bearing magnesia. In these the effect of solutions of known concentration of  $MgCl_2$  and  $MgSO_4$ , and of mixtures of the salts, both with and without the presence of  $NaCl$ , on powdered aragonite was tried. The concentration of the magnesium solutions used ranged from two to ten times the concentration of the magnesia in sea water. After a period of six months, residues from the experiments were thoroughly tested for dolomite. The results were entirely negative. No trace of dolomite could be found. Careful re-examination of the residues after a period of nearly three years still gave the same result. The analyses showed that the  $CaCO_3$  had reacted slightly with the solutions, but no  $MgCO_3$  had been deposited. Apparently the soluble trihydrate of  $MgCO_3$  had been formed. It then appears that dolomite cannot be prepared artificially under these conditions.

In a second set of experiments it was attempted to obtain dolomite as a direct chemical precipitate at ordinary temperatures and pressures. First solutions of the bicarbonates of calcium and magnesium, after being standardized, were mixed in molecular equivalent proportions so as to give the same ratio of  $CaCO_3$  to  $MgCO_3$  as exists in normal dolomite. The solution was then allowed to evaporate spontaneously during a

period of one month. It was noted that the carbonates came down separately with the  $\text{CaCO}_3$  much in advance of the  $\text{MgCO}_3$ . The precipitate then contained only the mixed carbonates—no dolomite was formed. Scheerer (40) previously obtained the same results in a similar experiment. Negative results were still obtained when a solution prepared as above was inoculated with a crystal of dolomite and allowed to evaporate. Nor could the double carbonate be prepared upon evaporating spontaneously a solution of the two carbonates obtained by the action of carbonated waters on normal dolomite even when a dolomite crystal was introduced and a concentrated solution of sodium chloride and magnesium salts was added.

The experimental evidence so far obtained, therefore, does not suggest the circumstances under which large masses of dolomite can be formed in nature under ordinary conditions either by the alteration of limestone or by chemical precipitation. It is to be regretted that a careful study of the process of dolomitization where it is going on in the seas to-day has never been made. Such a study would doubtless throw much valuable light on the problem. It may well be that bacteria play an important rôle in the production of dolomite as suggested by Nadson.

#### *Field Evidence.*

Realizing the importance of careful field studies of dolomitic formations in interpreting the conditions of their origin, the writer undertook a study of the dolomites of the Upper Mississippi Valley under the auspices of the Iowa Geological Survey during the field season of 1912. More recently a grant from the Esther Herrman Research Fund of the New York Academy of Sciences has made possible much more extensive field studies in the eastern and central states. Dolomites ranging in age from the Cambrian to the Mississippian have now been examined and many samples collected for detailed chemical and petrographic study. It is possible to outline in this paper only some of the more important results obtained.

It should be pointed out that the term dolomite is used here in the broad sense to include both normal dolomite and dolomitic limestone. It is not necessary to differentiate between these in a discussion of their origin.

The field studies undertaken during the course of this investigation have alone furnished irrefutable evidence that most of the dolomites examined, regardless of their age, are replacement products. The following facts support this contention: (1) the lateral gradation of beds of dolomite into limestone, sometimes very abruptly; (2) the mottling of limestones by

irregular patches of dolomite on the borders of dolomite masses; (3) the existence of remnants of unaltered limestone in dolomite, and of nests of dolomite in limestone; (4) the irregular boundaries between certain beds of limestone and dolomite; (5) the presence of altered oolites or fossils in many dolomites; (6) the protective effect of shale beds; and (7) the obliteration of structures and textures.

In some instances the relationship of dolomite to limestone is such as to indicate that the alteration was accomplished by solutions which migrated from above downwards after the limestone was formed, or at least in the closing stages of its formation.

It is an interesting fact that certain layers have sometimes been passed over during the dolomitization of adjacent ones, and show little or no sign of alteration. The so-called interstratification of limestone and dolomite cited by some as evidence in favor of some primary theory of origin is then, in some cases at least, rather a pseudo-inter-stratification produced by the selective dolomitization of an original limestone. Some layers which have been passed over have been noted to be coarser grained than the adjacent layers which have been altered and this would seem to explain their greater resisting power. At times, however, the unaltered layers do not appear to differ markedly from the altered ones. The phenomenon is then difficult to account for. Normally the contact lines between such interbedded layers of limestone and dolomite are fairly regular and definite, but in some instances they are known to be very irregular and may even simulate irregular contacts produced by disconformity. A remarkable example of a pseudo-disconformity produced by uneven selective dolomitization has been observed in the St. Louis limestone near Farmington, Iowa. Here a bed of altered limestone is found resting very irregularly on a bed of dolomite. The two beds are very different physically and might readily be taken at first sight for two distinct formations, but when the contact is traced laterally for a short distance the lower bed loses its dolomitic character and passes into a limestone very similar to and continuous with the bed above.

Another striking relationship of limestone to dolomite is exhibited in a certain layer of an interbedded series of limestones and dolomites of the Beekmantown in the old Walton Quarry near Harrisburg, Pa. The beds dip south here at an angle of 30°. The layer in question is represented by dolomite six feet in thickness in the upper part of the quarry face and on each side of it appear good limestone layers. Now in the lower part of the quarry the lower half of this layer passes abruptly into limestone and continues to the quarry floor as

two distinct layers each 3 feet thick. Samples of the dolomite at the point where it passes into limestone yielded 18.1 per cent of  $MgCO_3$ , while the limestone itself yielded only 0.83.

It will be noted that in the above instances the gradation of limestone into dolomite is abrupt, but in many cases the gradation takes place through transition zones of limestone mottled with dolomite. There can be no doubt but that these mottled limestones represent an incipient stage in the process of dolomitization and it is believed that many dolomites have passed through such a stage in the progress of their formation. In most cases the phenomenon of mottling appears to be of purely inorganic origin, having resulted from a process of dolomitization which began at certain favorable centers and spread outwards. In some cases, however, it has been produced by the selective alteration of areas suggesting algæ and fucoids in the limestone first, and the spreading out of the dolomite from these as nuclei. The Tribes Hill limestone, as developed at Canajoharie, New York, furnishes an excellent illustration of the mottling produced by the latter method. All stages of mottling from altered fucoid-like markings to a rock uniformly dolomitic may be traced in this.

It has been observed that the spreading of dolomitization from certain centers in a limestone may give rise to mottling on a large scale if these centers be few and far apart. For example there is a conspicuous bed of dolomite pseudo-boulders in the St. Louis limestone at Alton, Ill., which appears to have been formed entirely in this manner. These boulder-like masses range from a few inches up to six feet in diameter and contain 32.39 per cent of  $MgCO_3$ , while the limestone matrix bears only 3.39. That they were formed in place is clearly indicated by the fact that the contact of the boulders with the limestone matrix is occasionally gradational and that the stratification lines of the limestone may at times be traced directly through the boulders. In a layer of limestone a few feet above the boulder bed here a similar process of local dolomitization has given rise to the development of irregular lenses of dolomite.

It has often been noted during the course of the field studies that many dolomites known to be of secondary origin show little or no evidence of shrinkage and porosity determinations have since shown that the transformation of a limestone to dolomite, even subsequent to its deposition, need not necessarily be accompanied by a decrease in volume as pointed out by Beaumont and consistently adhered to by later writers on the subject. It seems probable, therefore, that the replacement may proceed at times according to the law of equal volumes as enunciated by Lindgren (41) and that the inter-



change need not be molecular. In view of this fact compact dolomites showing no shrinkage effects can no longer be regarded as primary.

Further studies will doubtless show that considerable shrinkage effects produced by dolomitization are not common. It is believed that many vesicular dolomites have resulted from atmospheric leaching long after their formation.

#### *Petrographic Evidence.*

The microscopic study of many thin sections of dolomitic limestone has not only further amplified and strengthened the field evidence but has also thrown new light upon the details of the process of alteration. By employing microchemical tests it has been possible to distinguish between calcite and dolomite in the sections and make clear the most intimate relationships of the two minerals. It should be stated, however, that these tests furnish no reliable guide to the exact amount of magnesia in the rock, for crystals containing less than 25 per cent of  $MgCO_3$  may behave essentially like normal dolomite. But this is to be regarded in truth as a distinct advantage, for alterations of only a slight degree are indicated as well as the more marked ones.

It must be admitted that if dolomite has a diverse mode of origin the microscope fails to reveal it. Careful examination of every variety of dolomite fails to show any positive evidence in favor of either the primary chemical or the elastic theory of origin. On the other hand, there is abundant evidence in favor of the alteration theory. It is true that certain dolomites, whose origin is not certainly known from their field relations, possess an extremely fine and uniform texture, and this feature has in fact led Daly (42) to believe that these represent original chemical precipitates. In order to test the validity of this argument the finest grained dolomite of unknown origin encountered by the writer in these studies was compared with the finest grained dolomite of known secondary origin. For example the Jefferson City dolomite of the Ozark region, whose mode of formation is not definitely known, possesses unusually dense and compact layers which are seen under the microscope to be made up of minute granules the majority of which are below  $.003^{mm}$  in diameter, some measuring only  $.001^{mm}$ . The granules are suggestive of an original chemical precipitate. The strength of this interpretation is weakened, however, by the fact that a dolomite of known secondary origin has been found in the Middle Devonian of Iowa which is equally as fine-grained. The latter dolomite has resulted from the alteration of a dense, lithographic-like limestone with the approximate retention of the original texture.

As regards the possibility that some dolomites may be of clastic origin, none has been found which exhibits any signs of clastic structure. But that the original structure might have been obliterated during recrystallization is easily conceivable in rocks of this type.

Turning now to the dolomites which from their field relations are known to be secondary after limestone we have much more definite data. Indeed in these, by virtue of the fact that the alteration has frequently been halted before it proceeded to completion, we are often able to trace all stages of dolomitization from a limestone showing only incipient alteration to a good dolomite. Thus, it is possible to describe the steps normally passed through during the transformation of a limestone to dolomite.

So far as the testimony of the microscope goes the fine-grained limestones are more susceptible to alteration than the coarser-grained ones, a fact which is in keeping with the laws of chemistry. The evidence also indicates that the alteration may not proceed in exactly the same manner in the two types of limestone.

The alteration of fine-grained compact limestones seems to be accompanied normally by a notable increase in size of grain. Usually the diameter of the dolomite crystals formed is many times as great as that of the original calcite grains. But in rare cases, such as that of the dense Middle Devonian dolomite referred to above, the original structure and texture seems to be approximately retained. In the dolomitization of such fine-grained limestones the replacement frequently begins at many centers throughout the rock and spreads outwards from these, or if the rock possesses fine stratification the replacement may follow closely these original lines of weakness in the early stages. In those cases where the alteration begins at certain centers and spreads out from these, fucoid-like markings occasionally serve as the nuclei as in the case of the Tribes Hill limestone. But as a general rule no organic influence is noted. Normally the limestone is altered uniformly in the process of spreading from the dolomite centers, but it cannot be said that it is altered completely, for the dolomite patches often possess less than twenty per cent of  $MgCO_3$ . Small remnants of limestone, however, may occasionally escape alteration and become incorporated in the dolomite patches. The boundary between the limestone and the spreading dolomite area may or may not be abrupt. When abrupt, the rock may assume the appearance of a breccia and the term "pseudo-breccia" may aptly be applied. When the boundary is gradational, on the other hand, rhombohedrons of dolomite, variable in size but usually nearly perfect in their development, are disseminated through

the limestone a short distance in advance of the main dolomite area. As the replacement proceeds the dolomite areas grow larger and larger and eventually meet and become confluent thereby giving rise to a rock which is uniformly dolomitic. Further addition of magnesia may then take place by altering the rock more completely.

In the coarse-grained limestones, especially those which were originally coarse-grained, such as the crinoidal limestones, on the other hand, mottling does not seem to be the rule in the early stages of alteration. In these the replacement appears to affect the matrix first and to spread rapidly through the rock. The coarser grains are next affected, being broken down into aggregates of small dolomite grains. In the end a coarse-grained limestone may be changed over into a uniformly fine-grained one.

In the dolomitization of limestones of both types the calcareous skeletons of organisms appear in most cases to successfully withstand alteration and these, owing to their greater solubility than dolomite, are then removed to leave molds by a process of atmospheric leaching when the formation passes into the belt of weathering.

#### *Conclusions.*

Considering all the evidence, it seems probable that the great majority of our dolomites had their inception in the alteration of limestones. It will not be denied, however, that some dolomitic formations of minor importance may have had a different origin. For instance, some impure dolomitic limestones associated with shales very probably represent original elastic deposits which have not suffered any alteration whatever, and there is some reason for believing that certain dolomitic limestones high in siliceous material, such as the Silurian waterlimes of New York State, may have had a similar origin.

The importance of marine and surface leaching in increasing the magnesia content of limestones originally low in magnesia should likewise not be overlooked. There can be no doubt that this process has greatly enriched the more vesicular dolomitic limestones in magnesia. But the leaching theory does not explain the ultimate source of the magnesia. It merely shows how the magnesia content of a limestone originally low in this constituent can be enriched.

To return now to the dolomites which have resulted from the alteration of limestone, there are many reasons for believing that the more extensive of these have all been formed beneath the sea, and that dolomitization affected by ground water is only local and very imperfect. Some of the features

which lend weight to this view are as follows: (1) The dolomite areas of mottled limestones are believed to have undergone recrystallization at the same time as the associated limestone areas as suggested by the occasional development of zonal growths of calcite and dolomite. (2) In imperfectly altered limestones the dolomite is seen to follow original lines of weakness rather than secondary structures such as joints or fractures. (3) In most cases of mottling the dolomitization appears to have progressed uniformly as we should expect it to in an uncrystallized rock, rather than to have progressed by forming veinlets and stringers in the early stages. (4) The existence of perfect rhombs of dolomite in many imperfectly altered limestones suggests that the latter had not yet solidified when the dolomite rhombs were formed. (5) The widespread extent and nearly uniform composition of many dolomites indicates that they must have been formed by an agent capable of operating uniformly over wide areas. (6) An adequate source of magnesia for transforming extensive limestone formations into dolomite is found only in the sea which contains many times as much of this constituent as ordinary ground water. (7) Many dolomites are directly and regularly overlain by pure limestone formations or by thick shale beds, proving that they must have been formed before these overlying beds were deposited.

Some dolomites of minor importance, such as those associated with ore deposits and probably most, if not all of those related to fractures (vein dolomites), must have been formed through the agency of ground water. But in general, ground water is incapable of carrying dolomitization far. Study of analyses of ground water, and of river water, shows these to be uniformly low in magnesia, this constituent normally being greatly exceeded in amount by lime. How, then, could such waters dolomitize limestone when they already contain lime far in excess of magnesia? The law of mass action speaks strongly against ordinary ground water being able to accomplish extensive dolomitization. In the case of mineral springs and the mineralizing solutions which are related to ore deposition, however, it is conceivable that magnesia might be present in sufficient proportions to accomplish local dolomitization and doubtless most vein dolomites have been so formed.

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ART. XXIX.—*Volcanic Domes in the Pacific*; by  
SIDNEY POWERS.

## INTRODUCTION.

SINCE the famous dome and spine rose on the summit of Mont Pelée on Martinique in 1902-3, five domes of a somewhat similar nature have appeared on volcanoes in the Pacific Ocean. Three spine-like domes have risen on the summit of Bogoslof volcano in Bering Sea, and two of them have been destroyed by explosions. The other two domes have appeared in Japan, one on the summit of Tarumai, in Hokkaido (Yezo), during the spring of 1909, the other on the side of Usu, also in Hokkaido, during 1910. It is the purpose of this paper to describe the latter two domes, which were seen by the writer in 1915, together with the other domes in Japan, those at Bogoslof, and those which formerly existed at Kilauea, Hawaii. A list of the known volcanic domes is appended with a brief discussion of the theory of origin of spines and domes in general. A portion of this material has not previously been published and a full list of known domes has never appeared.

Volcanic domes and spines are either masses of new, viscous, lava pushed out from the top or sides of volcanoes, or masses of material already on the volcanoes which are elevated by the push of newly injected magma from below. In every case described below, new lava has appeared at the surface either comprising the greater part of the elevated mass or in the form of volcanic bombs. Spines differ from domes in the form of the extruded mass: Spines (aiguilles, Beloniten,<sup>1</sup> Felszähne) are monolithic needles of new lava, such as the one on Mont Pelée, which may form the centers of domes as was seen in Perry Peak, Bogoslof Island, after the explosion of 1906-7; domes (Staukuppen, Quellkuppen, Tholoiden,<sup>1</sup> cumulo-volcanoes) are more rounded masses of new lava such as the trachyte "Puys" of the Auvergne region or portions of older lava or ejectamenta elevated by new lava beneath, as in the Usu uplift of 1910 and in the Kilauean domes.

## EXAMPLES.

*Tarumaidake.*<sup>2</sup> The volcano Tarumai is situated on Hokkaido (Yezo), the northern island of Japan, 30 miles north

<sup>1</sup> The terms Beloniten and Tholoiden were introduced by K. Schneider, *Die vulkanischen Erscheinung der Erde*, Berlin, 1911; but F. v. Wolf (*Der Vulkanismus*, vol. i, Stuttgart, 1914, p. 492) points out that the former term has been previously used with another meaning.

<sup>2</sup> Dake signifies hill or mountain in Japanese.

of Volcano Bay and 8 miles from the sea. During the last period of activity, in 1909, a volcanic dome rose in the summit crater to a height of about 400 feet. The dome (fig. 1) is now a steep-sided mass of blocks with a flat top from which steam issues.

Smoke was first seen on the summit of the mountain January 11, 1909, and ash fell on the 22nd and 27th of that month.<sup>3</sup> During February smoke and ash were reported on

FIG. 1.



FIG. 1. The volcanic spine which rose in the summit crater of Tarumai in 1909 (after Oinouye).

four occasions; on March 3 a noise was heard and on March 14 there was an earthquake, caused apparently by a gas explosion. During this period the new lava was rising in the vent, for on March 30 an explosion was accompanied by a heavy fall of ash to the southeast and bombs of new material were ejected. The mountain was ascended on April 4, but no fresh lava had yet appeared in the crater. On April 12 an explosion threw out ash, lapilli, and anorthite crystals from the new lava which was evidently just beneath the floor of the crater.

Fire was first seen on April 17, indicating that the new lava had reached the surface. A dome commenced to grow and it was seen over the rim of the crater on the 20th. Three days later an ascent of the mountain was made and a glowing, rounded dome was seen. A maximum height of 440 feet was reached about May 1, but a considerable settling of the center of the mass followed the rapid rise, forming a flat top and

<sup>3</sup>The outbreak is described by: H. Simotomai, *Der Tarumajausbruch in Japan 1909*, *Zeitschrift Ges. Erdkunde*, Berlin, 1912, pp. 433-444; I. Friedlaender, *Ueber einige japanische Vulkane*, *Mitt. Ges. Natur- und Völkerkunde Ostasiens*, vol. xii, Tokyo, 1909.

destroying the domical form. A final explosion on May 12 opened a large fissure in the floor of the crater near the dome and spread a covering of ash over the region on the northeast. From this fissure, a crack about 300 feet long with a maximum width of 15 feet and a depth of over 60 feet, steam was rushing in August, 1915.

Huge blocks of porous pyroxene-hornblende andesite of a light to reddish grey color compose the outside of the dome. The andesite is filled with anorthite crystals  $\frac{1}{4}$  to  $\frac{1}{2}$  inch in length and it shows banding due to variations in porosity. The dome may be composed of a uniformly solid mass of andesite as figured by Simotomai<sup>4</sup> or it may be formed around a central core as was Perry Peak, Bogoslof, described below.

Small domes of glassy andesite are reported on Eniwadake, an extinct volcano a few miles west of Tarumai.<sup>5</sup> The domes are located on the northwest side of the summit crater and on a small peninsula in Lake Shikotsu.

*Usudake.* The volcano Usu, in Hokkaido, five miles north of Volcano Bay, is situated on the south side of Lake Toya, one of the peculiar depressions like Lake Shikotsu in Hokkaido and Lake Ikeda in Kyushu whose bottom is below sea level. Usu (see fig. 2) consists of a large "somma" rim about  $2\frac{1}{2}$  miles in diameter within which are two rounded domes, O-Usu (fig. 3) on the east, 975 feet high, and Ko-Usu (fig. 4) on the west, 555 feet high. In 1910 an eruption took place north of the somma rim, opening about 45 small craterlets and uplifting a rectangular block of the mountain in a manner somewhat similar to uplifts which take place at Kilauea on the edge of the crater Halemaumau. O-Usu and Ko-Usu are volcanic domes like those of the Puy de Dôme region of France. The 1910 uplift was evidently caused by the intrusion of new magna which did not reach the surface.

The eruption of 1910 commenced with a seismic prelude characteristic of Japanese volcanoes, the first shocks being felt at the time the barometric pressure was low and the outbreak occurring when it was at a maximum (29.99 in.). The first earthquakes were felt July 21; 25 were recorded the following

<sup>4</sup>E. Reyer (Theoretische Geologie, Stuttgart, 1888, pp. 98-9, 152) suggested this structure for certain rounded masses in Bohemia—notably Schlossberg von Teplitz—first described as Quellkuppen but later shown to be erosion remnants of Miocene intrusives (v. Wolff, Der Vulkanismus, I, p. 484, 1914).

<sup>5</sup>I. Friedlaender, Ueber den Usu in Hokkaido und über einige andere Vulkane mit Quellkuppenbildung, Petermann's Mitt., vol. lviii (1), pp. 309-12, 1912.



day; 110 on July 23; 351 on the 24th; and 162 on the 25th, the day on which the eruption began, with the accompanying release of gas by explosions.<sup>6</sup> The first explosions took place on the north flank of Usu, about 1,300 feet south of Lake Toya and opened craterlets from which ash and rock fragments already at the surface of the ground were thrown out. New

FIG. 2.

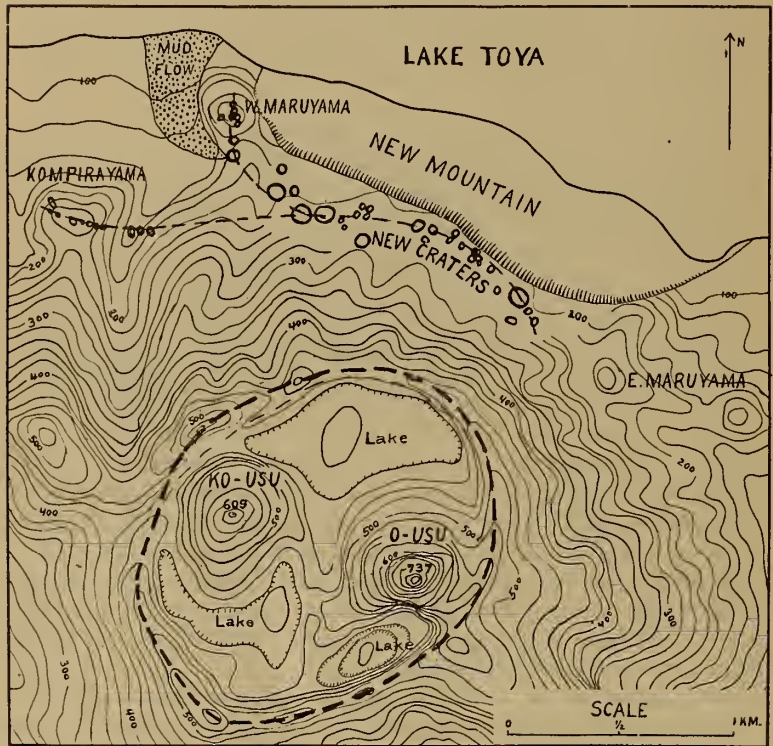


FIG. 2. Map of Usudake showing the volcanic domes O-Ussu and Ko-Ussu and New Mountain, which was tilted up in 1910. The old somma rim of the volcano is shown by heavy dashes. Contour interval 20 meters.

<sup>6</sup>F. Omori, The Usu-San eruption and the earthquake and elevation craters continued to form until the end of the year, but on the third day of the eruption smoking bombs of new hypersthene-phenomena, Bull. Imp. Earthq. Inves. Comm., Tokyo, vol. v, No. 1, 1911; D. Sato, Eruption of Mount Usu, Bull. Imp. Geol. Surv., Japan, vol. xxiii, 1910.

augite andesite were thrown out, indicating that the newly injected magma had arisen to within a short distance of the surface. Some of the craterlets were active for only a few hours, so that the trees on their sides were partly buried but

FIG. 3.



FIG. 3. The dome O-Usu as seen from the west. The south side of the dome has been uplifted and the west side steepened by an explosion (after Kato).

FIG. 4.



FIG. 4. The dome Ko-Usu looking northwest. The east side is supposed to have slightly subsided (after Kato).

not overturned, while others were intermittently explosive for several days, forming symmetrical cones and craters with diameters as great as 600 feet. In August, 1915, steam was still issuing from a few of the larger craters.

The elevation of the strip of land between the new craters and Lake Toya did not become noticeable until August 6,

1910, when it was found that the lake shore for a length of a mile had risen 3 feet. A maximum elevation at the shore of 10 feet at the east end of the uplifted area was reached August 21, followed by a gradual settling back of  $5\frac{1}{2}$  feet by November 10.

It was not until four days after the change of level of the shore-line was noticed, that attention was called to the formation of New Mountain north of a fault-scarp which developed between East and West Maruyama (fig. 2). New Mountain rose gradually, as a more or less rectangular block a mile long and 1,000 feet wide, to a maximum height of 310 feet. The fault-scarp disclosed beds of rock fragments and ash but no massive lava, and these beds were still steaming in August, 1915. The maximum height of 690 feet above Lake Toya (or 956 feet above sea-level) attained by New Mountain was not reached until November 9 and by April, 1911, the height had decreased 120 feet. A continuation of the uplift under Lake Toya was indicated by an increase in the amount of water in the lake.

As indicated above, the force causing the uplift of New Mountain appears to have been the intrusion of a mass of viscous magma which did not reach the surface, although bombs of the new lava were thrown out. The size of the area uplifted may be taken to indicate a large intrusion such as a laccolith, as Bailey<sup>7</sup> has suggested, but the arching characteristic of the beds above a laccolith was lacking. The partial subsidence of New Mountain may be compared to the change of form of the top of the Tarumai spine from a rounded dome to a plateau, and may have been caused by a partial withdrawal of the magma, or in part to contraction on cooling and loss of gas.

The volcanic domes O-U<sub>sn</sub> and Ko-U<sub>su</sub> rise to heights of 975 and 555 feet, respectively, above the floor of the crater. O-U<sub>su</sub> is the more perfect dome and its symmetry is broken only by an uplifted portion on the south side of the summit (fig. 3). There is no depression on the summit.<sup>8</sup> Ko-U<sub>su</sub> is an older and less perfect dome, similarly composed of hypersthene andesite. The east side has apparently been lowered by an explosion and a young crater with a diameter of 200

<sup>7</sup> E. B. Bailey, *Geol. Mag.*, vol. ix, pp. 248-252, 1912.

<sup>8</sup> I. Friedlaender (*Petermann's Mitt.*, vol. lviii (1), pp. 309-12, 1912) cites certain stream-worn pebbles on the summit as evidence that they were elevated to that position with the formation of the dome. It is apparent, however, that the dome was formed by new viscous magma and that the pebbles were carried up by the Ainus.

feet and 100 feet deep exists on the summit. As a Japanese painter who lived from 1765 to 1842 showed only Ko-Uzu in a sketch of the mountain, there is a slight possibility that O-Uzu rose during historic time.

*Kaimondake.* At the southern extremity of Japan in the line of volcanoes including Aso, Kirishima, and Sakurajima is the quiescent or extinct volcano Kaimondake, 3,030 feet in height. Friedlaender<sup>9</sup> has described the volcano as consisting of an ash cone rising to a height of about 2,200 feet where there is a crater wall, but the former crater is filled with an andesitic dome surmounted by a flat depression but not a crater. The dome is composed of very rough lava and it evidently represents such a dome as that on Tarumai. The last outbreak of the mountain was in 1615, and the last important eruption was in 885 A. D. At both these times ash was thrown out, but at the former eruption a summit glow was seen, suggesting that the dome appeared at that time.

*Sambondake.* About 100 miles south of the volcano Oshima (Vries Island) and 23 miles southwest of the island Miyake is a small group of rocks called Sambondake. The two larger masses are described as being composed of andesite, with the structure of dikes,<sup>10</sup> but the photograph of one of the masses (see fig. 5) shows that it strongly resembles in appearance the Mont Pelée spine.

*Chokai-San.* The volcano Chokai-San, in Ugo province, northern Japan, has been active seven times since 810 B. C., and ten days after the last eruption (1800-1), according to B. Koto,<sup>11</sup> a cone was raised on the east side of the summit crater, very much like the Tarumai dome.

*Kilauea.* Several times during the recorded history of Kilauea there have been uplifts of portions of the floor of the Kilauean sink surrounding the crater Halemaumau or of debris within the crater and once a dome formed of the consolidated surface of the lava lake was raised over Halemaumau.

In 1848 the first dome was formed. During the previous two years there had been an active lava lake in Halemaumau 2000 feet in diameter, the surface of which became crusted

<sup>9</sup> Peterm. Mitth., vol. lviii (1), pp. 309-12, 1912.

<sup>10</sup> I. Friedlaender, Mitt. Ges. Natur- und Völkerkunde Ostasiens, vol. xii, Tokyo, 1909.

<sup>11</sup> On the volcanoes of Japan, Jour. Geol. Soc. of Tokyo, vol. xxiii, p. 9, 1916. Professor Koto also mentions that Ma-yama, west of Kampu-San, northern Japan, is, according to tradition, a "puffed-up dome" (p. 9). Under the head of "Tholoide." Professor Koto classes those volcanoes which merely have a rounded form as well as those which are "volcanic domes" in the sense used in this paper.



over in 1848. The crust was elevated by a liquid lava beneath until it assumed the form of a dome 200 to 300 feet high and 2000 feet in diameter. By August the dome had increased in height until it was higher than the lower portions of the walls of the Kilauean sink. The sluggish basalt was seen

FIG. 5.

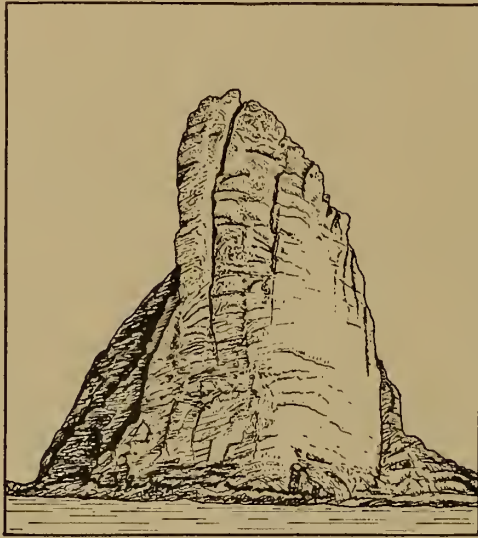


FIG. 5. Sambondake, an island in the Fujiyama-Bonin Island volcanic chain 30 miles south of Oshima, which may be a volcanic spine.

through cracks in the dome and occasionally it flowed out through these cracks and down the sides, increasing the size of the dome.<sup>12</sup>

The lava beneath the dome disappeared in the fall of 1848 and did not rise again until April, 1849, when, for a short time, very fluid basalt was thrown from openings in the top of the dome to heights of from 50 to 60 feet. With the next rise of the lava in 1852 the opening in the top of the dome had enlarged to a diameter of 200 feet. The sides of the dome were partly flooded by the rise of 1855 and they soon after fell into the lake.

<sup>12</sup>W. T. Brigham, *The volcanoes of Kilauea and Mauna Loa*, Mem. B. P. Bishop Museum, Honolulu, vol. ii, no. 4, p. 61ff., 1909.

An open dome was next formed over Halemaumau and it remained in place from 1872 until 1886. After the catastrophe of 1868 which drained the lava lake, Halemaumau became active in 1871 and 1872. In October of the latter year the crater had become an immense dome on whose summit were two lava lakes. The descriptions of this dome are imperfect, but it seems probable that the shores of the single lake of March, 1872, were elevated by the force of liquid lava below them. Four lakes developed on the dome and the tilted beds surrounding the lakes changed in height and form with the variations in level of the lakes. In 1880 the dome was regular in form with a number of crags elevated above the top of the dome. With the emptying of the crater in 1886 the remaining portions of the dome, 200 feet in height, collapsed.

A deep pit with the form of an inverted cone remained after the collapse of March, 1886, but four months later lava returned and the center of the pit had become a steep cone of talus blocks rising 140 feet and partly surrounded by a lava lake. The cone rose with the lava beneath until, by October, 1866, it became a rim of lava blocks 1000 feet in diameter and 250 to 450 feet in height with a central depression. The basin immediately surrounding the cone rose with it by bodily uplift and by flooding<sup>13</sup> so that the cone appeared conspicuously above the walls of the basin. By July, 1888, the walls of the basin had been eliminated and the summit of the cone was 158 feet higher than two years previously. The cone persisted until the collapse of 1891.

The ability of molten basalt to raise a dome over Halemaumau in 1848, to elevate the floor of the crater adjacent to the open lava lake in 1872, and to elevate a mass of talus into the form of a cone in 1886, is confirmed by an uplift in 1894. On March 21, the entire surface of the brimming lake appeared to be intensely active and agitated. "Suddenly on the north side stones, lava, and 'dust' were thrown high into the air with spouting columns of fire and in the space of less than four minutes the north bank of the lake was tilted to a height of 100 feet or more, leaving an abrupt wall over the lake with a steep and broken slope toward the north."<sup>14</sup> The uplifted area was 800 feet long by 400 feet wide.

One month after the uplift on the edge of Halemaumau the hill began to sink and by July 11 it had reached the level of

<sup>13</sup> Measurements by F. S. Dodge, cited by J. D. Dana, *Characteristics of volcanoes*. New York, pp. 109-10, 1891.

<sup>14</sup> An observation by Mr. W. R. Castle, cited by W. T. Brigham, *op. cit.*, pp. 185-6.

the other banks. With the sudden subsidence of the lake on that date the hill sank still farther, and the resulting depression may now be seen on the northeast side of the Halemaunau pit.

In December, 1914, a portion of the floor of the Halemaunau pit rose in a manner similar to the 1894 uplift, but more slowly. The origin may have been the differential loading of other portions of the floor of the pit by fresh flows or it may have been the intrusion of lava beneath. On December 4 with a lake 400 feet long and 150 feet wide, a portion of the floor beneath the main lake and a northeast arm commenced to rise as a crag 300 feet long and 100 feet wide. The relative movements of the crag and of the lake were irregular: in 14 days the crag remained 58 feet above the surface of the lake while that body rose 41 feet; in 9 days more (January 2, 1915) the lake rose 12 feet but the crag subsided 23 feet; and by March 15 when the lake had subsided 112 feet the crag had sunk only 45 feet.

A similar crag was formed in September, 1915, between the main lake and a northwest arm. A rectangular block 100 feet wide rose about 15 feet, as measured by the writer, between September 9 and 10 while the lake remained stationary except for the daily rises in the late morning and evening. A few days later the lake began to rise and the crag remained above the surface of the lake throughout the rising phase.

*Bogoslof.* Six peaks have risen from the sea on top of the submarine Bogoslof volcano since the early navigators explored Bering Sea, about 1768. These peaks have each been composed of solid rock and have probably been formed by the upthrust of viscous magma after the manner of the Mont Pelée spine. Three of the peaks remain and are connected to form one island by the debris from explosions which have destroyed two of the other spines.

The rise of the first peak, Ship Rock, was reported by the early mariners, and the rock was not washed away until 1888. Old Bogoslof, better known as Castle Rock, was pushed up in 1796. Various estimates of the size of this island were made before erosion began to wear it away, and it appears to have been 4,000 feet in diameter and 350 feet in height. There was no summit crater, the top being formed of pinnacles. New Bogoslof, also called Grewingk and Fire Island, appeared in 1883 as a craterless mass of andesite rising precipitously from the sea to a height of 800 feet. The name Fire Island was applied to the mass for it apparently increased in size by newly upthrust masses for several years with accompanying smoke, steam, and an occasional glow.

Perry Peak (Metcalf Peak) appeared in March, 1906, as an island 2,000 feet in diameter and 400 feet long, near the site of Ship Rock, midway between Castle Rock and Fire Island. The sides of the peak were quite smooth and the top was described as a "broken horn" as if the mass had been forced through an aperture in the submarine volcano. Gas must have accumulated in large quantities within the cold exterior of the spine, for after an existence of 10 months, an explosion blew away half of it.

Soon after the destruction of half of Perry Peak, a similar spine, McCulloch Peak, rose close by, partly over the place which the destroyed half of Perry Peak had occupied. The size of McCulloch Peak, when visited in August, 1907, was about that of the original Perry Peak. The shattered cross-section of the latter showed a central spine, like that of Mont Pelée, surrounded by debris which had fallen from and which had been blown from the sides and top of the spine during its upthrust.<sup>15</sup>

The life of McCulloch Peak, like that of Perry Peak, was 10 months, for an explosion destroyed the entire mass in September, 1907, piling high with debris the sand bars which had formed between Castle Rock, Fire Island, and the remnant of Perry Peak.

During the next few years the changes at Bogoslof are uncertain, but in July, 1908, it was reported that no trace of Perry Peak was visible, suggesting another explosion. On September 10, 1909, the bay which occupied the site of McCulloch Peak and of Perry Peak was reported to have become a lagoon in which two small islands had appeared. These islands continued to rise, so that in June, 1910, the larger was 178 feet in height, and the smaller 100 feet.

The lower peak was named Tahoma Peak in honor of the U. S. S. *Tahoma*, but the higher one is referred to as Perry Peak. On September 18 an explosion opened a crater in the higher peak, and ashes together with clouds of smoke and steam were ejected. The formation of a crater—so rare a phenomenon at Bogoslof—may have been caused by a more gradual escape of the confined gases than in the cases of Perry and McCulloch peaks.

<sup>15</sup> T. A. Jaggar, Jr., *Bull. Amer. Geogr. Soc.*, vol. xl, pp. 385-400, 1908. The earlier history of the volcano is described by C. H. Merriam, *Harriman Alaska Expedition of 1899*, vol. ii, and *Smithsonian Rept. for 1901*, pp. 367-375.



## SUMMARY.

The following table shows the size, composition, and important features connected with the various volcanic domes of the world. Through lack of sufficient data, the following domes are omitted: those of the Auvergne region of France, including Puy Chopine, Puy de Dôme, and Puy Sareony,<sup>16</sup> those in Italy, including Monte Tolfa, Monte Cerveteri,<sup>17</sup> Monte Santa Croce, Monte Lattani,<sup>18</sup> and Monte Venere<sup>19</sup>; that on Saba<sup>20</sup>; the dome of Chokai-san and the questionable spine of Sambondake discussed above; and those which may exist on the Lipari Islands,<sup>21</sup> Pantelleria,<sup>22</sup> or on Sardinia.<sup>23</sup> The lateral cone of the Vesuvius formed in 1895-9 grew exotically according to Dr. H. S. Washington, and does not represent a dome.<sup>24</sup> Certain volcanoes of Ecuador which have been described by A. Stübel,<sup>25</sup> as having no summit crater, appear to have suffered from glacial and other forms of erosion, and in two instances the rock at the summit is described as an agglomerate.

In attempting to draw any general conclusions about volcanic domes it is seen that very little is known concerning many of the examples cited. All of the volcanoes on which domes have appeared must be classed as old and 13 of the 25 are extinct. In at least 7 of the 13 extinct volcanoes, activity appears to have been closed by the formation of the dome or spine over the vent. Not all volcanoes, however, become extinct with the formation of domes, for Usu has been occasionally active during the Christian era, and a few minor eruptions have been re-recorded in the now quiescent or extinct Kaimondake.

Tarumai and Mont Pelée have furnished information concerning the mechanism of dome-formation. The eruption commences with earthquakes and explosions as the gas from the

<sup>16</sup> Michel Lévy, Eighth Int. Geol. Cong., Paris, 1900, Guide Book 14, pp. 7-12; P. Glangeaud, *Les volcans d'Auvergne*, Paris, 1910; A. Lacroix, *La montagne Pelée apres ses eruptions*, Paris, 1908; M. Boule, *La Géographie*, vol. xi, pp. 7-26, 1905.

<sup>17</sup> H. S. Washington, Italian petrological sketches, *Jour. Geol.*, vol. v, p. 350, 1897.

<sup>18</sup> *Idem*, pp. 241-4.

<sup>19</sup> *Idem*, vol. iv, pp. 828-30, 1896.

<sup>20</sup> E. O. Hovey, *Volcanoes of Martinique, Guadeloupe, and Saba*, Eighth Int. Geogr. Congr., Washington, pp. 447-51, 1904; K. Sapper, *In den Vulcangebieten Mittelamerikas und Westindiens*, Stuttgart, p. 219, 1905.

<sup>21</sup> A. Bergeat, *Staukuppen*, *Festband Neues Jahrb.*, 1907.

<sup>22</sup> *Idem*; also H. S. Washington, *Volcanoes and rocks of Pantelleria*, *Jour. Geol.*, vol. xxi, pp. 662, 1913.

<sup>23</sup> H. S. Washington, *Some lavas of Monte Arci, Sardinia*, this *Journal*, vol. xxxvi, pp. 577-90, 1913.

<sup>24</sup> Personal communication from Dr. H. S. Washington.

<sup>25</sup> *Die Vulkanberge von Ecuador*, Berlin, 1897, especially pp. 28, 405, 418.

Example	Elev. Feet	Ht. Dome Feet	Diam. Base	Age	Magma	Remarks
Tarumaidake	2540	440	1300	1909	Pyrox.-Hornb. andes.	Rose with many explosions; summit became flattened.
Usu: O-Usu	2420	975	1700	}	} Hyper. andes.	Younger, symmetrical dome.
Ko-Usu	2000	555	1700			
New Mt.	956	310	6760 × 1540			
Kaimondake	3030	700-1000	1200 ±	885?	Andesite	Fills summit crater; closed summit activity?
Kilauea:	3600 ±	250 ±	2000	1848-55	Basalt	Broad dome of frozen crust pushed up over lava lake.
1 { "Dome"	"	"	"	1872-86	"	Rim of open lava lake uplifted.
2 { "Dome"	"	140 +	"	1886-91	"	Talus raised as cone over lava lake.
3 { Debris cone	"	"	"	"	"	"
Bogoslof	350 +	350	4200 -	1796	Hornb.	Old Bogoslof
Castle Rock	800 ±	800	"	1883	andes.	New Bogoslof
Fire Island	400	400	2000	1906	Hornb.-pyr.	Half blown away after ten months.
1 { Perry Peak	400	400	2000	1907	andes.	Destroyed by explosion after ten months.
2 { McCulloch Pk.	400	400	2000	1909-10	"	Summit crater opened in 1910.
3 { Tahona Peak	178	178	1200 ±	"	"	Tower-like rock inside crater.
Panum Crater	150	150	1300 × 1800	"	Rhyolite	"
Mono Lake <sup>2</sup>						
Nameless crater		250			Augite andes.	Rose during closing stages of flow.
Pauline Lake <sup>3</sup>						
Mont Pelée <sup>4</sup>						
1 { Dome	4420	1130 -		1902-3	Hyp. andes.	Appeared in old crater.
2 { Spine	5170	760	1500 ±	"	"	Came through top of dome.
Soufrière <sup>5</sup>	4868	1000	3150	"	"	Fills old summit crater.
Nevado de Toluca <sup>6</sup>	15000	330			Hornb.-hyp. andes.	Within summit crater; closed activity.
Colima <sup>7</sup>	11900			1869	Hyp. andes.	Formed at close of flow.
Graham Island <sup>8</sup>	210	210	380	1831	Feld. basalt	Crater on the summit.
Pantelleria						
Santorin <sup>9</sup>	355	355	1300 × 1600	1866	Hyp. andes.	Rose with explosions; flow broke through.

<sup>1</sup> Appeared in approximately the same locality.<sup>2</sup> I. C. Russell, Criteria relating to solid massive eruptions, this Journal, vol. xvii, pp. 254-68, 1904.<sup>3</sup> Idem.<sup>4</sup> T. A. Jaggar, Jr., *ibid.*, vol. xvii, pp. 34-40, 1904;<sup>5</sup> A. Lacroix, La Montagne Pelée et ses éruptions, Paris, 1904;<sup>6</sup> E. O. Hovey, this Journal, vol. xvi, pp. 269-281, 1903.<sup>7</sup> E. O. Hovey, Bull. Amer. Geogr. Soc., 1904, pp. 1-18.<sup>8</sup> T. Florez, Tenth Int. Geol. Congr., Mexico, 1906, Guide Book 9;

H. F. Cleland, Pop. Sci. Mo., vol. lxxi, p. 185, 1907;

A. Bergcat, Staukuppen, Festband Neues Jahrb., 1907, pp. 310-29;

P. Waitz, Tenth Int. Geol. Congr., Mexico, 1906, Guide Book 13;

H. F. Cleland, *op. cit.*<sup>9</sup> H. S. Washington, this Journal, vol. xxvii, pp. 131-50, 1909.

F. Fouqué, Santorin et ses éruptions, Paris, 1879;

F. v. Wolff, Der Vulkanismus, Stuttgart, vol. I, p. 486, 1914.

rising magma reaches the surface. After the throat of the volcano is partly cleared by these explosions, the lava appears at the surface as bombs and usually as a mass of incandescent blocks which is elevated by the injection of magma from beneath. A monolithic mass of rock may be thrust through the dome, and, if so, by expansion and explosions of gas it becomes surrounded by a pile of debris. Once the dome appears at the surface, gas appears to play only a minor rôle in furthering the uplift, but a major rôle in causing the destruction of any projecting portions of the dome or even of the entire mass. As in the cases of Perry Peak and McCulloch Peak at Bogoslof, the gas rising from the deeper seated portions of the magma may apparently become confined under a hardened crust in such a quantity that the whole top is blown off.

Viscosity is the principal factor which determines whether the magma shall appear as a flow or a dome. At Santorin in 1866 a dome was formed, but the lava finally burst out the side as a flow, whereas at Colima in 1869 and at the crater near Pauline Lake, Oregon, the flow came first, and an increasing degree of viscosity finally led to the formation of a dome. Contrasted to these domes built by magmas of low fluidity, and frequently great porosity, stand the Kilauean uplifts caused by basalt, which, when liquid, is one of the least viscous of magmas. The frozen crust of a lava lake was elevated about 600 feet at one time, the floor of older lava surrounding an open lava lake was raised at another time, and still later a pile of talus in the form of an inverted cone was raised into a debris cone in the center of which the lava lake finally appeared. The uplifted masses at Kilauea and at New Mountain formed at Usu in 1910 differ from the other domes because consolidated lava or talus instead of newly intruded magma formed the uplifted mass. The principle of uplift, however, appears to be the same, because in each case new lava appeared later at the surface.

ART. XXX.—*New Zinc Phosphates from Salmo, British Columbia*; by ALEXANDER H. PHILLIPS.

DURING January, 1916, a small collection of ores and minerals, representing the occurrences and associations at the Hudson Bay Mine at Salmo, British Columbia, was received by the Geological Department of Princeton, from Mr. Dave McBurney. Included in this collection was a small specimen which, after analysis, was recognized as a new basic zinc phosphate. Mr. McBurney describes the occurrence of this mineral in a letter as follows: "We ran into this ore last October and most all of it was taken out and shipped. This ore was in a sort of a cave 16' by 24' and 8' high. When we broke into it, there were pillars of the ore reaching from the roof to the floor of the cave, also masses hanging down from the roof. . . . The main ledge of zinc carbonate ore passes directly over this cave. It is cut by two dykes at the cave, one dyke forming the wall and the other the roof of the cave. . . . On the floor there was a mass of very phosphatic clay, which carried 20 per cent zinc, and buried in the clay were great chunks of this ore." Mr. McBurney also adds, that the cave is on the 200-foot level. About one hundred tons of ore were taken from the cave, and the mine is absolutely dry, except where the two dikes cut the formation. A description of this new zinc phosphate has been sent to the Mineralogical Magazine by Dr. T. L. Walker of Toronto,\* and has been named *spencerite* by him and its formula fixed as  $Zn_3(PO_4)_2 \cdot Zn(OH)_2 \cdot 3H_2O$ .

The specimen of spencerite in the collection from Mr. McBurney was apparently formed on the floor of the cave, as it was coated with clay. It was a mass of radiated and reticulate crystals, some of which are nearly an inch and a half in length. The crystals are white, slightly greenish in the mass with a strong pearly luster on the good cleavage. There are no terminal faces, as the specimen has been much affected by solution, and there are solution cavities separating the spencerite from a thin botryoidal crust of calamine. Calamine is also included in isolated solution cavities of the spencerite and has been formed as a later product.

The spencerite is practically a chemically pure compound and as my analysis had been completed before hearing from Dr. Walker, I am adding the results here simply to corroborate his work. The specimen was air-dried and yielded:  $ZnO = 60.39$ ,  $P_2O_5 = 26.13$ ,  $H_2O = 13.44$ . The specific gravity as determined by methylene iodide is 3.123. Hardness about 2.75. Decrepitates strongly in the closed tube, yielding much water

\* From personal letter from Dr. Walker.



and becoming yellow while hot. A sample was tested for loss of water at various temperatures with the following results; expressed in percentages.

110°	120°	140°	167°	204°	244°	278°	Red heat
·19	·41	1·39	2·89	9·27	9·65	9·71	13·22

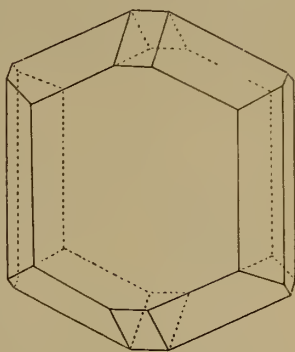
All the above results would indicate that the formula assigned to the mineral is undoubtedly correct.

*Hibbenite*.—Mr. McBurney very kindly responded to a request for more material with a specimen weighing a little over 500 gms. This specimen was, apparently, a portion of a rounded nodule of radiated spencerite crystals, enclosed also in a botryoidal crust of nearly pure white calamine (silicate). Some of the crystals showed cleavage surfaces nearly three inches in length. The specimen was much affected by solution, and was very friable in portions, some laminae being more soluble than others, breaking down into thin scales. Under the binocular a crystal angle quite different from the spencerite in appearance and slightly yellow in contrast to it was noted. Further search through the specimen yielded eight or ten of these crystals, varying from eight to twelve millimeters in length. These crystals I believe to represent another new basic zinc phosphate and I suggest the name *hibbenite* for it, in honor of Dr. John Grier Hibben, President of Princeton University.

*Habit*.—The habit is orthorhombic, tabular parallel to the macropinacoid,  $a$  (100), nearly as broad as long and approximately one quarter as thick along the brachyaxis, as broad along the macroaxis. They are all combinations of the pinacoids  $a$  (100) and  $b$  (010), the prism  $s$  (120), the pyramid  $p$  (111) and the macrodome  $d$  (101). The brachypinacoid is the dominant face, yielding the tabular appearance of the crystals. Implanted separately upon and evenly distributed over all the crystal faces are small, rounded lens-shaped crystals. They average about one millimeter across, have no definite orientation to the crystalline directions of the *hibbenite* or to each other and are so rounded by parallel growths that crystal forms or faces cannot be identified. These small crystals I believe to be also another new basic zinc phosphate. The *hibbenite* crystals are all simple in habit and separately imbedded in the spencerite. In several instances parallel growths were attached to the terminations and extending out in the matrix, ending in rounded granular stringers. These parallel growths were easily detached, leaving the terminal faces intact, but much pitted and scarred. The brachypinacoid,  $b$  (010), is inconspicuous, very narrow and striated parallel to the vertical axis. It occurs on about half of the crystals. The prism,

$s(120)$ , is always well developed, but strongly striated vertically. The alternations of growth between the prism and the brachypinacoid are so marked, as to round this portion of the prism zone almost circular. The pyramid,  $p(111)$ , is present on all the crystals and is the second best developed form. The faces are rounded and striated parallel to their intersections with the maeropinacoid. The form is equally developed at both terminations. The maerodome,  $d(101)$ , is small and variable, and while the angle fixes the face, as the unit dome, in several cases it appeared triangular, as if not in the same zone as  $p, p'$ . This is caused by the rounded nature of the pyramid faces and in the illustration the dome is shown as the unit dome in contact with maeropinacoid and its intersections with the unit prism parallel. The comparative development of all the forms is as represented in the illustration.

*Angles.*—While to the eye the various faces seemed perfect and bright enough to yield reflections, in the goniometer they give only a confused blur, with no indication of a signal whatever. The measurements are, therefore, very imperfect, measured mostly with a small Wollaston goniometer. The axial ratio and crystal angles are only approximate.



		Average	Limits	No.
$s \wedge s'$	(120) : (120)	80° 37'	79° 58' to 80° 50'	9
$a \wedge d$	(100) : (101)	50° 28'	49° 30' " 51° 25'	4
$d \wedge d'$	(101) : (101)	79° 24'	78° 20' " 80° 5'	3
$p \wedge p'$	(111) : (111)	77° 18'	76° 29' " 78° 30'	5

Axial ratio  $a : b : c = 0.589 : 1 : 0.488$ .

The combination of forms, the crystal angles and axial ratios are very near that of hopeite as given by J. L. Spencer.\*

*Chemical composition.*—Several crystals were ground, combined in one sample and analyzed with the following results:

	No. 1	No. 2	Theoretical
ZnO .....	57.51	57.60	57.625
P <sub>2</sub> O <sub>5</sub> .....	28.77	28.88	28.721
H <sub>2</sub> O .....	13.74	13.68	13.653
	<hr/>	<hr/>	<hr/>
	100.02	100.16	99.999

\* Mineralogical Magazine, vol. xv, p. 1.

The above represents the results arrived at from the analysis of the air-dried sample. The sample dissolved readily in dilute acids to a perfectly clear solution leaving no residue and qualitative tests revealed no other elements present, except in traces. The analysis yields the ratios of  $7\text{ZnO} \cdot 2\text{P}_2\text{O}_5 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ , or  $2(\text{Zn}_3(\text{PO}_4)_2) \cdot \text{Zn}(\text{OH})_2 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ , a formula which is very satisfactory, with the possible exception of the water. The water is somewhat variable with the condition of the sample. The crystals are filled with small cavities which contain water as shown under the microscope. Water was determined in another sample which had not been exposed to the air as long as the first sample, with the result that it yielded 13.90 per cent. Then a crystal was picked out of the matrix, ground, and the water determined at once with 14.8 per cent as the result. A portion of this crystal weighing .348 gms. was then tested for loss of water at different temperatures, for comparison with that of spencerite.

It lost at	110°	130°	210°	250°	275°	Red heat
	5.74%	7.24%	7.93%	10.05%	11.35%	14.71

The crystals are basic, as is shown both by the high temperature at which a considerable part of the water is given off and by the yellow color of the hot sample, due to the presence of zinc oxide.

*Physical properties.*—There are three cleavages parallel to the three pinacoids. Of the three, the brachypinacoidal cleavage is perfect, that parallel to the macropinacoid less so, and the basal cleavage is imperfect. The specific gravity, as determined on small fragments with methylene iodide, varied but little from 3.213. It fuses easily and becomes yellow while hot; decrepitates strongly in the closed tube, yielding much water. Hardness is about 3.75, scratching calcite easily.

*Optical properties.*—Hibbenite is a pale yellow, almost white, translucent, with a vitreous, though somewhat pearly luster. The double refraction is very weak. Extinction is parallel on all three pinacoidal sections, with the plane of the optic axes parallel to the base. The macroaxis  $b$  is the acute bisectrix. Optically negative.

The small lens-shaped crystals mentioned, as being implanted on the hibbenite crystals, are also found in the solution cavities of the spencerite and represents a secondary mineral, formed from solutions derived from the spencerite. While these crystals have been separated from the other material by means of methylene iodide, the sample was contaminated with considerable calamine. The analysis, however, indicates that they, also, are a new basic zinc phosphate. It is hoped that a pure sample may be separated and the chemical formula reported in the near future.

ART. XXXI.—*On the Separation of Cæsium and Rubidium by the Fractional Crystallization of the Aluminium and Iron Alums and its Application to the Extraction of these Elements from their Mineral Sources*; by PHILIP E. BROWNING and S. R. SPENCER.

[Contribution from the Kent Chemical Laboratory of Yale Univ.—ccclxxxi.]

ROBINSON and Hutchins\* have recommended the crystallization of the aluminium alums for the separation of cæsium and rubidium from potassium and lithium in lepidolite after the decomposition of that mineral by fluor spar and sulphuric acid. They have also called attention to the difference in solubility between the cæsium and the rubidium alums† and have suggested fractional crystallization for the separation of these elements. The marked difference in solubility between the potassium alum and the alums of cæsium and rubidium makes the method quite satisfactory for the separation of potassium from these rare alkalies, but the difference in solubility between the alums of cæsium and rubidium is not sufficiently great to bring about a rapid separation of these elements.

The work to be described was undertaken to obtain some definite information as to the value of the process of fractional crystallization when applied to the problem of separating the alkalies.

The process may be briefly described as follows:

A solution obtained from the decomposition of lepidolite by heating with fluor spar and sulphuric acid after the removal of the calcium sulphate was evaporated until on standing the mixed alums crystallized out. The mother liquor was poured off into a second flask and this liquid was evaporated until another crop of crystals was obtained and the new mother liquor poured into a third flask, and so on. The crystals in the first flask were dissolved in a small amount of water, by warming, and again allowed to crystallize, the supernatant liquid being poured into the second flask upon the crystals which had formed there; these crystals, in turn, were dissolved in this liquid and allowed to recrystallize; and the process was continued through all the series of flasks. The crystals separating in flask number one were repeatedly dissolved in fresh water and allowed to recrystallize in this way, and the mother liquor was kept moving along the series of flasks in succession.

By this method the more insoluble alum was concentrated at the upper end of the series while the more soluble alum moved toward the lower end.

\* Amer. Chem. Jour., vi, 74.

† Note: 100 parts of water at 15-17° C. will dissolve 0.62 parts of cæsium alum, 2.3 parts of rubidium and 13.5 parts of potassium alum.



After six such crystallizations applied to a solution of the alkalis from lepidolite, the crystals in the first flask showed only cæsium and rubidium when examined before the spectroscope on a platinum wire, and the crystals in the sixth flask gave a decided test for potassium and a very strong test for lithium, and showed only traces of cæsium and rubidium.

A mixture of cæsium and rubidium alums obtained by the above process was subjected to this same crystallization method. After about seven crystallizations, the crystals in the first flask were found to be pure cæsium alum but the crystals in the sixth flask, while strong in rubidium, still gave evidence of the presence of cæsium. The process of crystallization was continued until twenty-two fractions had been obtained before the cæsium had been completely removed. The crystals in the twenty-second flask proved to be pure rubidium alum, no evidence of the presence of cæsium being found.

Locke,\* in studying the properties of the alums, has called attention to the differing solubilities of these interesting compounds, and notes in particular the great difference of solubility of the cæsium and rubidium iron alums† as compared to that of the corresponding aluminium alums; and it has been suggested that this difference might be of analytical value.

In order to investigate this point a mixture of cæsium and rubidium iron alums was prepared and subjected to the same process described above. After four crystallizations, the crystals in flask number one gave no test for rubidium but showed abundance of cæsium; and after the process had been continued until eight fractions were obtained, the eighth fraction was found to be free from cæsium and contained pure rubidium alum.

A further experiment was made as follows: Ten grams of the mixed cæsium and rubidium alums from lepidolite were dissolved in water and the aluminium hydroxide was precipitated by ammonium hydroxide and filtered off. The filtrate, evaporated to about 130 cm<sup>3</sup>, was poured upon some crystals of ammonium ferric alum in quantity somewhat in excess of the amount necessary to allow the replacement of the ammonium by the cæsium and rubidium. The solution was then warmed until the crystals were dissolved. On cooling, crystals separated which, when examined, gave abundant evidence of cæsium but no test for rubidium.

This experiment suggested a convenient method for the formation of cæsium alum and also seemed to show that the more insoluble alums were readily thrown out of solution by treatment with strong solutions of the more soluble alums.

\* Amer. Chem. Jour., xxvi, 166.

† 100 parts of water at 25° C. dissolve 2.7 parts of cæsium alum and about 17 parts of rubidium alum.

This method was applied quite successfully to the extraction of cæsium from pollucite as follows :

The mineral was decomposed by hydrochloric acid, and after evaporation and the removal of silica the acid extract was poured upon crystals of ammonium aluminium alum and warmed until the crystals had dissolved. On cooling, cæsium alum separated in abundance ; and the mother liquor, although not free from cæsium, after one treatment consisted mainly of ammonium chloride. After about two recrystallizations the crystals obtained in the first treatment were found to give no test for either ammonium or chlorine and to be pure cæsium alum. The remainder of the cæsium was easily obtained by a few crystallizations of the mother liquor.

This method has advantages over the other methods for the extraction of cæsium from pollucite which involve the precipitation of the cæsium as the double lead or antimony chloride and the decomposition of these compositions by hydrogen sulphide or ammonium hydroxide.

A few experiments were made to determine the insolubility of the cæsium and rubidium in a saturated solution of ammonium aluminium alum. It was found that 1 cm<sup>3</sup> of a solution of RbCl containing 0.0002 grams Rb would give a perceptible precipitate when treated with 5 cm<sup>3</sup> of a saturated solution of ammonium alum, and that 1 cm<sup>3</sup> of a solution of CsCl containing 0.00005 grams Cs would give a precipitate of cæsium alum.

By the careful study of conditions and the use of the other alums it is hoped that these observations may lead to some advances in the analytical study of these elements, and we hope to give further attention to this problem.

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## SCIENTIFIC INTELLIGENCE.

### I. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Collection of Osteological Material from Machu Picchu* ; by GEORGE F. EATON. *Memoirs of the Connecticut Academy of Arts and Sciences*, vol. V, pp. 1-96, figs. 50, plates 39, charts 3. New Haven, Conn., 1916.—The monograph in hand is a creditable and well-illustrated report on the collection of osteological material gathered from Indian graves at Machu Picchu by the Peruvian Expedition of 1912, under the leadership of Professor Hiram Bingham, and the auspices of Yale University and the National Geographic Society.

The remains described were obtained from graves "found at various places on the steep sides of the Machu Picchu mountain,

from its very foot close to the Urbamba River up to an altitude of 1200 feet above the ruins." The burials were mostly in holes and dugouts, or caves, beneath bowlders, very much as in other, and in some instances widely distant, parts of the mountains of Peru. In the majority of cases the bodies were simply placed in these shelters without being interred. In numerous instances the skeletal remains were incomplete suggesting secondary burials, such as also were common in different parts of the Andean region. The total represents 164 individuals. Very curiously, of the 124 adults among these no less than 102 were female. The author is inclined to explain this by the presence at Machu Picchu of an Inca convent, in which case the female skeletons would be largely the remains of the inmates; another possible explanation being that a large percentage of the males were withdrawn from the community for military operations and would be buried in other parts of the country.

Anthropologically the crania represent partly the coastal or brachycephalic and partly the highland or relatively narrow type, showing on the whole a decidedly mixed population. Ten of the female and five male skulls show, besides, the Aymara deformation, while four of the females present a "flat-head" compression, such as was common in some regions along the coast. The period to which the Machu Picchu skeletal remains are referable is in the main probably the late pre-Columbian; but two of the burial sites yielded also objects which show contact with the Spanish.

The individual "caves" in which skeletal material was discovered are described in detail, thus giving the reader a faithful picture of the conditions and difficulties of the work of the anthropological collector in these regions; and added to this are descriptions of the archeological and animal remains found with the human bones. The former include some interesting articles of bronze and pottery, while among the latter occur several new species of smaller mammals.

The charts of measurements might have been supplemented to advantage by smaller, analytical tables; and one misses an index. But on the whole the memoir bears testimony of careful, painstaking work and is a welcome contribution to the anthropology of a region that so far was unknown to science. One can not but express in this connection the great pity that such highly promising explorations as those of Professor Bingham's expedition had to be abandoned, through the unfavorable attitude of certain citizens of the very country which would benefit most by their continuance.

ALEŠ HRDLIČKA.

2. *Geology, Physical and Historical*; by HERDMAN FITZGERALD CLELAND, Ph.D., Professor of Geology in Williams College. Pp. 718. figs. 588, pl. I. New York, 1916 (American Book Company).—This is an excellently arranged and handsomely printed text for college classes. Part I on Physical Geology embraces 355 pages with an appendix of 6 pages on the common

minerals. Part II on Historical Geology contains 307 pages. The book gives consequently about equal space and importance to the two great divisions of geology. The paper is of such a grade that the half-tone reproductions of photographs and wash drawings which constitute the bulk of the illustrations are of excellent quality. Certain of the full-page photographs of impressive features, such as that of the Yosemite, reach a height of artistic excellence. Numerous block diagrams bring out clearly the various features of erosion and structure. The number and instructional value of the illustrations show that the author, as a skilled teacher, has paid much attention to this side of the subject. The fragmentary fossils of the older texts have disappeared from this and in their places are restorations, wash drawings being given of invertebrates.

The text is equally clear and attractive. It presents the basic principles amply, but in a manner which the student can master and permits the teacher in lecturing to go directly into the more advanced phases or give special illustrations of such subjects as may suggest themselves. An excellent list of references is appended to each chapter which will be of value to the interested student for developing an acquaintance with the important literature.

J. B.

3. *Handbook and descriptive Catalogue of the Meteorite Collections in the United States National Museum*; by GEORGE P. MERRILL. Bull. 94, U. S. Nat. Mus. Pp. 207, pls. 41. Washington, 1916.—This is a very interesting catalogue of the meteorites in the U. S. National Museum. These include 329 falls and finds in the Museum collection proper and 83 more in the Shepard collection. The latter, brought together by Professor C. U. Shepard and bequeathed to the Museum by his son, includes 234 falls and finds. The total number is therefore 412 out of the 650 known in all the world. The descriptions are made more interesting by the liberal number of excellent plates exhibiting prominent specimens and sections from them. The Introduction of 27 pages gives a concise but valuable summary of the subject of meteorites; their classification, mineral and chemical composition, structure and phenomena of fall.

4. *A Student's Book on Soils and Manures*; by E. J. RUSSELL. Pp. ix, 201; with 34 text-figures. Cambridge, 1915 (Cambridge University Press).—The present work, by the Director of the Rothamstead Experimental Station at Harpenden, England, is a further evidence of the increased interest in the study of soils. It is issued in the Cambridge Farm Institute Series and, although intended primarily for the use of the practical farmer, contains information of much value to the botanist and chemist. The first part includes an account of the soil, discussing its composition, its organic constituents, and the changes produced by climatic factors. The second part takes up the control of the soil by cultivation, drainage and other processes. The third and last part is devoted to fertilizers, both inorganic and organic. The book shows clearly that the art of treating and improving soils from



the standpoint of the farmer is still in an experimental stage, and the much remains to be done before it can be placed on a thoroughly scientific basis.

A. W. E.

5. *Plant Anatomy, from the Standpoint of the Development and Functions of the Tissues, and Handbook of Micro-Technic*; by WILLIAM CHASE STEVENS. Third edition. Pp. xvii, 399; with 155 text-figures. Philadelphia, 1916 (P. Blakiston's Son & Co.).—The third edition of this very helpful text-book has been improved by the addition of a section dealing with the phylogeny of the vascular bundle. In other respects it is essentially the same as the second edition, although a few minor changes have been made. The work consists of two entirely distinct parts. The first, comprising thirteen chapters, deals with plant anatomy; the second, comprising five chapters, with micro-technic. From the standpoint of the teacher these two parts might well be issued separately. The part on plant anatomy, following the example of Haberlandt's *Physiologische Pflanzenanatomie*, emphasizes the relationship between the structure and the functions of plant tissues and organs and traces the development of the various tissues from a uniform embryonic condition. The second part includes an account of the reagents and processes used in the study of plants and a description of the micro-chemistry of plant products.

A. W. E.

6. *The Principles of Plant Culture; a Text for Beginners in Agriculture and Horticulture*; by E. S. GOFF. Eighth edition, revised by J. G. MOORE and L. R. JONES. Pp. xxiii, 295; with 177 text-figures. New York, 1916 (The Macmillan Company).—In the preface to the present edition of this useful text-book, Professor L. H. Bailey of Cornell University gives an account of the late Professor Goff's life and work and of his many services to agricultural and horticultural science. The book is intended especially for students who have had no previous training in botany and presents the essential features of plant anatomy, morphology and physiology, in clear and non-technical language. The various topics are treated from the standpoint of the practical cultivator, and the concluding chapters discuss the propagation of plants, grafting, transplanting, pruning, and the improvement of varieties by breeding.

A. W. E.

7. *Annual Report of the Board of Scientific Advice for India for the year 1914-15*. Pp. 191. Calcutta, 1916 (Superintendent Government Printing, India).—The Indian Board of Scientific Advice includes ten gentlemen having charge of the various scientific activities of the government, with F. Noyce, Esq., as ex-officio president. Meetings of the Board were held in May at Simla and in November at Delhi. The present volume includes contributions from many departments of natural and physical science, furnished by some ten different authors. These summaries are necessarily very brief, but they call attention to the main lines on which progress has been made during the year.

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# AMERICAN JOURNAL OF SCIENCE

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ART. XXXII.—*The Geologic Rôle of Phosphorus* ;\* by ELIOT  
BLACKWELDER.

PROGRESS in scientific research is attained largely by the most intensive study of minute problems; but it is also necessary that there should be frequent attempts to view these problems in their larger relations. Such undertakings are always the more hazardous for the student because they oblige him to reach out of his special field into domains with which he may have only a general acquaintance. In preparing this paper on the part played by phosphorus in geologic processes, the writer has tried not only to correlate his work with that of many other students in this and other countries, but also to understand the bearing of sister sciences upon the subject. He has done so with keen realization of the pitfalls that beset the path especially outside his own limited field.†

Phosphorus occurs naturally in many different forms and situations. Nevertheless, its varied transformations follow an orderly sequence, which is in harmony with the general scheme of rock metamorphism and biologic evolution. In a broad way, these changes form a cycle within which there are subordinate cycles, all having a common beginning, and probably capable of being brought to a common end. Any particular atom of phosphorus may follow one or more of the subordinate cycles while another atom may pursue a different route.

The primary occurrence of phosphorus in the earth, like the beginnings of most things in geology, lies wholly in the realm

\* Presented in summary before the Geological Society of America at Washington, December 29, 1915.

† For valuable information and advice the writer is indebted to his colleagues, Professors E. V. McCollum and E. B. Hart, of the University of Wisconsin, Mr. Chauncey Juday of the Wisconsin Geological and Natural History Survey, and Prof. W. A. Noyes of the University of Illinois.

of speculation. If the planetesimal theory of the earth's origin,—elaborated by Chamberlin and Moulton,—is true as regards its major points, the original material of the earth may be comparable to the meteorites which are still falling upon its surface from time to time. Nearly all modern meteorites contain minute quantities of phosphorus,—chiefly in the form of the iron-and-nickel phosphide (schreibersite). Individual meteorites vary in the amount of phosphorus which they contain. On the whole, the iron meteorites are generally richer in the phosphide than are the stony varieties, the range being from a trace in the latter to 1.25 per cent, expressed as  $P_2O_5$ , in the former.

On the basis of the planetesimal theory, Chamberlin has suggested that more or less of the original cosmic matter of the globe has been melted and worked its way outward to the surface. Meanwhile it should have differentiated until the uppermost part became a familiar volcanic magma. While there are weighty considerations in favor of this concept, it is admittedly speculative. Whether or not it be true, it is a fact that the nearest approach to a primary occurrence of phosphorus actually known to geologists, is its appearance in the igneous rocks, which have crystallized from a hot mineral solution (the "magma" of geologists) rising from the unknown depths of the earth's interior. All igneous rocks contain small quantities of phosphorus. According to Clarke's calculation, the average igneous rock of the world contains .29 per cent  $P_2O_5$ . The ratio is usually somewhat higher (.50–1.15 per cent) in the more basic igneous rocks such as gabbro and the peridotites. In all these rocks the phosphorus exists chiefly as the mineral apatite,—an anhydrous tricalcium phosphate chemically combined with calcium fluoride or chloride.

When magma crystallizes it emits large quantities of steam and other vapors. At the surface these are discharged into the atmosphere; but around deep-seated intrusions of magma the liquid and volatile constituents permeate the adjacent rocks. The mineral matter with which these solutions are highly charged crystallizes out selectively upon the walls of fissures and other openings through which the hot solutions pass, thus producing among other things the type of veins known as pegmatites. Most pegmatites contain such minerals as quartz, feldspar and mica; but in rare instances, apatite is the chief constituent. Like the other minerals, it usually occurs as large crystals, sometimes a foot or more in length. The so-called nelsonites\* of Virginia, which contain 5–16 per cent of  $P_2O_5$ , as well as certain vein deposits in Quebec and Norway, are

\* Watson, T. L., and Taber, S., The Virginia Rutile Deposits, Bull. U. S. Geol. Survey, No. 430, 1910, pp. 202–213.

evidently pegmatites. In similar veins some other phosphatic minerals, such as the valuable rare-earth phosphates monazite and xenotime, have been found, but they are decidedly rare.

Certain veins of much less frequent occurrence than the apatites consist largely or even entirely of the related minerals dahllite or staffelite,—considered by the French mineralogist Lacroix\* to be hydrous calcium carbo-phosphates, containing about 39 per cent  $P_2O_5$ . The mineral occurs in lamellar and

FIG. 1.

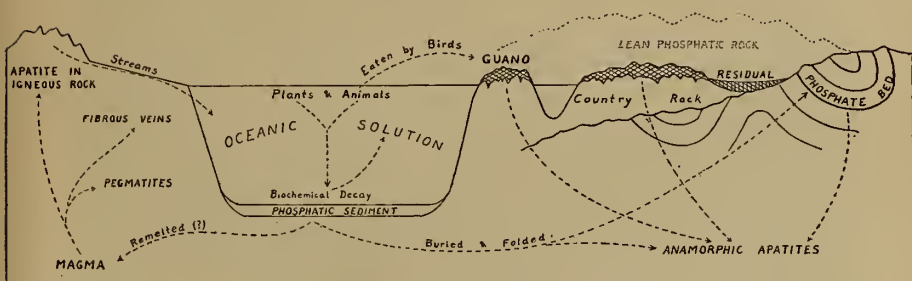


FIG. 1. Diagram illustrating the cycle of changes through which the element phosphorus is believed to pass. Solid phosphatic deposits are shown in bold-faced capitals and by cross-hatching. Arrows indicate the directions in which the more important processes move, but many changes of less importance have been eliminated for the sake of simplicity.

radiating aggregates of very minute fibrous crystals, rather than in coarse stout prisms like those of apatite. Although a vein of this type near Crown Point, New York, has been described by Emmons,† the only large and well-known examples are those of the province of Estremadura‡ in Spain, where they have been recognized for nearly 150 years. Several different hypotheses have been advanced to account for these Spanish veins, but most of them are clearly inadmissible. The facts that the veins are persistent with depth, contain quartz, and traverse such slightly altered rocks as quartzite, slate and limestone associated with granitic intrusions, suggests that they have crystallized from ascending magmatic solutions but at a moderate temperature. It is not certain, however, that they have not been produced by waters descending from the surface.

Under ordinary climatic conditions, rocks near the surface of the earth are subject to chemical decomposition. Percolat-

\* Lacroix, A., *Minéralogie de la France*, vol. iv, p. 555 et seq.

† Emmons, E., *New York State Geological Survey Report*, 1838, p. 252.

‡ Fuchs and de Launay, *Traité de Min. et Met.*, 1893, p. 353.



ing underground water containing more or less carbonic acid and other solvent materials is one of the chief agents in this decay. In such solutions both apatite and dahllite dissolve more readily than most other common minerals, although much less rapidly than the lime-carbonate minerals such as calcite. The phosphate-bearing solution then circulates through the rock and soils, to be disposed of eventually in several different ways.

Much of the dissolved phosphoric acid is taken up by plants, whose roots penetrate the soil, and by them is incorporated in the nuclear material of their cells, and particularly in their seeds. Animals taking the phosphorus indirectly from the plants upon which they feed use it not only in various cells and tissues, but also in bones and teeth. In the vast majority of cases, part of it is soon returned to the soil as a constituent of urine, fæces and dead organic matter, but bacteria then decompose its compounds and the phosphoric acid returns to the state of solution in ground water. Only rarely, when soon buried in mud, does it become fixed in land deposits in the form of bones and even mineralized fæces (coprolites). On the other hand, thin beds with very limited area, consisting largely of bones and teeth, have been found in a few places, such as Big Bone Lick in Kentucky.

By far the greater part of the phosphorus in ground water solution must either immediately or eventually go into the streams and find its way to the ocean. Of the vast quantity of dissolved mineral matter annually delivered to the sea by the run-off, it is estimated that about .45 per cent consists of phosphorus pentoxide. Using the best available figures for the amount of water thus brought to the ocean annually, it is calculated that if the phosphatic material in the form of solid tricalcium phosphate were loaded into standard railroad cars it would fill a train stretching continuously from Boston to Seattle and would be 7 to 12 times as great as the world's total production of phosphate rock in 1911. Nevertheless, so great is the volume of the oceans, and so vast the area of their floors, that if all this material were deposited in solid form uniformly over the bottom of the sea, it would build annually a layer less than one-fifth of a millimeter thick. Of the phosphorus poured into the sea, so large a proportion is utilized by living beings that the net working balance dissolved in oceanic water constantly averages less than .005 per cent, expressed as  $P_2O_5$ , or, in other words, about .18 per cent of the dissolved salts. In this solution, phosphorus seems to have reached the most dilute state in which it exists during the course of its complex migrations. Its subsequent transformations, now to be described,

generally tend to ever greater concentration, almost until the cycle is closed upon itself.

Soluble phosphates are absorbed by the various oceanic plants as well as by those on land. In some measure the phosphoric acid becomes chemically linked in organic compounds, but for the most part it probably remains in the ionized state. Living diatoms and other algæ contain, in both of these forms, from .1 to .2 per cent of  $P_2O_5$ , chiefly as a minor constituent of the cell nucleus. Although the marine animals have the power of absorbing phosphoric acid directly from the sea water, it so happens that they generally get a surplus of it as a constituent of the plants or other animals on which they feed, and hence do not exercise that power.

The round of transformations to which phosphorus is subjected in the ocean is extraordinarily complex. The plants which absorb the element are devoured by myriads of aquatic animals, each of which, in its turn, is liable to a similar fate. This endless process of devouring is recognized even in the ancient Chinese proverb to the effect that "the big fish eats the little fish, the little fish eats the shrimp, and the shrimp eats the mud." In the individual animal, the phosphorus forms a constituent of its cell nuclei, tissues and liquids. With the exception of casein and that of egg-yolk, the proteins do not contain phosphorus, but it forms a constituent of certain other organic compounds, such as lecithins. As solid calcium phosphate it resides in bones, teeth and more rarely in shells.

As phosphorus ascends in the evolutionary scale of animals, its concentration tends to increase, although irregularly. The protozoan, air dried, contains less than .6 per cent  $P_2O_5$ . According to Juday\* quantities of minute crustaceans from Lake Mendota contain in the air-dried condition 1.8 to 2.4 per cent of  $P_2O_5$ , or several times that of the protozoans. A Russian biochemist, Sempelovski, found in entire fresh specimens of a cartilaginous fish (the common skate) .91 per cent  $P_2O_5$ , whereas the average for eight Teleostean fishes with well-developed bones was about 1.5 per cent. Certain brachiopods, such as those of the family *Lingulidæ*—form shells of fibrocrystalline tricalcium phosphate—probably either the mineral dahllite or staffelite.

From its almost endless series of reincarnations in the ocean, phosphorus is allowed to escape from time to time by either one of two routes. The organisms in the sea may be eaten by land animals, chiefly birds, or the phosphates may become fixed in mineral form in the solid matter on the sea bottom, and eventually buried beneath the accumulating sediments. We may consider the second of these processes first.

\* C. Juday, personal communication.

As the writer has already remarked, the animals of the sea are almost never permitted to die of old age, but are devoured sooner or later by other animals. Any that happen to die in other ways are almost invariably eaten at once by scavengers. Even the bones of fishes are rapidly devoured by echini and certain other animals. It is conceivable, however, that in rare instances the quantities might be too great for the capacities of the scavenger population; and in that event a local accumulation of animal matter might result. The late Sir John Murray\* based upon this idea a hypothesis to explain the origin of the phosphatic nodules now dredged up from the sea bottom in several parts of the world. In another work†, he cited the remarkable case of the tile-fish, which in 1883 were killed by hundreds of millions along the Atlantic coast of the United States, presumably by a sudden fall of water-temperature brought about by the shifting of the position of the cold northern current between the Gulf Stream and the coast. Using Murray's figures for the area and number of the fish, the writer estimates that enough were killed at this time to make a layer of fish substance about four millimeters deep over the affected area, if all had fallen to the bottom and had been uniformly distributed. Other instances of this kind have been reported and fish are known to have been killed in great numbers by submarine earthquake shocks, submarine volcanic eruptions, and other catastrophes. It might be supposed that in such cases a layer of bones and teeth would be left upon the bottom of the sea, and if the process were repeated at intervals, the layer might gradually attain noteworthy thickness. It should be remembered, however, that the carcasses of dead vertebrates generally float, because distended by the gases of putrefaction; and both while floating and after lodgment upon the shore they are subject to the attack of scavengers as well as to the final decomposing action of micro-organisms. As a final result, but little of the original fish remains except the points of the teeth, which being almost wholly mineral matter apparently contain too little nutritive substance either to attract the spoilers or to serve the purposes of bacteria. Under these circumstances, it is difficult to imagine how a layer of carcasses could be deposited in the open sea. On the assumption, however, that it is possible, Murray outlined a process of fermentive decay and chemical interchange which is essentially that to be detailed below. It is chiefly this source of supply that is here laid open to question.

As an incident in the normal life of vast numbers of organisms, both on the sea floor and in the upper waters, shells and

\* Murray, Sir John, Challenger Expedition Report, Deep Sea Deposits, pp. 396-399.

† Murray, Sir John, Geogr. Journ., vol. xii, p. 113, 1898.

little pellets of excrement are incessantly falling to the sea bottom. Some of the dredgings of the Valdivia expedition\* showed that over large areas of the sea bottom, the latter material forms an appreciable part of the soft ooze, and, in several places the sediments consist almost entirely of such pellets. They have been attributed in large measure to holothurians, echinoids, and marine worms. No chemical analysis of this material is available, but it is well known that animal excreta in general contain a noteworthy proportion of phosphoric acid. Although the phosphorus in the excreta of nearly all animals below the Mammalia seems to exist chiefly in the form of insoluble organic phosphates, bacteria are able to decompose these compounds, usually with the formation of ammonium phosphate which is immediately returned to the oceanic solution and there doubtless exists in the ionized condition. Under ordinary circumstances, as pointed out by Sir John Murray in the Challenger Reports,† even bones, teeth and shells lying upon the sea bottom gradually lose their phosphoric acid. Hence this faecal material probably does not accumulate to any considerable depth. In fact, over most of the ocean bottom it is destroyed about as fast as it is produced. In so far as this action prevails, phosphorus cannot well become a solid part of the sediments deposited on the sea floors.

Nevertheless, we find among the rocks derived from oceanic sediments in many parts of the world, beds several feet thick which are rich in lime-phosphate and extend rather uniformly over thousands of square miles. They contain marine fossils which indicate that they have accumulated upon the sea bottom. It is therefore evident that locally there must be conditions which cause the fixation of the phosphoric acid among the bottom sediments. Some students of these deposits have ascribed them to the direct deposition of phosphatic shells, bones and teeth, and others have made appeal to the agency of mineral springs. Generally they have sought an explanation for the abundance of the phosphorus. As the writer has already shown, however, the quantity of phosphorus dissolved in seawater is always sufficient to produce in a few thousand years even the thickest known phosphate beds; and hence we need only to account for the special conditions which cause it to be precipitated on the sea floor. There is excellent reason to think that the immediately controlling conditions are chemical or biochemical, but these chemical conditions in turn depend upon physiographic and climatic factors difficult to analyze and estimate. The study of the latter is a task for the geologist.

\* Murray, Sir John, and Philippi, E.. *Wissensch. Ergebn. der deutschen Tiefsee Exped.*, Bd. x, Lf. 4, 1905, p. 103. (Carl Chun, editor.)

† *Loc. cit.*



In its simpler aspects, the chemistry of the marine deposition of phosphates has been plausibly interpreted by a number of European students of the question, even as far back as 1870. The following is a modification of their views, based on modern information. The process and results of bacterial decomposition of organic matter vary according to the conditions as well as the particular class of bacteria that are at work. In air and aerated water, decay is generally complete, resulting in the production of carbon dioxide, water, soluble nitrates, sulphates,

FIG. 2.

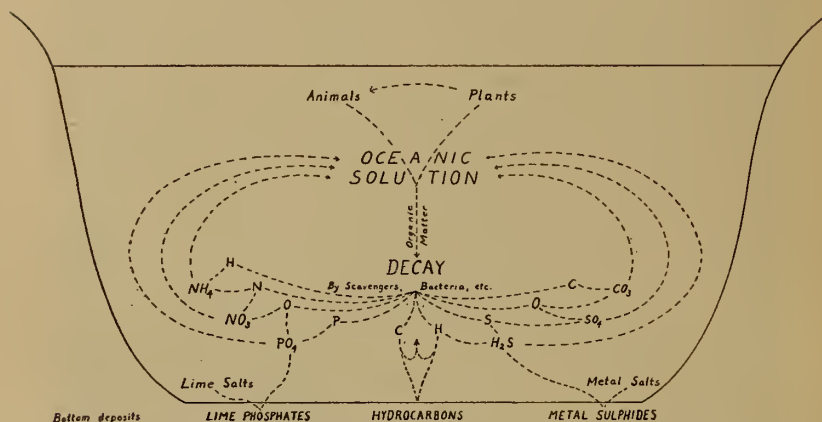


FIG. 2. Diagram to illustrate the process and results of the decay of organic matter on the sea bottom. In reality the process is much too complex to be represented in this way. (The materials which become fixed in the bottom layers are shown in capitals on the lower line. Other marine sediments, such as particles of sand, mud, shells and bones, have been omitted from consideration.)

phosphates, etc. In the absence of oxygen, however, the anaerobic bacteria somewhat more slowly break down the organic compounds and produce a different series of end products, of which the most important are various hydrocarbons, nitrogen, ammonia, and hydrogen sulphide, with only so much of the carbonic oxides as the available oxygen in combination permits. In so far as free oxygen is present in only small quantities, there should be a compromise between the two processes.

Some of the most obvious characteristics of our marine phosphatic rocks show that they have been associated in origin with the anaerobic phase of bacterial action. Almost invariably they are black in color and, owing to the fact that they contain noteworthy quantities of hydrocarbon oils, tars and gases,

they are famous for their bad odor. In central Wyoming,\* phosphate rocks of this kind contain so much oily matter that they are being successfully exploited for petroleum. Although such phosphates contain a few fossils such as fish teeth, brachiopods and larval gastropods, they are invariably devoid of sessile bottom-inhabiting organisms, a fact which suggests that the bottom layer of sea water lacked the oxygen necessary to support life.

2 The deficiency of oxygen is, therefore, the controlling chemical condition, for it not only determines that the bacterial decay shall be of the anerobic type, but also prevents animal scavengers from devouring such organic matter as may fall to the bottom, for no animal can be active in an oxygen-free medium. Through the work of Birge and Juday† on the Wisconsin lakes, and that of other students of lake phenomena, it is now well understood that mechanical circulation of the water is the only factor that serves to prevent this deficiency of oxygen from becoming general in all waterbodies. At the present time most parts of the ocean bottom are thus supplied with enough oxygen to support their benthic faunas. It is carried in by the slow convective circulation downward from the polar regions and upward near the equator. In order to account for the oceanic phosphate deposits, therefore, we must apparently discover those rare areas of the sea bottom where this circulation is not effective. Deep inclosed gulfs or seas, such as the Black Sea, to-day afford some of the conditions, but not all of them. The bottom sediment of the Black Sea‡ is now a lifeless mud blackened by hydrocarbons and charged with hydrogen sulphide. There is, however, some condition lacking, for the deposition of phosphates in the Black Sea is not indicated by the dredgings thus far reported.

3) Passing by this question as a room for which the key is yet to be found, we may consider the manner in which phosphorus comes to be fixed in the oceanic sediments under anerobic conditions wherever they may be developed.

As was long ago pointed out by Bonney,§—under ordinary circumstances all of the products of decay are likely to either remain in solution or escape as gases rather than to be precipitated. Under special conditions, however, most of them remain in solid form and others react with the sediments of the bottom or with materials in solution, in such a way as to form insoluble products. For example, hydrogen sulphide, in-

\* Woodruff, E. G., *The Lander Oil Field, Fremont County, Wyoming*, Bull. U. S. Geol. Survey, No. 452, 1911.

† Birge, E. A., and Juday, C., *The Inland Lakes of Wisconsin*, Bull. No. 22, Wis. Geol. & Nat. Hist. Survey, 1911.

‡ Andrussov, N., *La Mer Noire, Guide des Excursions der 7<sup>m</sup>e Congrès Géologique International*, No. 29.

§ Bonney, T. G., *Cambridgeshire Geology*.

teracting with the iron compounds, forms the mineral pyrite, which is common in certain types of black shales. In a similar way, phosphoric acid in the presence of ammonia reacts with various substances, and especially lime carbonates, in such a way as to produce phosphatic minerals, of which the commonest is collophanite,—said to be hydrous calcium carbo-phosphate. These changes have been carried out experimentally in the laboratory by several investigators, and the necessary conditions are such as may readily occur on the sea bottom where organic decomposition is in progress. The calcareous shells and fragments lying on the ocean floor thus become phosphatized, and even such organic materials as excretory pellets and pieces of wood are known to have been altered in the same way. Bones, which initially contained about 58 per cent tricalcium phosphate, have their organic matter completely replaced by phosphatic minerals, thus raising the ratio to 85 per cent or more. In addition, collophanite is precipitated in concentric layers around particles of sand or any solids, forming round or elliptical granules which resemble the oölitic grains in certain limestones. By the enlargement of these coatings, the granules, shells, teeth and other objects are cemented into hard nodules or even into continuous beds of phosphatic rock. Such nodules have been dredged up from the bottom of all the oceans in moderate depths, and are not uncommon in certain kinds of marine limestones and shales now on land.

The marine phosphatic sediments now constitute our greatest bodies of commercial rock phosphates, exemplified in the phosphate beds of Tunis, Algeria, England, and—most extensive of them all,—those of the Rocky Mountains of Idaho, Utah and Wyoming. In many other places, such as the Carolinas, Florida, Belgium, and northern France, marine sediments containing only 1 to 5 per cent  $P_2O_5$  have, through secondary concentration in later ages, produced rich phosphatic deposits.

Reference has already been made to the fact that, through the agency of land-animals such as birds, the phosphorus may escape from the charmed circle of its metamorphoses in the ocean. Upon islands where they are out of reach of predaceous animals, seabirds congregate in extraordinary numbers, and the amount of excrement annually deposited by them upon the surface of these islands is large. Ridgeway\* cites evidence that it accumulates locally at the rate of about  $1\frac{1}{2}$  inches per year. The material is comparatively rich in phosphorus, owing in part to the fact that the birds feed largely upon the bony fishes; but it seems to exist chiefly in the form of insoluble organic phosphates which are not affected by unaided rain

\* Quoted by G. P. Merrill, *Non-metallic Minerals*, p. 267.

water. In humid regions, however, bacterial fermentation decomposes these compounds, and the soluble resultants, including phosphoric acid, are removed by rain water so rapidly that no appreciable residue is left.

On those arid islands, however, which are situated under the trade winds and "horse latitudes," neither fermentation nor solution is favored, and hence the guano accumulates from year to year. The well-known deposits on the islets off the coast of Peru, in the Leeward Islands of the Caribbean Sea, and on many of the East Indian islands, serve as examples. As compared with its ratio in the fishes and other marine animals, the concentration of the phosphorus in the freshly deposited excrement of the fish-eating birds is about the same,—averaging but little more than one per cent  $P_2O_5$ . In the thoroughly dry guano of the desert islands off the Peruvian coast, where almost no chemical change has taken place, it contains 10–16 per cent  $P_2O_5$ , as well as a noteworthy quantity of nitrogenous and other organic compounds.

On the other hand, where underground water has access to the older portion of the deposit, the guano is more or less fermented, probably by such micro-organisms as the bacteria, with the result that the nitrogenous matter is largely converted into nitrates and ammonia, while the phosphorus forms calcium, magnesium and ammonium phosphates. The occasional rains dissolve out the more soluble ammonium phosphates and nearly all the nitrates, leaving the relatively insoluble alkaline-earth phosphates to form a residue of solid "stone guano." The latter contains from 28 to as much as 39 per cent  $P_2O_5$ , largely in the form of hydrous acidic and basic calcium phosphates, closely, and probably chemically, associated with more or less lime-carbonate. The commercially exploited guanos on Baker island in the tropical Pacific, and many others, appear to have passed through this type of alteration.

The strongly phosphatic solutions thus derived from the guano sink downward through the underlying rocks and produce characteristic alterations in them. Where the rock is limestone, it is somewhat rapidly converted into a mass of calcium phosphates, in which the mineral species are various, although collophanite seems to predominate. On Christmas Island in the western part of the Pacific Ocean, Willis\* found that coral limestone had been changed to calcium phosphate to a depth of from 2 to 3 feet within 20 years. In the laboratory, Collet† immersed a coral skeleton in a weak solution of ammonium phosphate, with the result that the coral was 60 per cent phosphatized in only two months. Still more remark-

\* Willis, J. L., *Ottawa Naturalist*, vol. vi, p. 18, 1892.

† Collet, L. W., *Proc. Royal Soc. Edinburgh*, vol. xxv, p. 882.



able cases have been reported in which refractory volcanic rocks such as andesite and trachyte have been phosphatized by solutions descending from guano beds.

For many years it was generally supposed that the rich and important phosphate deposits of Florida and the Carolina coast had been produced by solutions from guano beds percolating down into limestones, and thus changing them into calcium phosphate; but now it is fairly well established that the phosphatic solutions were derived not from guano, but from marine clays, containing 1-5 per cent  $P_2O_5$ . It has been demonstrated that these clay beds originally overlie the limestone but have been rather generally stripped off by erosion in more recent time. Although poor in phosphates the clays are hundreds of feet thick and have, therefore, yielded a vast amount of phosphoric acid. In other countries, there are many illustrations of the phosphatized limestone type, and in most cases, as in Florida, the source of the phosphorus was not guano, but a lean phosphatic clay or chalk. The plateau of southern France, the Lasne valley in Germany, and southwestern Belgium furnish well-known examples.

Where the slightly phosphatic original rock was chalk or limestone, a variation of the process has been brought about because the lime carbonate is relatively more soluble than the lime phosphate. Therefore, during the slow process of solution by rainwater descending from the surface, the calcium phosphate, although actually decreased in total quantity, has been relatively concentrated by differential solution. Cases of this kind have been reported from southern England, northern France, and Belgium.

Phosphate beds of both of these secondary types are irregular in thickness, and rest upon a most uneven and cavernous surface of the corroded limestone beneath. The deposits often contain phosphatized bones and shells of animals really belonging to a geologic age much more recent than the limestone of which they appear to form a part. These have slumped in from the surface and been thus mixed with what is in reality only a special type of residual soil.

Although the concentration of phosphorus thus brought about by the phosphatization and differential solution of limestones is never quite equal to that in the leached guanos, it may rise to over 36 per cent  $P_2O_5$ , a ratio which indicates almost pure collophanite. Sellards\* finds reason to think that the amorphous and probably colloidal mineral collophanite is gradually converted into a fibrous crystalline mineral (stafelinite?) which has about the same composition. If this opinion

\* Sellards, E. H., 5th Ann. Rep. Florida State Geol. Survey, 1913, pp. 37-66.

is correct, it affords another illustration of the well-known tendency of colloidal or amorphous minerals to assume the crystalline state with the lapse of time.

With certain minor exceptions the transformations of phosphorus that take place on the surface of the earth have now been reviewed. It remains to trace the element downward into the interior of the crust and at the same time more deeply into the realm of inference. Phosphatic deposits of any of the types already described may have sediments deposited upon them until, in the course of geologic ages, they may be buried thousands of feet below the surface. In that region pressures are great, temperatures are much increased, and the activity of solutions is greater than, or at least different from, that above. In the past, some of the older phosphate beds have in addition been subjected to overwhelming compressive forces, the origin of which is still a debatable subject with geologists, although we see plenty of evidence of their operation in the folded rocks of our mountain systems. It is now well known that under these conditions of the interior of the earth, minerals of various kinds undergo radical changes. Some, like calcite, merely recrystallize in more compact form. Others recombine to form new minerals, while still others are metamorphosed by either losing or gaining constituents. Although no case of this kind for phosphates has yet been proven, it is entirely in harmony with the established principles of rock metamorphism for us to suppose that the phosphatic sediments would, under these conditions, be reorganized. The hydrous minerals and the carbonates characteristic of the surface should become dehydrated and decarbonated. As a result, collophanite and staffelite as well as many other minerals of less importance, should pass over into the anhydrous calcium fluophosphate, apatite, in which the proportion of  $P_2O_5$  may rise to 42-43 per cent,—which is apparently the maximum concentration attainable in rocks. It was suggested many years ago by Sir William Dawson\* and others that some of the rich apatitic beds that are intimately associated with the ancient Grenville marbles and gneisses near Ottawa, Canada, are really the highly metamorphosed representatives of phosphatic sediments which were once deposited on the bottom of the sea. No weighty arguments against their hypothesis have been advanced.

There is still another fate that may befall the phosphatic deposits either before or after recrystallization. Rocks of any kind in the crust are liable sooner or later to be invaded by

\* Sir J. W. Dawson, Note on the Phosphates of the Laurentian and Cambrian Rocks of Canada, Quart. Journ. Geol. Soc. of London, vol. xxxii, pp. 285-291, 1876.

large bodies of fluid magma, issuing from the interior of the earth, at initial temperatures well above a thousand degrees centigrade. It now seems proven beyond dispute that such igneous bodies flux their way through the overlying rocks, absorbing them or dissolving them as they rise. Phosphatic minerals thus dissolved would later recrystallize out along with the other constituents of the magma when it became a solid igneous rock. It would then also appear as the mineral apatite, which is apparently one of the few phosphates adapted to these conditions of high temperature. As the constituents of the magma obey the laws of solutions and are diffused uniformly through the liquid, the apatite, like the feldspars, quartz, and mica, would be evenly distributed throughout the resulting igneous rock in the form of minute crystals. In so far as this occurrence takes place, it closes the cycle, for it will be remembered that almost at the outset of this review, phosphorus appeared in the form of microscopic apatite prisms as a constituent of the typical igneous rock. Meanwhile, however, the phosphorus may have passed through the complex series of migrations and transformations over and over again, on and near the surface of the earth. Even if the cycle should thus become closed, it would be closed only temporarily, for a new cycle would be initiated just as soon as the apatite of the second generation became subject to the process of weathering.

Madison, Wisconsin,  
July 11, 1916.

ART. XXXIII.—Notes on Radiolarian Cherts in Oregon;  
by WARREN D. SMITH.

THE age of certain cherts found in our West Coast stratigraphy has long been a matter of conjecture. Diller described occurrences of these in both the Port Orford Folio (U. S. G. S.) and that for Roseburg and assigned provisionally the rocks to the Cretaceous. No genera or species were given, as far as I know, nor were any very definite field relations mentioned, on account of the unsatisfactory nature of the exposures.

During the summer of 1915, the writer was in the field for the Oregon Bureau of Geology and Mines investigating some problems connected with the stratigraphy of the Cascades, during the course of which he obtained some data relative to these cherts which may be of interest now and are here given with the permission of the Director of that Bureau.

In the cow pasture back of Mr. Engles' house at Peel P. O., about 25 miles east of Roseburg on the Little River, a branch of the Umpqua, there is an almost hopeless mixture of rocks, hornblende schists with small patches of these cherts inclosed by them.

At the time of the writer's visit to Peel, he was fortunate in being able to see these outcrops after some excavating had been done for road metal. The value of this for road surfacing is due doubtless to the combination of the chert and the iron, for they are ferruginous at this place. An examination of the outcrops as opened up by them showed the stratification lines very plainly. The strike was found to be N. 8° E. and the dip 70°–90°. The direction of the dip varies, in places being to the N. W., and a few feet away, about the same amount in the opposite direction. About a quarter of a mile farther up the Little River, Eocene sandstone and shales were found dipping about 20° to the east (as already noted by Diller), so that if these beds do not reverse their direction of dip in the intervening distance (no outcrops visible to determine this) they would come far above these chert beds and there would be a marked angular unconformity between them.

Thin sections of these cherts were made which showed species of the following genera of radiolaria: *Cenosphæra*, *Dictyonitra* and *Spongodiscus*. In most cases, however, only small round areas filled with cryptocrystalline silica showed where the tests had been.

Identical forms have been found by the writer\* in material lithologically similar and in about the same stratigraphic posi-

\* Smith, W. D., Philippine Jour. Science, vol. v, No. 5, p. 327.



tions in the Philippine Islands. Not only do we find the same sort of formation in those islands, but in Borneo,\* Java, Molluccas, Ceram,† etc.

Both Martin and Hinde have assigned these cherts to the Jurassic or Triassic and, following them, the writer has done the same in the Philippines. The radiolarian-bearing rocks of Roti and Savu (D. E. I.) are associated with beds of limestone containing Halobias and Daonellas. The cherts, as described, are strikingly similar lithologically to our West Coast rocks of this character.‡ We are nevertheless well aware that fossil radiolaria are far from being satisfactory index fossils.

These notes are here given in the hope that they will throw some light on this part of West Coast stratigraphy. To one who has dealt with geological problems on both sides of the Pacific, there is a remarkable similarity in the stratigraphic columns of the two.

University of Oregon, Eugene, Ore.

\* Hinde, *App. I*, 9, Molengraaf's Borneo, 1902.

† Marten, K., *Reisen in den Molukken*, Leiden, p. 164, 1902.

‡ Hinde, *Radiolarian rocks, etc.* *Jaerboek van het Mijnewesen in Nederl. Oost-Indie*, xxxvii, 1, 2, 1908.

ART. XXXIV.—*On the Rates of Solution of Metals in Ferric Salts and in Chromic Acid*; by R. G. VAN NAME and D. U. HILL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—celxxxii.]

FORMER papers from this laboratory have dealt with the rates of solution of metals in iodine.\* The present investigation is an application of the same method to further measurements of the rates of solution of metals in oxidizing solutions, and was undertaken on account of the probable bearing of the results upon the so-called Diffusion Theory of heterogeneous reactions.

It will be recalled that this theory is based on the hypothesis that in a reaction between two phases, let us say a solid and a liquid, the stirring of the liquid is not effective up to the actual boundary surface, but that there remains a narrow zone or layer of liquid, adjacent to the solid, which is so far unaffected by the stirring that the transport of dissolved substances through this layer, to or from the solid, must be brought about essentially by diffusion. From this point of view the observed velocity of a reaction between a solid and a dissolved substance should be the resultant of two consecutive reactions, (a) the diffusion process, and (b) the chemical reaction † proper, which occurs at the surface of the solid. The slower of these two reactions will obviously determine the reaction velocity actually observed.

Many instances have come to light in recent years in which this hypothesis seems to give the best explanation of the facts. As an example the above mentioned work on rates of solution of metals in iodine may be cited, in which it was shown that eight different metals, Ag, Hg, Cu, Ni, Co, Fe, Cd and Zn, all dissolved at the same (equivalent) rate in a solution of iodine in potassium iodide. This fact seems to show that the rate of diffusion of the iodine is here actually the determining factor.

Such results are, of course, conditioned upon the absence of any interfering secondary effects, which are often encountered in practice and may obscure or wholly conceal the influence of diffusion. The formation of an insoluble coating on the solid is a common type of interference. Other types will be referred to later. As a rule, however, such cases show characteristic

\* Van Name and Edgar, this Journal (4), xxix, 237, 1910; Van Name and Bosworth, this Journal (4), xxxii, 207, 1911; Van Name and Hill, this Journal (4), xxxvi, 543, 1913.

† The term "chemical reaction" in this connection is used in the broader sense, and may in certain cases include processes not always classed as chemical, such as solution in water, or crystallization from solution. No such cases, however, are included in the present investigation.

peculiarities which make it easy to determine the cause of the abnormal results. These anomalous cases can only be interpreted individually, and must, for the present, be excluded from our general discussion.

The hypothesis of a diffusion layer, together with its immediate consequences, is usually enough to account for the observed results. Nernst, however, whose opinion carries special weight since he is to a large extent the originator of the diffusion theory,\* has introduced a second hypothesis. Nernst argues that at the boundary surface between two phases considerable differences in chemical potential must exist between points infinitely near together, which should make the velocity of the chemical reaction infinite, or at least in practice extremely high.† Consequently the diffusion process will always be slow in comparison, and will therefore determine the observed reaction velocity in all cases except, of course, the anomalous ones already mentioned.

If this hypothesis of Nernst's is to be understood literally it means that the observed velocity of a reaction between a solid and a dissolved substance will never represent, even approximately, the true rate of the chemical reaction. No place is left for cases other than those in which the velocity is governed solely by diffusion, and those rendered abnormal by disturbing influences. From this it follows that when the same dissolved substance reacts with different metals the velocity of the reaction, in all cases free from secondary disturbances, should be the same irrespective of the specific nature of the metal. This test of Nernst's hypothesis is applied in the experiments to be described.

## EXPERIMENTAL PART.

The method and apparatus used have been described in a previous article.‡ Such minor modifications in the procedure as were found desirable in dealing with the different reactions will be mentioned in their proper connection. The different metals, in the form of circular disks 0.5<sup>mm</sup> in thickness and 38.3<sup>mm</sup> in diameter, were exposed to the action of the solution, under carefully regulated conditions as to temperature, rate of stirring, and position of the disk. Samples of the solution,

\* Noyes and Whitney (*Zeitschr. phys. Chem.*, xxiii, 689, 1897) were the first to suggest the conception of a diffusion layer, but they applied it only in a special case. Nernst, in 1904, gave the idea a more exact formulation, showed its wide applicability, and made it the basis for a "general theory of heterogeneous reactions." (See following footnote.)

† *Zeitschr. phys. Chem.*, xlvii, 52, 1904, also "Theoretical Chemistry," 3d Eng. ed., p. 586.

‡ This Journal (4), xxxii, 207, and in part, *ibid.*, xxix, 237.

which was initially 600 cm<sup>3</sup> in volume, were taken at convenient intervals with a 20 cm<sup>3</sup> pipette, and the velocity constants  $k$  calculated in the ordinary way from the observed concentrations at the beginning and end of the five to ten-minute time intervals. The rate of stirring was kept at 200 revolutions per minute in all experiments, and although the variations were usually very small they were systematically determined and corrected for by the method described in the article just cited. The temperature was 24.6° C. in all experiments with ferric salts, and 25° C. in all those with chromic acid.

#### *Rates of Solution in Ferric Sulphate.*

Previous experiments on the rate of the reaction between ferric sulphate and metals have been made by T. E. Thorpe\* (1882), and by C. G. Schleuderberg† (1908). Thorpe compared the action of the ferric salt on zinc, magnesium, and iron, but under poorly defined experimental conditions, further complicated by the evolution of hydrogen. Schleuderberg studied only the reaction between ferric sulphate and copper, so that his work affords no comparison between the rates for different metals. Though primarily interested in testing for a possible effect of light on the reaction velocity, he was led to the conclusion that diffusion was the determining factor.

In the experiments of the writers, the ferric alum solutions used were approximately 0.05 molar with respect to  $RFe(SO_4)_2$ , and contained, besides, various known amounts of free sulphuric acid together with a little ferrous sulphate to take up dissolved oxygen. Several liters of solution were prepared at one time, and the total iron concentration determined once for all by reducing duplicate samples in a Jones Reductor and titrating with 0.02 normal permanganate. The ferrous iron concentration at various stages of the reaction was found by direct titration with the same permanganate solution in the presence of phosphoric acid, and the ferric iron obtained by difference. In the tables  $C$  is the total iron, and  $c$  the (variable) amount of ferrous iron contained in 20 cm<sup>3</sup> of solution, all expressed in cubic centimeters of the 0.02 normal permanganate. The values of  $C-c$  were used in calculating  $k$ .

To prevent oxidation of the ferrous salt in the solution by the stirring in contact with air, an atmosphere of carbon dioxide was maintained above the liquid by passing a brisk current of the gas into the reaction vessel throughout the experiment.

In most of the experiments the ferric alum used was the potassium salt. Those, however, in which the sulphuric acid

\* Jour. Chem. Soc. Lond., xli, 287.

† Jour. Phys. Chem., xii, 574.



was 5 molar were made with ammonium ferric alum, after special tests had shown that the two alums gave practically identical results.

*Cadmium.*—Experiments with metallic cadmium (Kahlbaum's) are recorded in Table I. Here, and in all the following tables,  $k_1$  is the observed velocity constant, uncorrected,  $k$  is the same corrected for variations in the rate of stirring, and  $K$  the averaged value of  $k$  for the single experiment. By way of illustration, data for Experiment 1 are given in full. For the rest only the corrected velocity constants are recorded.

TABLE I.

Metal: CADMIUM.		RFe(SO <sub>4</sub> ) <sub>2</sub> , 0.05 molar.							
		H <sub>2</sub> SO <sub>4</sub> , 0.01 molar.							
No. of Exp.	C = 50.00								K
1.	$v =$	580	560	540	520	500	480	460	
	$\Delta t =$	7	6	6	6	6	6	6	
	$c =$	0.47	2.78	4.73	6.72	8.72	10.69	12.69	14.61
	$k_1 =$	3.96	3.93	4.04	4.11	4.06	4.18	4.04	
	$k =$	3.94	3.93	4.01	4.11	4.09	4.14	4.02	<b>4.03</b>
2.	$k =$	4.01	3.99	4.01	3.93	3.92	4.10	4.04	<b>4.00</b>
3.	$k =$	4.01	4.01	4.05	4.22	4.29	4.12	4.29	<b>4.14</b>
4.	$k =$	3.98	3.98	4.08	4.12	4.09	4.02	4.06	<b>4.05</b>
5.	$k =$	4.13	4.00	4.23	4.34	4.48	4.20	4.39	<b>4.25</b>
6.	$k =$	4.00	3.98	4.20	4.33	4.50	4.34	4.22	<b>4.22</b>
		H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.							
7.	$k =$	4.14	4.10	4.25	4.20	4.19	4.25	4.09	<b>4.17</b>
8.	$k =$	4.18	4.04	3.97	4.19	4.21	4.20	4.12	<b>4.13</b>
		H <sub>2</sub> SO <sub>4</sub> , 1.25 molar.							
9.	$k =$	3.48	3.46	3.53	3.56	3.61	3.58	3.61	<b>3.55</b>
10.	$k =$	3.46	3.47	3.51	3.60	3.62	3.53	3.51	<b>3.53</b>
		H <sub>2</sub> SO <sub>4</sub> , 5 molar.							
11.	$k =$	1.78	1.76	1.75	1.84	1.68	1.78	1.68	<b>1.75</b>
12.	$k =$	1.75	1.76	1.74	1.75	1.79	1.80	1.81	<b>1.77</b>

Although it might be expected that an increase in acidity would raise the reaction velocity, it is seen in the table that precisely the reverse is true, at least for concentrations of sulphuric acid above 0.25 molar. This effect will be observed in all cases where free sulphuric acid is present, whether the oxidizing agent be ferric salt or chromic acid.

*Iron.*—Results obtained with metallic iron are shown in Table II, the first experiment, as before, being recorded in detail as an example. The calculation of the constants from the titrations is here somewhat different, since for every two molecules of ferrous iron formed by reduction of the ferric sulphate one more is formed by solution of the metal. The concentration of ferric salt at any instant is therefore measured by the value of the expression  $C - c_0 - \frac{2}{3}(c - c_0)$ , in which  $C$  is the total iron,  $c_0$  the initial ferrous iron, and  $c$  the ferrous iron at time  $t$ , all expressed in the same units. In the table these units, as before, are cubic centimeters of 0.02 normal permanganate, and the values refer to 20 cm<sup>3</sup> of solution. The metal used was "American Ingot Iron," a special grade of commercial iron which has a purity of about 99.9 per cent.

TABLE II.

No. of Exp.	Metal: IRON.		R <sup>1</sup> Fe(SO <sub>4</sub> ) <sub>2</sub> , 0.05 molar.						K
	C = 50.00	c <sub>0</sub> = 0.44	H <sub>2</sub> SO <sub>4</sub> , 0.01 molar.						
1.	$v =$	580    560	540	520	500	480	460		
	$\Delta t =$	8        8	8	8	8	8	8		
	$c =$	4.36	8.20	11.93	15.68	19.15	22.68	25.67	
	$k_1 =$	3.90	3.93	3.90	3.99	3.78	3.59	3.73	
	$k =$	3.87	3.91	3.89	3.99	3.79	3.58	3.73	<b>3.82</b>
			H <sub>2</sub> SO <sub>4</sub> , 0.05 molar.						
2.	$k =$	3.97	3.97	3.64	(lost)	3.76	3.96	3.80	<b>3.85</b>
			H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.						
3.	$k =$	4.00	3.92	3.95	3.98	3.91	3.94	3.99	<b>3.96</b>
4.	$k =$	3.91	3.90	3.82	3.80	3.85	3.92	3.92	<b>3.87</b>
			H <sub>2</sub> SO <sub>4</sub> , 1.25 molar.						
5.	$k =$	3.42	3.38	3.31	3.42	3.35	3.35	3.34	<b>3.37</b>
6.	$k =$	3.45	3.38	3.29	3.44	3.33	3.45	3.31	<b>3.38</b>
			H <sub>2</sub> SO <sub>4</sub> , 5 molar.						
7.	$k =$	1.77	1.79	1.74	1.79	1.75	1.78	1.69	<b>1.76</b>
8.	$k =$	1.75	1.71	1.69	1.67	1.63	1.64	1.62	<b>1.67</b>
9.	$k =$	1.79	1.74	1.74	1.72	1.73	1.72	1.74	<b>1.74</b>
10.	$k =$	1.80	1.79	1.76	1.76	1.76	1.76	1.78	<b>1.77</b>

For the lower acidities, 0.01 and 0.05 molar, the results are less trustworthy than the rest and probably slightly too low, for the disk became covered during the experiment with a blackish coating which seemed to consist chiefly of hydroxide, since it turned to a rust-red color on drying. In the presence of 0.25 molar sulphuric acid the coating was very slight, and at higher acidities entirely absent.

*Nickel.*—Table III contains the results of the experiments with metallic nickel. Two samples of “pure nickel” were used, one furnished by Kahlbaum, the other of unknown origin, both of which seemed to give practically the same results. The former was used in Experiments 1 and 2, the latter in Nos. 3, 4, and 5, and also in the experiments with chromic acid, to be described later.

In no case was the action of the solution on the metal per-

TABLE III.

No. of Exp.	Metal: NICKEL.		R <sup>1</sup> Fe(SO <sub>4</sub> ) <sub>2</sub> , 0.05 molar.						K
	<i>k</i> =		H <sub>2</sub> SO <sub>4</sub> , 0.01 molar.						
1.	<i>k</i> =	3.75	3.75	3.53	3.29	3.27	3.33	2.98	<b>3.41</b>
				H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.					
2.	<i>k</i> =	3.82	(lost)	3.53	3.36	3.15	3.18	3.15	<b>3.36</b>
3.	<i>k</i> =	3.86	3.54	3.49	3.42	3.31	3.22	3.11	<b>3.42</b>
				H <sub>2</sub> SO <sub>4</sub> , 1.25 molar.					
4.	<i>k</i> =	3.24	3.19	3.07	2.93	2.89	2.82	2.78	<b>2.99</b>
				H <sub>2</sub> SO <sub>4</sub> , 5 molar.					
5.	<i>k</i> =	1.71	1.69	1.56	1.52	1.49	1.45	1.45	<b>1.55</b>

Initial velocities by extrapolation: Exp. 1, **3.80**; Exp. 2, **3.75**; Exp. 3, **3.75**; Exp. 4, **3.27**; Exp. 5, **1.71**.

fectly normal and uniform. In the presence of 0.01 and 0.25 molar sulphuric acid distinct black coatings formed on the disk, while even at the highest acidity, 5 molar, the disk acquired a brownish discoloration and, ultimately, a minutely spotted appearance. Examined under low magnification these spots were seen to consist of irregular rounded hollows, each containing traces of a brown deposit.

As the probable result of these irregularities in the action, we find in all cases that the velocity constants decrease as the experiment progresses, though less rapidly in the more strongly acid solutions. However, the constants for each single experiment, when plotted with time as the other coördinate, lie fairly close to a straight line, so that by extrapolating this line back to time zero we obtain a corrected value for the reaction velocity which represents, at least approximately, the rate at which the reaction would proceed under the given conditions if the sources of disturbance were absent. The initial reaction velocity for each experiment, as obtained by such extrapolation, is recorded at the foot of the table. Although, owing to irregularity in the constants, this procedure sometimes fails to give sharp results, these extrapolated values are certainly more accurately and fairly representative of the single experiments, in

the present case, than are the average values of their constants, and will therefore be given the preference in comparing nickel with the other metals.

It should be noted that this process of extrapolation affords a general method for correcting the observed reaction velocities for the effect of all disturbances which are initially absent but are produced by the progress of the reaction. It will be used in a number of the cases to follow.

*Tin.*—Metallic tin was found to dissolve readily, retaining a clean bright surface, in the ferric sulphate solutions used. The results as recorded in Table IV were calculated by using for the concentration of ferric salt the expression  $C - c_0 - \frac{1}{2}(c - c_0)$  in which  $C$  and  $c_0$  are the initial concentrations of ferric and ferrous salt respectively, and  $c$  is the titer of the solution at

TABLE IV.

Metal: TIN.		R <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> , 0.05 molar.							K
No. of Exp.		H <sub>2</sub> SO <sub>4</sub> , 5 molar.							
1.	C = 62.00	c <sub>0</sub> = 2.46							
	v =	580	560	540	520	500	480	460	
	Δt =	10	10	10	10	10	10	10	
	c =	5.91	9.48	13.00	16.53	20.13	23.80	27.40	
	k <sub>1</sub> =	1.71	1.75	1.71	1.71	1.75	1.78	1.72	
	k =	1.71	1.74	1.71	1.71	1.75	1.78	1.72	1.73
2.	k =	1.76	1.76	1.75	1.75	1.71	1.74	1.71	1.74
3.	k =	1.75	1.70	1.73	1.69	1.67	1.71	1.66	1.70
		H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.							
4.	k =	4.07	4.03	4.09	4.10	4.18	4.22	4.35	4.15
5.	k =	4.07	4.04	4.11	4.14	4.28	4.27	4.36	4.18

Initial velocities by extrapolation: Exp. 4, 3.97; Exp. 5, 3.95.

time  $t$ . This method of calculation is based on the reaction  $2\text{Fe}^{+++} + \text{Sn} = 2\text{Fe}^{++} + \text{Sn}^{++}$ , that is, it takes no account of the possibility of oxidation beyond the stannous stage.

The assumption here involved, that stannous sulphate is not oxidized by the ferric sulphate, may seem at first sight to be unwarranted, even as an approximation, for the reaction between stannous chloride and ferric chloride, as shown by the work of Kahlenberg\* and of A. A. Noyes,† is fairly rapid and practically complete, and is, moreover, accelerated by hydrochloric acid. We have found, however, that under the conditions of our experiments the oxidation of stannous sulphate by ferric sulphate is extremely slow. The following observations

\* Jour. Amer. Chem. Soc., xvi, 314, 1894.

† Zeitschr. phys. Chem., xvi, 550, 1895.



will serve to illustrate this fact: After an experiment on the rate of solution of tin, the solution remaining in the apparatus, and containing a large excess of ferric sulphate, was always found to give a brown precipitate with hydrogen sulphide, even after standing over night. Again, a mixture of stannous sulphate with a small amount of ferric sulphate, strongly acidified with sulphuric acid and colored red by thiocyanate, retained its color for many hours, but bleached rapidly as soon as a little potassium chloride was added, thus showing conspicuously the much greater velocity in the presence of chloride ion.

It is certain, therefore, that comparatively little stannic sulphate can have been formed during the short time occupied by the experiment (about 70 minutes). Nevertheless it is desirable to consider what effect the oxidation of the stannous sulphate by the ferric sulphate would tend to have upon the observed reaction velocity. The important point here is the fact that this reaction produces no change in the titer of the solution toward permanganate. Consequently, the analyses yield us no information concerning the extent to which ferric sulphate has been replaced by stannic sulphate, but give only the sum of the two. Both react with metallic tin, and with the same ultimate result so far as the yield of products which reduce permanganate is concerned, but the specific rates at which ferric sulphate and stannic sulphate, respectively, react with the metal, may be, and probably are, quite different. We may therefore conclude that the only direct effect on the observed reaction velocity to be expected in a case of this kind, due to the second stage of the reaction, is a downward or an upward trend of the velocity constants, according as the original oxidizer, or the one replacing it, reacts most rapidly with the metal.\*

Experiments 1, 2, and 3, of Table IV show no such trend in the constants, and the averaged values of  $k$  may accordingly be assumed to be practically free from error due to the second stage of the oxidation. In Experiments 4 and 5 the constants show a slight rise, so that here the initial reaction velocities, obtained by linear extrapolation in the way described above, furnish the safest basis for comparison with the other metals, and will be so used. Whether the observed rise in the constants is due to the second stage of the reaction or to some other cause, no serious doubt attaches to the initial velocities, which are entirely consistent with the values given by the other metals.

\*It is evident that this will in many cases be determined more by rapidity of diffusion than by oxidizing activity.

*Copper and Silver.*—The results obtained with copper and with silver are much alike and can conveniently be considered together. They are recorded in Table V, together with two experiments on the rate of solution of zinc. The silver used was from a sample of high purity which gave no test for copper. For the copper disks the best obtainable grade of commercial sheet copper was employed, but the sample was not

TABLE V.

$R^1Fe(SO_4)_2$ , 0.05 molar.

		<i>Copper.</i>							K
No. of Exp.	$k =$	$H_2SO_4$ , 0.25 molar.							
1.	$k =$	3.83	3.58	3.78	3.68	3.54	3.61	3.64	<b>3.67</b>
2.	$k =$	3.76	3.64	3.69	3.60	3.55	3.62	3.51	<b>3.62</b>
		$H_2SO_4$ , 1.25 molar.							
3.	$k =$	3.31	3.21	3.26	3.22	3.24	3.41	3.02	<b>3.24</b>
4.	$k =$	3.36	3.25	3.22	3.18	3.16	3.13	3.02	<b>3.19</b>
		$H_2SO_4$ , 5 molar.							
5.	$k =$	1.73	1.67	1.64	1.66	1.69	1.46	1.60	<b>1.63</b>
6.	$k =$	—	1.64	1.68	1.59	1.63	1.63	1.53	<b>1.62</b>
7.	$k =$	1.68	1.66	1.65	1.60	1.61	1.59	1.62	<b>1.63</b>

Initial velocities by extrapolation: Exp. 1, **3.75**; Exp. 2, **3.73**; Exp. 3, **3.27**; Exp. 4, **3.33**; Exp. 5, **1.74**; Exp. 6, **1.70**; Exp. 7, **1.69**.

*Silver.*

		$H_2SO_4$ , 0.25 molar.							
8.	$k =$	1.60	1.60	1.44	1.34	1.29	1.19	1.08	<b>1.36</b>
		$H_2SO_4$ , 1.25 molar.							
9.	$k =$	1.61	1.49	1.35	1.36	1.23	1.14	1.18	<b>1.34</b>
10.	$k =$	1.61	1.53	1.48	1.41	1.29	1.27	1.15	<b>1.39</b>
		4 gram. $Ag_2SO_4$ added at the outset.							
11.	$k =$	0.73	0.63	0.62	0.59	0.56	0.52	0.41	<b>0.58</b>
		$H_2SO_4$ , 5 molar.							
12.	$k =$	1.28	1.16	1.11	1.08	1.06	1.06	1.05	<b>1.11</b>
13.	$k =$	1.25	1.16	1.17	1.10	1.04	1.05	1.02	<b>1.11</b>

Initial velocities by extrapolation: Exp. 8, **1.67**; Exp. 9, **1.61**; Exp. 10, **1.65**; Exp. 12, **1.23**; Exp. 13, **1.24**.

*Zinc.*

		$H_2SO_4$ , 0.01 molar.							
14.	$k =$	4.41	4.32	4.35	4.56	4.56	4.57	5.00	<b>4.46</b>
15.	$k =$	4.27	4.38	4.13	4.07	4.48	4.34	4.39	<b>4.29</b>

subjected to any special tests for purity. Both silver and copper retained a bright clean surface in dissolving in the ferric sulphate, but both gave in all cases velocity constants which decreased as the experiment progressed, though this effect was much more marked with silver than with copper.

For silver, at least, the explanation is clear, since the reaction between silver and ferric ion has been shown to be far from complete. Noyes and Brann\* found that only about one-fourth of the ferric ion was reduced at 25°. The rate of the chemical reaction proper must therefore decrease with increase in the silver content of the solution, which accounts for the falling constants in our silver experiments. The correctness of this explanation is placed beyond question by Experiment 11, in which silver sulphate, added at the outset, produced a large decrease in the reaction velocity.†

By analogy, the decrease in the copper constants should be explainable in the same way. Electrochemical evidence tending to confirm this is found in Table VI, where it is shown that a copper electrode becomes more positive toward a solution of ferric sulphate when copper sulphate is added, thus proving that the reaction is to some extent reversible. Silver and cadmium electrodes show a like behavior. All potentials in the table are referred to the normal calomel electrode as +0.560 volts, but no corrections have been applied for diffusion potentials. The values lay no claim to accuracy, as the concentra-

TABLE VI.

Metal.	Solution.	Single Potential volts
SILVER	1/20 m. KFe(SO <sub>4</sub> ) <sub>2</sub> , 1/4 m. H <sub>2</sub> SO <sub>4</sub> , .....	+0.937
"	" " " " 1 1/4 " " .....	+0.919
"	" " " " 5 " " .....	+0.883
"	" " " " 1/4 " " 1/200 m. Ag <sub>2</sub> SO <sub>4</sub> , .....	+0.948
COPPER	" " " " 1/4 " " .....	+0.540
"	" " " " 1 1/4 " " .....	+0.525
"	" " " " 5 " " .....	+0.508
"	" " " " 1/4 " " 1/100 m. CuSO <sub>4</sub> , .....	+0.549
CADMIUM	" " " " 1/4 " " .....	-0.205
"	" " " " 1 1/4 " " .....	-0.224
"	" " " " 5 " " .....	-0.236
"	" " " " 1/4 " " 1/100 m. CdSO <sub>4</sub> , .....	-0.200
SILVER	0.015 m. CrO <sub>3</sub> , .....	+0.968
"	" " " " 5 " " .....	+0.894
"	" " " " " " " 1/200 m. Ag <sub>2</sub> SO <sub>4</sub> , .....	+0.905

\* Jour. Am. Chem. Soc., xxxiv, 1016, 1912.

† A part of the silver sulphate added was still undissolved at the start, but dissolved during the course of the experiment. This was no doubt the cause of the falling constants.

tions of the solutions were only approximate, and the potential readings changed somewhat with the time, but the effect of the added salts is unmistakable. It is also clear that the electrode in all cases becomes less positive or more negative to the solution as the acidity increases, a fact to which we shall have occasion to refer later.

The reaction between ferric ion and a metal would, in general, be expected to be more complete the less noble the metal, and this probably explains why the tendency of the reaction velocity to decrease during the course of the experiment, though large enough to affect the results in the case of silver, and (to a smaller extent) also in the case of copper, was not appreciable with tin, nickel, iron, and cadmium.

On account of this decrease in the constants it is clear that the extrapolated initial velocities, in all the silver and copper experiments, are the values which properly represent the individual experiments.

*Zinc.*—For the experiments with zinc the metal used was the very pure commercial grade from the "Bertha" mine in Pulaski, Virginia. This was cast into thin plates and then ground and filed to the desired shape and thickness. Unfortunately it proved impossible to obtain the rate of solution of zinc, free from the disturbing influence of an evolution of hydrogen, which was given off in appreciable quantity even in ferric sulphate solutions to which no acid had been added. It has been shown in a previous paper\* that the evolution of a gas tends to raise the observed reaction velocity, and by an uncertain amount, so that the velocity constants obtained in Experiments 14 and 15, in the presence of 0.01 molar sulphuric acid, are probably slightly too high.

These two experiments are the only ones recorded in this paper which are affected by this source of error. None of the other metals gave an appreciable evolution of hydrogen under the conditions of experiment.

#### *Rates of Solution in Ferric Chloride.*

No change in the conditions or general procedure described above for ferric sulphate was made in the experiments with ferric chloride, except that in making the titrations definite amounts of manganous sulphate, sulphuric acid, and phosphoric acid were added to the sample, instead of phosphoric acid alone. This modification, made necessary by the presence of chloride, involved a slight sacrifice in the accuracy of the analyses. Table VII contains the results.

The experiments with cadmium call for no special comment. In the experiments with metallic iron the disks remained

\* This Journal, xxxii, 217. See also, *ibid.*, xxxvi, 544.



wholly free from the black coating formed in some cases in the sulphate solution. As before, the expression  $C - c_0 - \frac{2}{3}(c - c_0)$  was used in calculating the velocity constants for iron.

Copper dissolving in an acidified ferric chloride solution is oxidized in two stages, the case being therefore unlike that of copper in ferric sulphate, but closely analogous to that of tin in ferric sulphate. As in the latter case, the titer of the solution toward permanganate is not changed by the second stage of the oxidation, so that the analyses do not distinguish between ferric

TABLE VII.  
FeCl<sub>3</sub>, 0.05 molar.

No. of Exp.	<i>Cadmium.</i>							
	K							
	HCl, 0.5 molar.							
1. $k =$	4.17	4.08	4.16	4.16	4.13	4.18	4.20	<b>4.15</b>
2. $k =$	4.09	4.28	4.15	4.27	4.21	4.18	4.12	<b>4.19</b>
	HCl, 0.1 molar.							
3. $k =$	4.32	4.16	4.37	4.12	4.14	4.25	4.29	<b>4.24</b>
4. $k =$	4.12	4.15	4.17	4.18	4.12	4.14	4.12	<b>4.14</b>
	<i>Iron.</i>							
	HCl, 0.5 molar.							
5. $k =$	4.26	4.30	4.29	4.15	4.39	4.50	4.41	<b>4.33</b>
6. $k =$	4.24	4.34	4.39	4.37	4.40	4.40	4.44	<b>4.37</b>
	HCl, 0.1 molar.							
7. $k =$	4.18	4.10	4.18	4.35	4.18	3.83	4.22	<b>4.15</b>
8. $k =$	4.08	4.11	4.06	4.12	4.17	4.16	4.15	<b>4.12</b>
	<i>Copper.</i>							
	HCl, 0.5 molar.							
9. $k =$	4.26	4.22	4.32	4.42	4.33	4.49	4.41	<b>4.35</b>
10. $k =$	4.14	4.25	4.29	4.37	4.28	4.22	4.20	<b>4.25</b>
	HCl, 0.1 molar.							
11. $k =$	3.43	3.28	3.26	3.17	3.16	3.09	2.99	<b>3.20</b>
12. $k =$	3.56	3.32	3.30	3.23	3.15	3.02	3.11	<b>3.24</b>

Initial velocities by extrapolation: Exp. 9, 4.20; Exp. 10, 4.20; Exp. 11, 3.40; Exp. 12, 3.48.

chloride and cupric chloride, but give their sum. The velocity constants have been calculated in exactly the same way as in the tin experiments. In fact, the sole difference between the two cases is that here the second stage of the reaction is comparatively rapid. A good deal of cupric chloride must therefore have accumulated in the solutions, reaching, at the close of Experiments 9 and 10, in which this effect was largest, a concentration considerably larger than that of the ferric chloride itself.

It is evident that this substitution of cupric for ferric chloride would tend to cause a progressive change in the reaction velocity during the experiment. A careful consideration of the probable effect of the various factors influencing the result seems to show that such changes as those observed in Experiments 9 to 12, in which the direction of the change depends upon the acidity, are not incompatible with the point of view which we have adopted. We shall, however, make use of only the extrapolated initial velocities, so that the cause of the changes in velocity is for our purpose of minor importance.

*Discussion of Results Obtained with Ferric Salts.*

Table VIII contains a summary of the results given in the previous tables, each velocity constant being the averaged result of the various experiments performed under the conditions specified. These values have been obtained by one or the other of the two following methods: (a) For groups of comparable experiments in which the results were normal they are the averages, for all members of the group, of the average reaction velocity in each single experiment. (b) For groups of experiments in which the constants showed an unmistakable trend upward or downward they are the averages of the initial velocities as found by linear extrapolation. Although where method (b) is used the constants so calculated must be given the preference as more truly representative, the values calculated by method (a) are placed beside them, enclosed in parentheses, for comparison.

Considering first the upper section of the table, containing the ferric sulphate constants, we observe that in the presence of 5 molar sulphuric acid five metals give practically the same velocity, which, from the point of view of the diffusion theory, would be interpreted to mean that here the rate of diffusion of the ferric sulphate is determining the velocity. With decreasing acidity, however, the agreement becomes poorer, the metals tending to draw apart and to show individual velocities whose order is that of the electromotive series, the more positive metal dissolving more rapidly. It is evident here that the specific nature of the metal has a distinct influence on the reaction velocity.

Such results as these are seemingly in direct contradiction to Nernst's hypothesis of infinitely high reaction velocity at the boundary surface between two phases. Nernst's hypothesis, as we have already seen, demands that in all normal cases, that is, in all cases not affected by secondary disturbing influences, the observed reaction velocity shall be determined by the rate

of diffusion of the active substance, and shall be practically independent of the nature of the solid. Now it cannot be denied that disturbing influences may have slightly affected some of the results in the table; in particular, the nickel constants are rather uncertain. On the other hand, there was no evidence whatever of interfering effects in the cadmium experiments. Moreover, the distinctly systematic nature of the results in the table argues against the possibility that any considerable number of them represent "anomalous" cases. Finally, the decreasing constants obtained with silver were clearly traced to the retardation of the chemical reaction by the accumulation of silver sulphate, which would have only a trifling effect on the rate of diffusion. In short, these results furnish grounds for seriously doubting the general validity of Nernst's hypothesis.

A study of the table seems to show that at one extreme we have velocities determined largely or wholly by diffusion, at the other, velocities determined chiefly by the rate of the chemical reaction, and between them velocities in which we can readily detect the simultaneous effect of both influences. Although these results do not cover the full range from a purely chemical reaction velocity to a pure diffusion velocity it is evident that the transition from one to the other is gradual, not abrupt.

This point becomes clearer on further analysis of the results. An increase in the concentration of free sulphuric acid above 0.25 molar produces in all cases a marked decrease in the observed reaction velocity. In general, the activity of an oxidizing agent is increased by a rise in the concentration of hydrogen ion. It will hardly be doubted that this rule applies in the cases with which we are dealing, and we should, therefore, expect that the free energy of the reaction with the metal would increase with increasing acidity. This is supported by the potentials in Table VI so far as inferences can safely be drawn from the behavior of electrodes which are imperfectly reversible. This table contains the single potentials of silver, copper, and cadmium against solutions of the same composition as those used in the reaction velocity measurements. As we have already noted, the values show that with increasing concentration of sulphuric acid the metal in all cases becomes less positive or more negative toward the solution, that is, the change is in the direction of increasing free energy.

For our purpose, however, the important question is the effect of an increase in acidity upon the velocity of the chemical part of the reaction with the metal. Although, in general, there is no necessary correspondence, even in sign, between variations in reaction velocity and variations in the magnitude

of the change in free energy, there would seem to be here a rather strong probability that the chemical reaction in most or all of the cases with which we shall have to deal is accelerated rather than retarded by an increase in acidity. At all events we shall make this assumption as a working hypothesis, and shall adhere to it consistently throughout.

TABLE VIII.  
Summary of Velocity Constants.

		<i>Ferric Atom.</i>		
Conc. of H <sub>2</sub> SO <sub>4</sub>	0·01	0·25	1·25	5 molar.
Zinc.....	4·38			
Cadmium.....	4·12	4·15	3·54	1·76
Iron.....	3·95 (3·82)	3·92	3·37	1·74
Nickel.....	3·80 (3·41)	3·75 (3·39)	3·27 (2·99)	1·71 (1·55)
Tin.....	....	3·96 (4·16)	....	1·72
Copper.....	....	3·74 (3·64)	3·30 (3·22)	1·71 (1·63)
Silver.....	....	1·67 (1·36)	1·63 (1·36)	1·24 (1·11)
		<i>Ferric Chloride.</i>		
Conc. of HCl			0·1	0·5 molar.
Cadmium.....			4·19	4·17
Iron.....			4·14	4·35
Copper.....			3·44 (3·22)	4·20 (4·30)

We must assume then that sulphuric acid tends to accelerate the chemical reaction with the metal, but we find in Table VIII that if the acid is present in more than 0·25 molar concentration it exerts a strong retarding influence on the rate of solution. From the standpoint of the diffusion theory the explanation of this effect is clear. The important factor here is the viscosity of the solution, which is increased in the ratio of about 2·5 : 1 when the sulphuric acid concentration rises from 0·25 molar to 5 molar. An increase in the viscosity retards the diffusion process by lowering the rate of diffusion, and perhaps, to a slight extent, by increasing the thickness of the diffusion layer,\* and in this way depresses the rate of solution of the metal, this effect here outweighing any acceleration of the chemical part of the reaction resulting from the higher acidity.

A predominance of the diffusion effect, however, does not necessarily exclude the influence of the chemical reaction, for we find that velocity constants in the same vertical column (that for 0·25 molar sulphuric acid, for instance), though they differ among themselves in a comparatively systematic manner according to the specific nature of the metal, thus showing the

\* See Van Name and Hill, this Journal, xxxvi, 552-4.



influence of the chemical reaction velocity, are all lowered by an increase in the viscosity. In other words, these results illustrate the case, alluded to above, of a reaction velocity determined by the simultaneous influence and mutual relation of both factors, diffusion process and chemical reaction.

Nor is there any reason for believing that such cases are unusual. On the contrary, it seems proper to regard the observed velocity as being normally the resultant of the simultaneous action of the two factors just mentioned. Cases in which one factor predominates to the virtual exclusion of the other are, therefore, merely limiting cases, though no doubt they occur very often in practice.

This point of view appears to us to be the most reasonable and helpful one in dealing with heterogeneous reactions of the general type under consideration, and will be the one employed throughout the present paper, in interpreting experimental results.

The results obtained with ferric chloride, summarized in the lower section of Table VIII, tend to confirm, so far as their evidence goes, the conclusions drawn above from the experiments with ferric sulphate. These values are probably less accurate than those for sulphate solutions, and less stress can be laid upon small differences. They prove that cadmium and iron dissolve in ferric chloride at the same rate in the presence of 0.1 molar hydrochloric acid, and probably also when the acid is 0.5 molar. This indicates that in these cases the observed reaction velocities are essentially rates of diffusion. It is not clear whether the effect of this increase in acidity is to raise or to lower the observed velocity, but the change is at all events small, as would be expected in a case in which the viscosity change is almost negligible (about 3 per cent).\*

The same increase in acidity produces a marked rise in the rate of solution of copper. We would avoid laying any emphasis on the absolute values of these copper constants, on account of the complications already mentioned. Nevertheless, it may be pointed out that the relations of these two velocities to one another, and to the corresponding values for cadmium and iron, involves nothing unexpected or inconsistent with the point of view stated above. The lower value for copper in 0.1 molar hydrochloric acid, as compared with cadmium and iron, seems to be due to the influence of the relatively slower rate, in the case of copper, of the chemical part of the reaction, this rate being accelerated by the increase in acidity to 0.5 molar, up to the point where the rate of diffusion

\* In a like manner, the fact that the ferric sulphate constants change so little between 0.01 and 0.25 molar sulphuric acid, may be ascribed largely to the smallness of the accompanying viscosity change.

predominates, thus tending to bring copper into agreement with the other two metals.

#### Rates of Solution in Chromic Acid.

In the experiments with chromic acid as oxidizing agent the solutions were initially about 0.015 molar with respect to  $\text{CrO}_3$ , and contained also definite known amounts of free sulphuric acid. The precaution, employed with ferric salts, of keeping an atmosphere of carbon dioxide above the liquid during the reaction, was, of course, unnecessary in working with chromic acid, but in other respects the procedure remained as before. As compared with the case of ferric salts, a higher concentration of hydrogen ion is essential for the reaction to proceed smoothly, and a further difference exists in the fact that the acidity decreases during the reaction. But unless the initial acidity is low this decrease is relatively small. In the experiments accepted as trustworthy, the initial acidity was always 0.5 normal (0.25 molar  $\text{H}_2\text{SO}_4$ ) or above, and the decrease in acidity, even in the extreme cases, was only about 6 per cent, an amount too small to have any marked effect upon the observed reaction velocity.

The analyses of the solution samples for chromic acid were carried out by one or the other of the two following methods: (a) Treatment with an excess of potassium iodide and titration of the liberated iodine with thiosulphate, (b) Treatment with a known volume of standard ferrous sulphate, and titration of the unoxidized ferrous sulphate with permanganate.

Method (a), which was conducted according to the directions of Seubert and Henke,\* was applicable only in certain cases, and seemed to have no advantage in accuracy over method (b). The experiments in which method (a) was used are designated in the tables by asterisks. Full experimental data are given for Experiment 1, the values of  $c$  being volumes of 0.02 normal thiosulphate used, which are evidently proportional to the concentrations of chromic acid at the corresponding times, and can therefore be directly substituted in the velocity equation in calculating  $k$ .

Method (b) was applicable in all cases, and was on the whole preferred, after experience had proved that the presence of the green chromic salt in the solution did not seriously diminish the sharpness of the permanganate end point. Data for a typical experiment (No. 4 of Table IX) are given in detail, the values of  $c$  being here cubic centimeters of 0.02 normal permanganate used in titrating 20  $\text{cm}^3$  of the given ferrous sulphate solution after the addition of the 20  $\text{cm}^3$  sample

\* Zeitschr. angew. Chemie, 1900, 1147.

of solution to be analyzed, together with a little phosphoric acid. The concentration of chromic acid is measured, in terms of the ferrous sulphate solution, by the expression  $20 - xc$ , in which  $x$  is the volume of the ferrous sulphate equivalent to 1 cm<sup>3</sup> of the permanganate. This expression was used in calculating the velocity constants.

*Cadmium and Copper.*—Table IX gives the results obtained with cadmium and with copper in solutions 0.25, 1.25, and 5

TABLE IX.  
CrO<sub>3</sub>, 0.015 molar.

No. of Exp.		Cadmium.							K
		H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.							
1.*	$r =$	580	560	540	520	500	480	460	
	$\Delta t =$	10	10	10	10	10	10	10	
	$c =$	48.11	42.68	37.74	33.14	28.96	25.13	21.72	18.60
	$k_1 =$	6.94	6.88	7.02	7.00	7.08	6.99	7.13	
	$k =$	6.96	6.88	7.02	7.00	7.08	6.99	7.13	<b>7.01</b>
2.*	$k =$	7.04	7.13	7.00	7.08	6.99	7.00	7.05	<b>7.04</b>
		H <sub>2</sub> SO <sub>4</sub> , 1.25 molar.							
3.	$k =$	5.16	5.41	5.31	5.29	5.47	5.23	5.37	<b>5.32</b>
		H <sub>2</sub> SO <sub>4</sub> , 5 molar.							
		1 cm <sup>3</sup> KMnO <sub>4</sub> = 0.388 cm <sup>3</sup> FeSO <sub>4</sub> .							
4.	$v =$	580	560	540	520	500	480	460	
	$\Delta t =$	10	10	10	11	9	10	10	
	$c =$	6.25	8.32	10.28	12.30	14.50	16.22	18.14	20.03
	$k_1 =$	2.71	2.60	2.71	2.73	2.63	2.68	2.68	
	$k =$	2.71	2.59	2.71	2.73	2.63	2.69	2.68	<b>2.68</b>
5.	$k =$	2.64	2.61	2.70	2.57	2.72	2.70	2.58	<b>2.65</b>
		H <sub>2</sub> SO <sub>4</sub> , 0.05 molar.							
6.*	$k =$	8.59	8.54	8.33	7.94	8.23	7.54	7.81	<b>8.14</b>
7.*	$k =$	8.48	8.65	8.16	7.82	7.82	7.89	7.39	<b>8.03</b>
* Chromic acid determined by iodometric method.									
<i>Copper.</i>									
		H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.							
8.	$k =$	7.18	6.79	7.06	7.05	6.73	7.21	6.95	<b>7.00</b>
9.	$k =$	6.75	6.96	6.91	7.07	6.88	6.84	6.87	<b>6.90</b>
10.	$k =$	6.96	6.86	6.95	6.99	7.00	7.09	6.85	<b>6.96</b>
		H <sub>2</sub> SO <sub>4</sub> , 1.25 molar.							
11.	$k =$	5.47	5.29	5.39	5.31	5.34	5.23	5.36	<b>5.34</b>
		H <sub>2</sub> SO <sub>4</sub> , 5 molar.							
12.	$k =$	2.73	2.67	2.72	2.73	2.78	2.72	2.76	<b>2.73</b>
13.	$k =$	2.71	2.64	2.76	2.75	2.76	2.69	2.67	<b>2.71</b>
		H <sub>2</sub> SO <sub>4</sub> , 0.05 molar.							
14.	$k =$	2.44	4.02	5.50	6.20	6.76	7.02	7.11	<b>5.58</b>

molar with respect to sulphuric acid. Both metals under these conditions behaved normally, giving satisfactorily constant reaction velocities, and the values obtained for the two metals are, moreover, in excellent agreement with one another throughout.

On the other hand a few experiments conducted in solutions only 0.05 molar with respect to sulphuric acid gave distinctly abnormal results, the reaction velocities showing progressive variation and no approach to agreement between cadmium and copper. Since these experiments were plainly affected by specific disturbances arising from insufficient acidity, the results, though included in the table, are of little significance.

*Iron.*—The experiments on the rate of solution of iron in chromic acid are complicated by the fact that the oxidation takes place in two stages. Two examples of such two-stage reactions have already been considered, tin in ferric sulphate and copper in ferric chloride, but in both cases the method of analysis was such that the second stage of the oxidation had no direct effect upon the titer of the solution. Consequently, the concentration of the oxidizing agent, as calculated from the titrations and used in calculating the velocity constant, was in reality the combined concentrations of two oxidizing agents present in unknown proportions in the solution, namely, the ferric salt, and the higher oxidation product of the dissolving metal. (See p. 308.) In the present case it is the concentration of the chromic acid alone which is given by the titrations, and therefore both stages of the oxidation change the titer of the solution. This difference must be borne in mind in comparing the results.

Now in general, in a two-stage reaction of this type between a metal and a dissolved oxidizer, if the second stage is sufficiently rapid the lower oxidation product will be oxidized where it is formed, that is, at the surface of the metal. Thus it may happen that a metal in passing through two stages of oxidation gives the same velocity constant as a metal undergoing only one stage, the observed velocity being that of the diffusion process. Such an instance is apparently offered by the case of tin in chromic acid, to be discussed later. On the other hand if the second stage of the oxidation is not quite rapid enough to produce the result just mentioned, some of the molecules of the lower oxidation stage will not be oxidized until they have diffused part way through the diffusion layer, or perhaps have passed through it into the solution. The effect in either case is to shorten the average length of the diffusion path for the molecules of the oxidizing agent and therefore to raise the observed reaction velocity. The reaction between tin and iodine dissolved in potassium iodide solution



TABLE X.  
 CrO<sub>3</sub>, 0.015 molar.

No. of Exp.	H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.								K
1.	1 cm <sup>3</sup> KMnO <sub>4</sub> = 0.385 cm <sup>3</sup> FeSO <sub>4</sub> .								
	<i>v</i> =	580	560	540	520	500	480	460	
	$\Delta t$ =	10	10	10	10	10	10	10	
	<i>c</i> =	6.95	13.87	20.02	25.60	30.60	35.10	39.17	42.70
	<i>k</i> <sub>1</sub> =	9.67	9.85	10.36	10.93	11.82	13.25	14.86	
	<i>k</i> =	9.66	9.85	10.37	10.94	11.83	13.25	14.86	<b>11.54</b>
2.	<i>k</i> =	9.61	10.39	10.34	11.02	12.10	14.09	15.22	<b>11.82</b>
	H <sub>2</sub> SO <sub>4</sub> , 5 molar.								
3.	<i>k</i> =	3.78	4.16	4.14	4.14	4.08	4.27	4.49	<b>4.15</b>
4.	<i>k</i> =	3.96	4.10	4.12	4.19	4.39	4.52	4.49	<b>4.25</b>
5.	<i>k</i> =	3.93	3.99	4.11	4.32	4.31	4.24	4.48	<b>4.20</b>
	<i>Nickel.</i>								
	H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.								
6.*	Disk immersed in dil. HCl in contact with zinc.								
	<i>k</i> =	5.75	5.95	5.80	5.40	5.80	5.54	6.12	<b>5.77</b>
7.*	Disk treated as in Exp. 1.								
	<i>k</i> =	4.71	6.00	6.92	6.76	7.05	6.80	6.80	<b>6.43</b>
8.*	Disk treated as in Exp. 1.								
	<i>k</i> =	5.92	4.56	3.48	2.71	3.27	3.40	3.51	<b>3.84</b>
9.*	Disk cleaned with 2:1 HNO <sub>3</sub> after each reaction period.								
	<i>k</i> =	0.49	1.54	1.35	0.03	1.71	0.09	1.04	<b>0.89</b>
10.*	Disk cleaned with warm 1:2 HNO <sub>3</sub> after each reaction period.								
	<i>k</i> =	0.37	5.96	6.01	5.67	4.48	3.68	4.82	<b>4.43</b>
	H <sub>2</sub> SO <sub>4</sub> , 5 molar.								
11.	<i>k</i> =	2.55	2.64	2.70	2.66	2.58	2.78	2.56	<b>2.64</b>
12.	<i>k</i> =	2.61	2.71	2.72	2.71	2.69	2.75	2.71	<b>2.70</b>
	<i>Tin.</i>								
	H <sub>2</sub> SO <sub>4</sub> , 5 molar.								
13.	<i>k</i> =	2.76	2.72	2.80	2.72	2.68	2.68	2.78	<b>2.73</b>
14.	<i>k</i> =	2.84	2.74	2.78	2.72	2.66	2.73	2.74	<b>2.74</b>
	<i>Silver.</i>								
	H <sub>2</sub> SO <sub>4</sub> , 0.25 molar.								
15.	<i>k</i> =	4.51	4.30	4.28	4.24	4.52	4.54	4.40	<b>4.40</b>
16.	<i>k</i> =	4.31	4.43	4.02	4.25	4.03	4.22	4.15	<b>4.20</b>
17.	<i>k</i> =	4.35	4.17	4.35	4.10	4.21	4.24	4.17	<b>4.23</b>
	H <sub>2</sub> SO <sub>4</sub> , 5 molar.								
18.	<i>k</i> =	(1.53)†	1.26	1.20	1.18	1.21	1.23	1.24	<b>1.22</b>
19.	<i>k</i> =	(1.52)†	1.28	1.29	1.21	1.21	1.18	1.19	<b>1.23</b>

Initial velocities by extrapolation: Exp. 15, **4.40**; Exp. 16, **4.27**; Exp. 17, **4.28**; Exp. 18, **1.22**; Exp. 19, **1.31**.

\* Chromic acid determined by iodometric method. † Not included in average.

probably belongs in this category, as has been shown elsewhere.\* There is, moreover, reason to expect similar behavior from iron in chromic acid, for Benson† has shown that the reaction between chromic acid and ferrous sulphate progresses in dilute solutions at a rate sufficiently slow to be easily measurable.

The results obtained, shown in Table X, Experiments 1-5, are in accordance with this view. Not only are the constants higher throughout than with the other metals under like conditions, but they also show the continuous rise which would be predicted from the accumulation of ferric salt, which itself reacts with the metal, producing ferrous salt in constantly increasing proportion compared with the chromic acid, and thus causing a progressive shortening in the average length of the diffusion path.

In Experiments 1 to 4 the titrations were carried out during the progress of the experiment, and with very little delay. Now Benson has shown, in the article just cited, that ferric salts have a retarding effect upon the oxidation of ferrous salts by chromic acid. If in our analyses the time allowed for the completion of this reaction had been too short this would have produced high and rising velocity constants. That the high and rising constants actually observed were not due to this is proved by Experiment 5, in which the solution samples, after mixing as usual with a known amount of ferrous sulphate, were allowed to stand for  $2\frac{1}{2}$  hours before titrating back with permanganate. It is evident that this modification made no appreciable difference in the results.

*Nickel.*—The experiments with nickel in chromic acid were carried out in solutions either 0.25 or 5 molar with respect to sulphuric acid. In the former solution the velocity constants were in all cases irregular and abnormally low; in the latter the results were apparently normal and agreed well with the values obtained with cadmium and with copper under like conditions.

The nickel disks after use always showed traces of a blackish deposit or, in the stronger acid, of a brownish discoloration, these surface coatings resembling closely in appearance and amount those observed with nickel in ferric sulphate solutions of like sulphuric acid concentration (see page 306). The effect of these coatings upon the reaction velocity was apparently negligible in 5 molar sulphuric acid, and even in the weaker acid they were probably responsible for only a small part of the abnormality observed.

The chief cause of the low and variable results obtained in the presence of 0.25 molar sulphuric acid was the tendency of

\* This Journal (4), xxxii, 216, 1911. † Jour. Phys. Chem., vii, 1, 1903.

the nickel disks to become passive. In Experiments 6, 7, and 8, to insure activity of the disk at the start, after cleaning in the usual manner it was immersed in dilute hydrochloric acid and thoroughly rubbed under the acid with a zinc rod. This treatment did not make the constants regular. Since low constants are found following much higher ones (notably in Experiment 8) passivity must have been produced in the chromic acid solution. That the reaction velocity also increases at times during the course of the experiment is perhaps explained by the fact that a partly passive disk in sulphuric acid would constitute a short-circuited element of which the active areas would be the anodes, and the adjacent passive areas would consequently be subject to cathodic reducing effects which would tend to destroy their passivity in so far as it was not re-established by the chromic acid. No explanation is offered for the fact that these two opposing tendencies produce fluctuations in the degree of passivity. It may only be suggested that the variations are in some way connected with the gradual uncovering of impurities in the metal.

In Experiments 9 and 10 the attempt was made to restrict so far as possible the formation, on the disk, of the blackish deposits above mentioned, by removing the disk from the solution at the end of each reaction period and cleaning with nitric acid. The treatment with a zinc rod was omitted. Neither hot concentrated hydrochloric acid nor iodine in potassium iodide solution would remove the deposit completely. Concentrated nitric acid removed it easily and gave the metal a perfectly clean surface, but a disk so cleaned was invariably wholly passive and was no longer attacked by the chromic acid solution. Nitric acid of two-thirds strength was accordingly selected for trial in Experiment 9 but proved too strong, the results showing practically complete passivity during two of the reaction periods, and a very low activity during the rest. The more dilute nitric acid used in Experiment 10 produced high passivity during the first reaction period, but the later constants showed no more passivity than might be expected, according to the results of Experiments 6, 7, and 8, from the action of the chromic acid alone.

For Experiments 11 and 12 the sulphuric acid concentration was increased to 5 molar with very beneficial results. The absence of any indication of passivity in these experiments seems to prove that this concentration of sulphuric acid was sufficient to entirely overcome the tendency of chromic acid to produce passivity in the nickel disks. The rate of the reaction shows a satisfactory constancy, and the mean value of the velocity constant agrees with the values obtained with several other metals under like conditions.

*Tin.*—The study of tin in chromic acid solution was confined to the two experiments numbered 13 and 14 in the table, both conducted in the presence of 5 molar sulphuric acid. The results are in both cases apparently normal, and the reaction velocity has the expected value. This behavior on the part of a metal-forming soluble and stable salts of two different valencies indicates one of two possibilities; either (*a*) the second stage of the oxidation does not occur to a measurable extent (the case observed with tin in ferric sulphate), or, (*b*) the second stage is so rapid that no appreciable diffusion of stannous salt away from the metal can occur. As the reaction between stannous sulphate and chromic acid is practically instantaneous there can be little doubt that explanation (*b*) is the correct one here.

*Silver.*—Experiments with silver in chromic acid gave the values recorded in Nos. 15-19 of Table X. In general, the results resemble those given by silver in ferric sulphate, both in the relatively low reaction velocities observed, and in the fact that the velocity tends to decrease as the silver salt accumulates in the solution. On account of this decrease the reaction velocity characteristic of a given experiment is best represented, as in a number of cases already considered, by the "initial velocity," found by extrapolating back to time zero.

### GENERAL DISCUSSION OF RESULTS.

A summary of the reaction velocities in chromic acid is given in Table XI. Comparison with the results obtained in ferric

TABLE XI.  
Summary of Velocity Constants.

Conc. of H <sub>2</sub> SO <sub>4</sub>	<i>Chromic Acid.</i>		
	0.25	1.25	5 molar
Cadmium .....	7.02	5.32	2.67
Nickel .....	(irregular)	(irregular)	2.67
Tin .....	....	....	2.74
Copper .....	6.95	5.34	2.72
Silver .....	4.28	....	1.22

sulphate, as summarized in Table VIII, shows a marked similarity between the two series, although chromic acid always gives higher velocities than ferric sulphate under like conditions. The chief points of similarity are the following:

(*a*) In each series there is an approximate agreement, in the presence of 5 molar sulphuric acid, between the values for cad-



mium, nickel, tin, and copper, the differences being either within the experimental error or, at most, exceeding it but slightly.

(b) The values for silver are in all cases decidedly lower than for the other metals under like conditions.

(c) The agreement between different metals tends to become closer the higher the acidity.

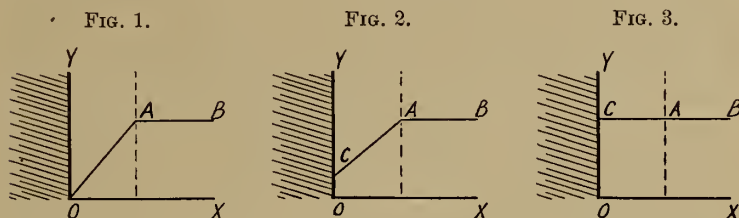
Slight deviations from (c) appear in several cases, but are generally smaller than the experimental error, the only clear exception being the one which occurs with silver in chromic acid, due to the unexpectedly low value 1.22. This exception will be discussed on a later page.

Following the point of view explained on page 316, the observed reaction velocity is to be regarded as the resultant of the rates of two different simultaneous processes, the diffusion and the chemical reaction. The agreement between different metals in the strongly acid solutions indicates a nearly or wholly complete dependence, under these conditions, of the observed rate upon that of the diffusion process. On the other hand, the systematic differences which appear between the rates for different metals in the less strongly acid solutions, show clearly that in these cases the diffusion process is not the sole controlling factor, and point to the conclusion that the chemical reaction is here slow enough to have a specific influence upon the observed result. Especially significant in support of this inference is the fact that the sequence of the metals, when arranged in the order of their observed reaction velocities, is very nearly the same as that of the electromotive series, the agreement being as close as could be expected when due allowance is made both for the normal error of experiment and for the additional uncertainty which attaches to several of the values on account of specific complications already described.

So far, our explanation is well supported by the results. One important point, however, remains to be considered. It has been shown that the reaction velocity in all normal cases obeys the equation for a reaction of the first order, thus proving that the rate is proportional at every instant to the concentration of the oxidizing agent. According to the view of Nernst this is due to the high velocity of the chemical reaction, which keeps the concentration of the oxidizer at the surface of the metal at practically zero. The observed reaction velocity is then the rate at which the oxidizer is supplied by diffusion, and this in turn is proportional to the difference in concentration between the two sides of the diffusion layer, which by hypothesis is equal to the concentration in the main body of the solution. It is evident that this explanation holds only when the velocity of the chemical reaction is very great com-

pared with that of the diffusion process, a condition which Nernst assumes to be always fulfilled except when secondary effects interfere.

Such a case, as Brunner\* has shown, may conveniently be represented by a diagram, fig. 1, in which the abscissas represent distances from the surface of the metal, and the ordinates concentrations. The shaded portion is the metal, OY its sur-



face, the dotted line is the outer limit of the diffusion layer, and the broken line OAB the concentration of the oxidizer at different points.

In the case of our results this explanation is applicable only to those experiments in the strongly acid solutions, in which, within certain limits, the reaction velocity is independent of the nature of the metal. Under conditions where different metals show different specific velocities (exemplified by the experiments at the lower acidities), the above explanation can not apply, yet we find that in general *the reaction velocity in such experiments obeys the expression for a reaction of the first order quite as well as when the velocity is independent of the metal.*

The point of view which we have adopted (pp. 316 and 324) assumes that the influence of the metal manifests itself in such cases because the chemical reaction is not sufficiently rapid in comparison with the diffusion process. In other words, the concentration of the oxidizing agent at the surface of the metal is not zero but has at every instant a finite value determined by the relative velocities of the two consecutive reactions involved. How this state of affairs can be reconciled with the observed obedience to the laws of a monomolecular reaction, is a point which calls for explanation.

The case with which we are dealing, represented on a diagram of the same type as fig. 1, gives fig. 2, in which the ordinate OC represents the concentration at the surface of the metal. Similarly fig. 3 shows the possible case of a reaction whose chemical stage is extremely slow in comparison with the dif-

\* Zeitschr. phys. Chem., xlvii, 68, 1904.

fusion stage, thus giving a concentration at the surface of the metal which is not sensibly different from that in the solution. The possibilities represented by these three figures will be hereafter referred to as cases I, II, and III, respectively.

For Case I, Nernst's explanation, given above, is sufficient to account for the fact that the reaction velocity obeys the equation for a monomolecular reaction. In Cases II and III, however, there is a finite concentration of the reagent at the surface of the metal. This can only occur when a part (in Case III, nearly all) of the molecules of the reagent which strike the surface of the solid phase fail to react with it, and hence remain in the solution. Now the frequency of the impacts will be proportional to the concentration of the reagent in the layer of liquid immediately adjacent to the solid, and the percentage of such impacts which result in reaction will, in a given case, be practically constant, independent of that concentration. It follows, therefore, that the rate of the chemical stage of the reaction will always be proportional to the concentration of the oxidizing agent in the layer of liquid which is in contact with the solid, that is, the concentration at the inner surface of the diffusion layer.

Our results seem to furnish no example of Case III, but it is clear that here, just as in Case I, the rate would be proportional to the concentration of the solution, for this is the same as the concentration at the surface of the solid, which, in turn, determines the rate.

It only remains to be explained why Case II\* shows the same behavior. As we have already shown that the rate must be proportional to the concentration at the surface of the metal, the problem resolves itself into proving that the concentration at the surface of the metal is proportional at every instant to the concentration in the solution. It is a simple matter to show that this is necessarily true except during a preliminary period of extremely short duration.

Let  $C_m$  represent the concentration of the oxidizer at the surface of the metal, and  $C_s$  its concentration in the solution. Further, let  $dm_1$  be the weight of the oxidizer diffusing to the metal during the time interval  $dt$ , and  $dm_2$  the weight used up during time  $dt$ .

The rate of the diffusion process is proportional to the difference in concentration on opposite sides of the diffusion layer. Hence

$$dm_1/dt = K_1(C_s - C_m),$$

\*Case II is evidently the general one, I and III being merely limiting cases.

and since the rate of the chemical reaction proper is proportional to  $C_m$

$$dm_2/dt = K_2 C_m.$$

Since a preponderance of either process tends to retard it and to accelerate the other, it follows that condition must sooner or later establish itself in which the rate at which the oxidizer is supplied is practically equal to that at which it is used up. Moreover, owing to the exceedingly small volume of the diffusion layer compared with that of the whole solution, this balance will be established almost instantly. Thereafter we can set, without any appreciable error,

$$K_1(C_s - C_m) = K_2 C_m,$$

whence

$$\frac{C_s}{C_m} = \frac{K_1 + K_2}{K_1}, \text{ a constant.}$$

That is, the concentration at the surface of the metal is proportional to that in the solution, which was to be proved.

The same reasoning must evidently hold for any reaction between a solid phase and a dissolved reagent, provided, of course, that the case is not complicated by secondary interfering effects, such as the formation of an insoluble product, or the occurrence of further chemical reactions in the solution. (See p. 329.) We may, therefore, conclude that *obedience to the equation for a reaction of the first order is to be expected in all normal cases of this type, quite irrespective of the relative rates of the diffusion process and the chemical reaction proper.* This feature of our experimental results is thus fully explained.

In the discussion of our results we have employed a hypothesis which is neither a part of the diffusion theory nor a necessary consequence of it, namely, the assumption that an increase in acidity tends to accelerate the chemical stage of the reaction. (See p. 315.) This may or may not be true in general, but seems to apply here, for the mutual relation of the velocities recorded in Tables VIII and XI (barring minor differences explainable by experimental error) is in qualitative agreement with what would be expected if increasing acidity accelerated the chemical reaction, the effect of increasing viscosity being to retard the diffusion process, as we have already seen.

Only one value, the one referred to above as exceptional, fails to conform to this explanation. This is the velocity for silver in chromic acid in the presence of 5 molar sulphuric acid, which is unexpectedly low, as the following comparison



shows: In ferric sulphate the ratio  $Cd : Ag$ , as would be expected, is lower in 5 molar than in 0.25 molar acid (1.42 and 2.48 respectively). In chromic acid, on the contrary, the corresponding ratios are 2.19 and 1.64, thus showing that the higher acidity has here failed to bring silver into closer agreement with the other metals.

We must not overlook the fact that from the standpoint of the diffusion theory alone there is no reason for regarding this particular value as anomalous. It becomes so only when considered in the light of that theory combined with our assumption concerning the effect of acidity upon the velocity of the chemical stage of the reaction. Whether this result is to be regarded as an exception to the rule assumed, or is, rather, to be ascribed to the effect of some unknown disturbing factor, is a question which can hardly be settled without more experimental evidence.

#### *The Influence of Adsorption.*

In discussing our experimental results we have thus far taken no account of the possible influence of adsorption effects. A supplementary hypothesis based on adsorption will now be briefly considered. It does not alter or supersede any of our previous conclusions, but is offered in order to show that a conception of the mechanism of heterogeneous reactions based on adsorption is not incompatible with the diffusion theory, but rather supplements it.

Our solutions contained in all cases free acid, usually in relatively large proportion, amounting in some instances to several hundred times the concentration of the oxidizing agent itself. Let us assume that the metal is covered by an adsorbed layer of molecules of sulphuric acid. Similar relations are to be understood for the hydrochloric acid used in the experiments with ferric chloride. Following the point of view suggested by Langmuir,\* we may imagine these acid molecules to form a layer, one molecule deep, in chemical combination with the outer layer of atoms of the metal, which by virtue of their position possess residual combining power. Since the hydrogen of the acid molecules will be virtually competing with the metal for the negative radical of the acid, this hydrogen will be rather loosely combined, and will undergo oxidation very readily.

The fraction of the whole number of what Langmuir calls "elementary spaces" so covered by adsorbed molecules will depend upon their concentration in the solution and upon the

\* Jour. Am. Chem. Soc., xxxviii, 1147, 1916.

nature of the metal, and is probably greater the more easily oxidizable, i. e. the more electropositive the metal. When this fraction is near unity the surface of the solid will practically consist of readily oxidizable hydrogen atoms which undergo immediate oxidation on suitable contact with a molecule of the oxidizer, so that the latter will be used up at the surface of the solid as fast as supplied by diffusion. This explains Case I. When the fraction is below unity the surface is only partly covered and some accumulation of the oxidizer at the surface results, the molecules which do not encounter active hydrogen on contact with the solid reacting slower, or not at all. This gives Case II, or, in the limit, Case III. The oxidation of the hydrogen of an adsorbed acid molecule is followed by the prompt escape into the liquid of the molecule of metallic sulphate or chloride so formed, since owing to the low concentration of that kind of molecules in the liquid they would be less strongly adsorbed than the acid molecules.

The fact that in Case II the observed reaction velocities for different metals follow the same order as the electromotive series can be ascribed either to the dependence of the amount of adsorption upon the electromotive behavior of the metal (see above), or to the influence of the secondary reaction, that is, the one which results when a molecule of the oxidizer finds its way into direct contact with the metal. This reaction may reasonably be assumed to be more rapid the more electropositive the metal.

The view that the velocity of the chemical reaction increases with the acidity, which we found it expedient to adopt in the general discussion of our results, would evidently be a necessary consequence of this adsorption hypothesis. Finally, since this hypothesis involves nothing to limit or alter the rôle of diffusion, the explanation, from the present point of view, of those phenomena which we have ascribed to the influence of diffusion calls for no change.

In short, it makes little difference here, in employing the diffusion theory, whether we consider the case from the standpoint of adsorption or not. In general, however, the combination of the two points of view should lead us farther than either one alone.

#### *Status of the Diffusion Theory. Normal and Abnormal Cases.*

An important result of this investigation is the proof of the existence of cases in which we are almost inevitably led to the conclusion that the reaction at the boundary surface is one of limited velocity. Opinions may differ as to whether these

cases represent real or only apparent exceptions to Nernst's hypothesis that the attainment of equilibrium at the boundary surface between two phases is practically instantaneous. It is after all largely a matter of definitions. The practical bearing of these cases, however, is obvious. They show that we can not assume, as an over-strict interpretation of Nernst's viewpoint might lead us to do, that every case in which different solids react at different rates with the same dissolved substance can be ascribed to some tangible and experimentally demonstrable interfering effect.\* If the cases in point are due to secondary interference it must be interference of a sort which only Maxwell's demon could recognize as not being a normal part of the mechanism of a reaction of the given type. In order to avoid such fine and elusive distinctions it is much better to admit the existence of phenomena which may or may not be theoretically equivalent, but are certainly practically equivalent, to a limited reaction velocity at the actual boundary surface.

What, then, is the status of the diffusion theory? It is evident that by this modification the diffusion theory loses a good deal of its simplicity and beauty, but its usefulness is not seriously impaired. We must now admit, as strictly normal, cases in which the influence of diffusion upon the observed rate of the reaction has any value between 100 per cent and zero. It may be that values close to 100 per cent will prove far more common in practice than lower ones, or, in other words, that Nernst's hypothesis is sustained much more often than it is contradicted, but its validity in a given case cannot always be assumed *a priori*.

Finally, in employing the diffusion theory we must be on our guard against cases in which the normal relation between diffusion and reaction velocity is disturbed by secondary interfering effects. Since it is desirable to be able to predict these exceptions in advance, a knowledge of the different known types, and of their specific effects upon the results, is important. The present investigation has furnished examples of four. These are

(a) Insolubility of one of the products of the reaction, with consequent formation of a coating on the solid phase.

(b) Occurrence of the reaction in two stages of which the second is of limited velocity and is not confined to the actual contact surface.

\* If, however, the solid is somewhat soluble in the pure solvent we are really dealing with a two-stage reaction, and agreement between the rates for different solids would not necessarily be expected, even when the second stage is instantaneous. (Example: Solution of different slightly soluble acids in the same dissolved base.)

(c) Passivity.

(d) Evolution of a gas.

These four types seem to include all that have thus far been reported.\* Of these, passivity is indicated by a marked dependence of the initial reaction velocity upon the preliminary treatment of the metal, and a two-stage reaction can be detected either by analysis of the solution or by the abnormally small effect of variation in the rate of stirring upon the observed reaction velocity.† Insoluble or gaseous products will usually show their presence by visible effects. All of these types of interference are of such a nature that they could generally be predicted in advance.

### Summary.

Measurements have been made of the rates at which different metals react with the same oxidizing solution in the presence of varying concentrations of free acid. The solutions used were (a) ferric sulphate and sulphuric acid, (b) ferric chloride and hydrochloric acid, and (c) chromic acid and sulphuric acid. The chief experimental results are the following:

1. When the acidity is sufficiently high, a number of metals give the same reaction velocity under like conditions, showing that diffusion is here the determining factor.

2. With decreasing acidity such agreement tends to disappear, and the observed velocities then depend upon the nature of the metal, the order being approximately the same as the electromotive series and the velocity greater the more electro-positive the metal.

3. The rate of the reaction in normal cases is proportional to the concentration of the oxidizing agent, not only under conditions where different metals give the same rate, but also where the rate depends upon the specific nature of the metal.

From these and related facts the following conclusions are drawn. They apply only to normal cases, that is, to those in which the progress of the reaction is not interfered with by mechanical effects, such as insoluble coatings and the like.

\* Nernst, in his "Theoretical Chemistry," 3d English Ed., p. 587, specifically mentions only the first two.

† An interesting case of a two-stage reaction is that of arsenic trioxide when dissolving in water. After dissolving as  $\text{As}_2\text{O}_3$  it undergoes hydration either in the solution or, possibly, as E. Brunner has suggested, wholly in the diffusion layer. This second stage is of course not detectable by chemical analysis. See Drucker, *Zeitschr. phys. Chem.*, xxxvi, 201 and 693, 1901; L. Bruner and Tolloczko, *Zeitschr. anorg. Chem.*, xxxvii, 455, 1903; E. Brunner, *Zeitschr. phys. Chem.*, li, 494, 1905.



4. The velocity of a reaction at the actual boundary surface between a solid and a liquid is not necessarily extremely rapid, even when there is no mechanical interference with its progress.

5. When a solid reacts with a dissolved reagent and the reaction velocity at the boundary surface is limited, a balance is quickly established between the consumption and the supply (by diffusion) of the reagent, such that its concentration at the boundary, under otherwise constant conditions, is always proportional to its concentration in the solution.

6. The rate of the reaction at the boundary surface may in some cases be low enough, compared with the rate of the diffusion process, to be an important, or even the predominant factor in determining the observed reaction velocity. A sound interpretation of the diffusion theory must take account of this possibility, which has heretofore been neglected.

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ART. XXXV.—*Sulphatic Cancrinite from Colorado*; by  
ESPER S. LARSEN and GEORGE STEIGER,\* U. S. Geological  
Survey.

A number of specimens of the uncomphgrite,† collected by the author (E. S. L.) from Beaver Creek, a tributary of Cebolla Creek, on the Uncomphgre quadrangle, Gunnison County, Colorado,‡ showed a small amount of a secondary mineral which could not be determined optically. A single specimen from the northeast slope, about 50 feet below the crest, of the hill that is surrounded by contour 8,500, and is about half a mile southeast of the mouth of Beaver Creek, was made up largely of a coarse-grained aggregate of this mineral. From this specimen material suitable for chemical and optical study was obtained and the mineral proved to be a cancrinite in which nearly half the  $\text{CO}_2$  was replaced by  $\text{SO}_4$ .

In the field this specimen was thought to be an altered uncomphgrite and the microscopic study confirms this. The specimen is made up in large part of the sulphatic cancrinite apparently derived from the original melilite, and contains also considerable apatite, perofskite, and perhaps melilite.

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

† Larsen and Hunter, *Journal Washington Academy of Sciences*, vol. iv, p. 473, 1914.

‡ This work was carried on as a part of the areal mapping of the Uncomphgre quadrangle, under the direction of Dr. Whitman Cross.

*Physical properties.*—The sulphatic cancrinite is nearly colorless; has a hardness of about 5; and fuses readily with intumescence. It is readily soluble in acid with effervescence and yields gelatinous silica on heating. The specific gravity is 2.443.

Optically it differs considerably from cancrinite; both minerals are uniaxial negative, but the mean index of refraction of sulphatic cancrinite is considerably lower than that of cancrinite, and the birefringence is much lower. The following data for sulphatic cancrinite are from the analyzed material. The different grains differ slightly—perhaps  $\pm 0.002$ —in index of refraction. The optical properties of cancrinite and natrodavyne are given for comparison.

Sulphatic cancrinite Colorado	Cancrinite	Natrodavyne
$\omega = 1.509$	1.524	1.522
$\epsilon = 1.500$	1.495	1.527
$\omega - \epsilon = .009$	.029	.007
Optical character +	+	-

Sulphatic cancrinite shows a poorly developed cleavage parallel to the prism faces; rod-like inclusions and negative crystals are commonly arranged parallel to the prismatic axis.

*Chemical Properties.*—The results of a chemical analysis made by George Steiger on carefully selected material which contained very little impurities are given in column 1 of the following table. Column 2 gives the combining ratios corre-

Analyses and ratios of sulphatic cancrinite and of cancrinite.

	Sulphatic cancrinite		Average of three cancrinites*		Cancrinite Litchfield, Maine †	
	Analysis	Combining ratios	Analysis	Combining ratios	Analysis	Combining ratios
SiO <sub>2</sub>	33.70	34.9	37.31	37.3	36.19	36.3
Al <sub>2</sub> O <sub>3</sub>	29.40	18.0	28.22	16.6	29.24	17.4
CaO	4.18	4.6	5.18	23.0	4.72	5.1
Na <sub>2</sub> O	18.52	18.7	16.88	---	19.20	18.7
K <sub>2</sub> O	1.45	1.0	1.74	---	.14	.1
H <sub>2</sub> O-	.72	---	---	---	---	---
H <sub>2</sub> O	4.24	14.7	4.53	15.1	4.15	14.0
TiO <sub>2</sub>	.07	---	---	---	---	---
CO <sub>2</sub>	3.18	4.5	5.89	8.0	6.11	8.4
SO <sub>3</sub>	4.65	3.6	---	---	---	---
SrO	.08	---	---	---	---	---
	100.19	100.0	99.75	100.0	99.75	100.0

\* One from Ditro, two from Brevik. † Steiger, analyst.

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sponding to this analysis and the succeeding columns give the analyses and ratios of typical cancrinites for comparison.

Little can be said regarding the chemical constitution of sulphatic cancrinite further than comparing it with cancrinite. The close agreement of its combining ratios with those of cancrinite, about half of the  $\text{CO}_3$  being replaced by  $\text{SO}_4$ , has suggested the name sulphatic cancrinite. No simple ratios appear in the combining equivalents of analyses of cancrinite. Clarke\* has applied the formula  $\text{Al}_2(\text{SiO}_4)_3 \cdot \text{Na}_4\text{H}(\text{AlCO}_3)$  to cancrinite, while Dana considers it to be represented by  $\text{H}_6\text{Na}_6\text{Ca}(\text{NaCO}_3)_2\text{Al}_8(\text{SiO}_4)_6$ . Clarke considers part of the groups  $-\text{Al}=\text{CO}_3$  to be partly substituted by  $-\text{Al}=\text{SiO}_3$  and some of the soda replaced by lime. The formula of cancrinite is evidently complicated, our present knowledge throwing but little light on its constitution, and were it not for the well-defined crystallographic properties of the mineral suspicion might point to its lack of homogeneity.

*Conclusion.*—The data as yet available are not sufficient to show clearly the relation between cancrinite and sulphatic cancrinite. That the two are closely related, both the chemical and optical properties show rather conclusively and they may form a complete isomorphous series from normal cancrinite to a mineral in which all the carbonate is replaced by sulphate. The sulphatic cancrinite described in this paper contains nearly equal parts, molecularly, of  $\text{SO}_4$  and  $\text{CO}_3$  and may represent an intermediate compound having the same relation to the end members as diopside has in the pyroxene group.

Sulphatic cancrinite has a much lower birefringence than cancrinite and it is not unlikely that a member of the group somewhat richer in sulphate has zero birefringence and that the pure sulphate member is optically negative.

\* Clarke, F. W., The constitution of the silicates, U. S. Geol. Survey Bull. 125, p. 23, 1895.

ART. XXXVI.—An Early Pliocene One-Toed Horse, *Pliohippus tullianus*, sp. nov.; by EDWARD L. TROXELL.

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- I Introduction.
- II *Pliohippus tullianus* sp. nov.
  - The teeth.
  - Skull.
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    - Ramus, atlas and axis.
  - Fore limb.
    - Radius and ulna.
    - Metacarpals.
    - Third phalanx, hoof.
  - Measurements.
- III Geology of the Oak Creek formation.
  - Character of the deposits.
  - Associated fauna.
  - Age of the beds.
- IV General Conclusions.

I INTRODUCTION.

NINETY years ago the first fossil horse was discovered in America, but not until 1856, when Dr. J. W. Leidy described the type of *Protohippus perditus*, did the presence of a race of extinct horses especially attract the attention of anyone. For the last half century the interest in these animals has been steadily growing and in very recent years expeditions have been sent out for the single purpose of securing their skeletons.

The discovery last summer of a skeleton in the Early Pliocene, with but one toe on each foot, yet allied to the protohippine horses which are known to be mostly tridactyl, furnishes a new type of more than ordinary importance. The species is described at this time as a matter of expediency, under the genus *Pliohippus* Marsh, in order not to encroach upon Professor Osborn's revision of the horses which is about to be published.

It gives me pleasure to name the new species in honor of Professor Richard S. Lull of Yale. *Pliohippus tullianus*, then, sp. nov. is the chief subject of this paper.

The list of those who contributed to the success of the summer's expedition or who have aided in the preparation of this article is even longer than can be recorded here. The Rev. A. B. Clark of Rosebud took an interest in my work and directed me to the region where the specimen was found. Professors E. C. Case, H. H. Bartlett and Dr. F. E. Robbins, of Michigan University, have examined my manuscript and their kindly criticisms have been invaluable. Dr. W. D. Matthew and



Professor Lull have generously helped me in many ways, especially in the beginning of the work. Professors Schuchert and Osborn very kindly allowed me to study the material in their respective museums.

## II *Pliohippus lullianus* sp. nov.

The specimen here described was the skeleton of a young colt about ten months old. The milk teeth are all visible and some are slightly worn; the first permanent true molar is well formed and about ready to be cut—it has, however, no apparent cement. The loose epiphyses and the incompletely ossified bones also attest the immaturity of the individual.

*Vestigial teeth.*—The canine teeth of both the upper and lower series are scarcely so large as the lead of a pencil, diameter  $1.3^{\text{mm}}$ , but are about  $7^{\text{mm}}$  in length. In life it is quite probable that they did not appear above the gum, but lay along the alveolar border and, of course, were not functional. The first deciduous molar, commonly called the wolf tooth, in the upper jaw is large,  $17^{\text{mm}}$  antero-posteriorly, and in a later stage of wear might have been functional. The corresponding tooth in the lower jaw, like the canines, is vestigial; it measures  $1.5^{\text{mm}}$  in diameter and standing erect in front of the larger tooth, protrudes  $2^{\text{mm}}$  from the bone. The length, root and all, is about  $7^{\text{mm}}$ . This tooth is not quite so large as one from a small skull of *Mesohippus*; the latter has a distinct crown, while in the former the diameter is uniform throughout.

*Permanent molars.*—Two uncut, permanent molars were secured, one upper and one lower. Although the upper molar is broken, it shows well certain characters which will be diagnostic of the species. The crown in its present development is less than  $40^{\text{mm}}$  long; it is slightly curved antero-posteriorly, but the pronounced transverse curve of the horses' teeth of that period is not conspicuous; however, since the tooth is not fully formed this observation may be of less importance.

The diameter of the tooth at the crown, measured over the styles, is  $30^{\text{mm}}$ ;  $1^{\text{cm}}$  lower it is  $27^{\text{mm}}$  and here the width across mesostyle and protocone is  $25^{\text{mm}}$ . With still further wear the longitudinal diameter would become less than the transverse. The lakes are broad and very simple in pattern; the horns are quite long and smoothly curved, while the enamel in places is very thick. The protocone, which does not extend anterior to its junction with the protoconule, is very long ( $10^{\text{mm}}$ ), but rather narrow transversely ( $5^{\text{mm}}$ ). The sides are parallel for quite a distance, making it unlike the round or oval cone of *Protohippus*. There is a sharp, thin fold, the plicaballum, between the protocone and the metaconule, which is commonly

seen in *Equus* but not in *Asinus*. The parastyle is broad, nearly 4<sup>mm</sup>, and has two sharp corners; the mesostyle is sharp but not prominent, while the metastyle is merely the rounded corner of the tooth.

The first true molar of the lower jaw was preserved in good condition, but it had not attained its full development. It is thin, the width being but one-third the antero-posterior diameter (30<sup>mm</sup>) at the crown; in this respect and also in the great inner extension of the parastylid, it resembles the three-toed horses. In the new species there is no well defined keel or loop antero-exterior to the protoconid. An inconspicuous groove separates the metaconid from the metastylid; it is sharp but not deep and fades out after running slightly more than half the length of the crown. This is like *Protohippus* and results from the narrowness of the metaconid-metastylid column (10<sup>mm</sup>) and its nearness to the protoconid and hypoconid; the latter are about equal in size. Near the root the entostylid blends into the entoconid and here the longitudinal diameter of the tooth is reduced to 25<sup>mm</sup>. There is no cement on the tooth.

*Skull*.—The antero-orbital fossa shows distinctly the lachrymal and malar parts which are commonly seen in Pliocene horses. Although they form a continuous cavity, the two pits are separated by a faint ridge running from the infra-orbital foramen and the posterior border consists of two distinct, overhanging shelves.

The presence of a large depression in this region precludes the possibility of long crowned teeth like those of the modern horse, for both would have to occupy the same space. The exact purpose of this pit is not known, but it is generally thought to have been the seat of a scent gland, which, like the larmier of the deer, was peculiar to animals living in a wooded or hilly country. Presumably, as the horses came to live on the open plains they had less need for such a device to assist in recognizing members of the race, but they had greater need for the long grazing teeth; so that in later generations the pit gave place to the longer crowns, while the increased range of vision in the open country made it no longer necessary to depend on the sense of smell. Even in the life of the individual it is possible that the pit became somewhat obliterated as the lengthening of the skull made room for the incoming molars; we find the lachrymal and malar pits seemingly best developed in young animals. According to Owen (*Anat. of Verts.* III, pp. 633) the presence of the "maxillary" pit in the antelope is associated with those animals which go in pairs.

It has been suggested that the antero-orbital pit may have marked the insertion of a muscle in an animal with a rather

long proboscis, but this seems very doubtful. In the present specimen the bone is thin and its surface is smooth; generally a place of muscle attachment is rugose, thick and porous. The

FIG. 1.

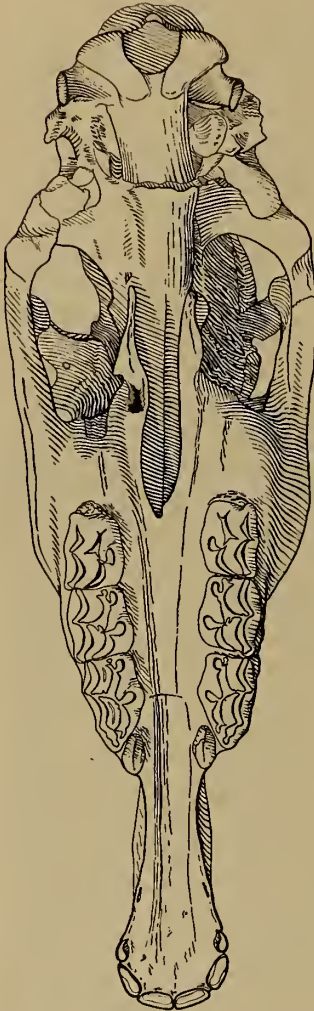


FIG. 1. SKULL. Ventral view. One-third natural size.

FIG. 2.



FIG. 2. SKULL. Side view, showing large pre-orbital pit. One-third natural size.

facial pits and narrow muzzle give the skull a very thin appearance above and in front of the molar teeth. In a mature specimen the region in front of the orbit would have been much longer, in order to furnish room for the six permanent molars instead of the three deciduous ones.

The antero-orbital pit is of little value as a means of identifying the species, the genus, or even the sub-family, for it seems to be a variable feature depending on age or sex. We find both portions well developed in *Protohippus* and *Merychippus*

FIG. 3.



FIG. 3. RAMUS. Side view. One-third natural size.

FIG. 4.

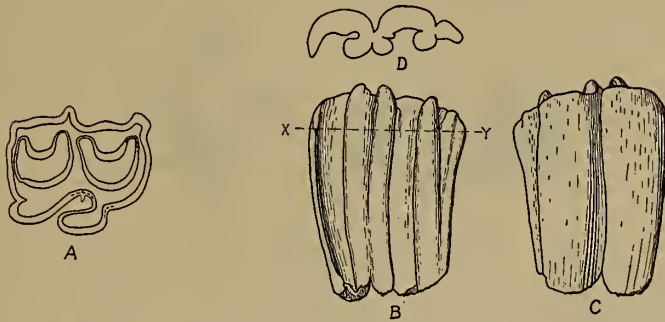


FIG. 4 PERMANENT MOLARS. Two-thirds natural size.

A, a section 1<sup>cm</sup> from the crown of first true, upper molar. B and C, inner and outer side views of first true, lower molar. D, a section on line, X-Y, of B.

and the lachrymal pit is even conspicuous in some of the Anchitherinae, especially in that aberrant form, *Hypohippus*.

On its lower border the ramus has a single large curve in front of the angle; it is like that of *Asinus* and *Hippanion*



rather than *Equus*, but in the present specimen it may be a character of youth. In the atlas the anterior notch is not closed to form a foramen, in which respect it resembles the more primitive forms. Likewise the intra-vertebral foramen in the axis is not inclosed, showing that it is either primitive or immature.

*Fore limb.*—The bones of the limb are very slender. In length the cannon bone nearly equals that of *Equus scotti*, but

FIG. 5.

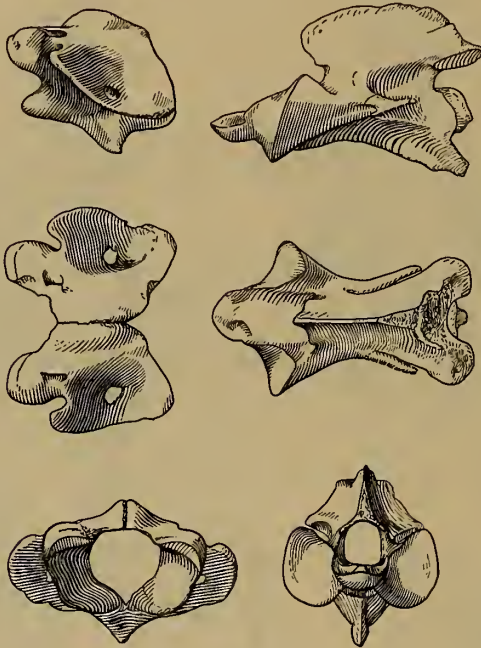


FIG. 5. ATLAS AND AXIS. Lateral, dorsal and anterior views. One-third natural size.

the width is scarcely more than half as great. The distance from the hoof to the elbow, which constitutes about half the height of a horse, in the new species is 23 inches; therefore the whole height is approximately 3 feet and 10 inches. Since the scapula and humerus are not so long relatively, this dimension may be less.

It is important to note that the distal segments, especially the cannon bones, are long, suiting the animal to greater speed, and here may be seen evidence that the race had changed its

habitat. Slenderness and lightness in general are cursorial adaptations to the needs of the individual; for instance, where food and water are scarce the animal has to go farther to satisfy its wants. Moreover, life in the open country was imperilled by preying animals and the little horses had less opportunity to hide and dodge about among bushes or over hilly country; to offset this disadvantage they had to be able to outdistance any pursuers.

Aside from the actual rate of speed, the long-limbed animals seem to be better suited to long continued effort. The slenderness of the cannon bone sometimes goes beyond the point of fitness for speed; the Arab, which is probably our swiftest horse, has only a moderate speed index: 7.26; on the other hand the ass, with a higher index: 8.68, is noted for its endurance but not for its actual speed. It is equally true that where food is scarce nature has to economise, hence the slender, small-boned type is better suited to the environment where less material is available for building up the frame.

As a matter of fact the limbs of *Plihippus tullianus* are not out of harmony with the general build; it stands three feet and ten inches, while an ordinary horse may be five feet high. The linear dimension of the former is  $\frac{3}{4}$  that of the latter; if all the proportions are the same the relative weights would be as the cubes of 3 and 4, that is as 27 and 64; the larger horse would weigh over twice as much and would therefore need greater strength of limb. However, the present specimen, being a colt, does not show the development of the adult, so it is quite probable that later the bones would have increased considerably in diameter, while changing only slightly in length.

*Radius and ulna.*—A unique feature in this one-toed horse is the complete ulna, separate throughout from the radius. As in the modern horse, the proximal and distal portions serve as part of the articulations; unlike it, the middle portion is not fused to the radius but lies along its posterior surface, a mere remnant of a former functional member.

The shaft of the ulna in its smallest part is 2<sup>mm</sup> wide and a little more than half as thick. The distal epiphysis is a long segment (3.4<sup>mm</sup>) which joins the shaft well above the epiphysis of the radius and conforms to the contour of the latter. The radius is quite slender through its middle portion, but the ends are large; the junction planes of the epiphyses mark the largest parts. The form would change somewhat with age as the shaft fills out to correspond to the heavier joints.

*Metacarpals.*—The especial character which distinguishes this specimen is its monodactyly. It has commonly been predicted that one-toed specimens of the Protohippinae would be

Measurements of the Radius.	
Shaft ant-post.....	17 <sup>mm</sup>
Proximal and ant-post.....	33
Distal end ant-post.....	40
Shaft transverse.....	24
Proximal end transverse.....	58
Distal end transverse.....	56
Length.....	263

FIG. 6.



FIG. 6. RADIUS AND ULNA. Rear, side and front views. One-third natural size.

found, but no positive evidence of this feature has, heretofore, been presented.

The splints, Metacarpals II and IV, unlike those of *Equus* extend the lengths of the cannon bone, but like those of the modern horse they bear no digits on the ends. These slender

bones are large proximally, but at once decreasing in size they run at a uniform diameter to the middle; in the next fourth of the distance they decrease to a width of about  $3^{\text{mm}}$  and a thickness of less than  $1.5^{\text{mm}}$ . The distal ends are enlarged to

FIG. 7.

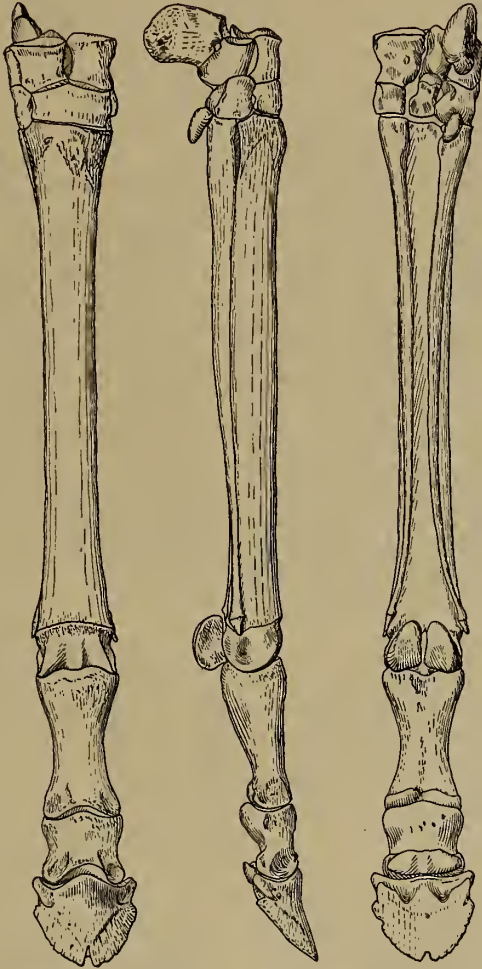


FIG. 7. RIGHT MANUS. Front, side and back views. One-third natural size.

receive the pointed epiphyses, the larger one of which measures  $6^{\text{mm}}$  in length. They show no evidence of articular facets; in fact their very sharp ends eliminate the possibility of their ever having borne phalanges.



Metacarpal IV has a diameter greater by 1.5<sup>mm</sup> than that of II. This difference in size is the character upon which Marsh sought to found *Plihippus gracilis*, but the species has been ruled out (Lull, Gidley) and the feature upon which it had been established is considered of little importance except as it signifies the unsymmetrical reduction of the foot. The dissymmetry of the foot is also shown by the presence of a small nodule of bone representing the fifth metacarpal; while on the other side the remnant of metacarpal I is not even positively known in the earliest forms of *Eohippus*, showing that the first digit was much more progressive in its reduction. The vestigial metacarpal V has two articular facets joining it with the unciform and metacarpal IV. It harps back to the period of *Eohippus*, when for the last time the front foot bore the phalanges of a fourth toe.

*Third phalanx.*—The hoof of *Plihippus lullianus* is very flat, especially in comparison with that of *Equus scotti* or *E. caballus*. The angle of the front slope in the new type is about 27½° and in this respect approaches that of *Mesohippus*: about 22½°. In *Equus* this angle measures over 45°. The feet have a different structure as a result: in *P. lullianus* and the earlier genera the second phalanx hangs on the back of the hoof with no part of the articular surface horizontal, while in the modern genus a part of the weight transmitted falls directly upon the hoof bone, a device better suited to the greater weight. The cleft in the anterior border of the ungue of the new type is a very primitive feature, one not found in *Equus* but common in the earlier forms.

Measurements in millimeters:—

Cannon bone	<i>Asinus</i>		<i>P. lullianus</i>		<i>E. scotti</i>	
		ratio %		ratio %		ratio %
Width distal .....	35.8	84	30	52	57.7	
Diameter of keel, ant-post. ....	27.8	94	26	61	42.7	
Shaft transverse .....	22.0	86	19	46	41.0	
Proximal width .....	38.5	88	34	59	57.3	
Proximal ant-post. ....	25.3	99	25	60	41.5	
Length .....	191.0	115	219	90	244.0	
Speed index .....		8.68		11.53		5.95

First phalanx		<i>P. lullianus</i>		Second phalanx		<i>P. lullianus</i>	
Proximal width .....	32			Proximal width .....		31	
Distal width .....	29			Proximal, ant-post. ....		20	
Shaft width .....	19			Length .....		26	
Proximal, ant-post. ....	25						
Shaft, ant-post. ....	12			Third phalanx, hoof			
Length .....	56			Altitude .....		20	
				Width .....		40	
				Length .....		36	

Comparative measurements of types: *P. lullianus* nov. *P. pernix* Marsh

		ratio %	
Ant-post. diameter of wolf tooth.....	16	81	13
Ant-post. diam. of first upper true molar	27	81	22
Ant-post. diam. of second deciduous molar	36	86	
“ “ “ “ premolar ----			31
Extent of four upper deciduous molars .	107	82	
“ “ “ “ premolars.....			88
Extent of three lower deciduous molars.	89	83	
“ “ “ “ premolars .....			74
Length of radius.....	263	96	253
Width of proximal end.....	59	83	49
Width of articulation, distal.....	44	81	40
Length of cannon bone.....	219	86	189
Length of first phalanx.....	56	98	55
Length of second phalanx.....	26	96	25
Length of hoof bone.....	36	106	38
Width of hoof.....	40	125	50
Length of skull.....	380	108	410

### III. *Geology of the Oak Creek Formation.*

The skeleton of the new type was found in the eastern part of the Rosebud Indian Reservation, near the town of Mission, South Dakota. This Reservation, at least the western part in the Miocene formation of the valley of the Little White River, has long been a favorite hunting ground for specimens of extinct animals.

The region east of Mission is slightly rolling but a very fertile farming country. Because it is so productive of vegetation, it was generally considered an unprofitable place to hunt for fossils, for only at infrequent intervals along the crests of the hills is the bed rock of the later formations well exposed. Most of this land has been allotted to the Indians, whose present peaceful life is in great contrast to that of the time of Marsh and the other early explorers.

A table land, whose northern escarpment extends in a direct line for quite a distance and rises about 200 feet above the valley floor, forms a divide between the Keyapaha and the valley of Oak Creek. In nearly every direction the flat topped hills can be seen, all apparently conforming in height.

Few geologists have visited this area, but one, A. B. Reagan,\* while carrying on his missionary work among the Indians, paid much attention to the earth formations and collected many

\* Albert B. Reagan, *American Geologist*, vol. xxxvi, pp. 229, 1905.

fossils. He identified and described the Miocene formation, but in the region east of his district he erroneously assumed that the rocks were of Cretaceous age; the fact is that a later formation exists there and the fauna indicates the Early Pliocene.

The rock is entirely of sandstone and most of it is very fine-grained. The variety of the grains, their rounded form and the absence of larger components, suggest the probable eolian origin of the formation, although the sand was shifted and finally deposited by running water. The lower strata are much harder because the grains are much more firmly cemented together; the rock of the main quarry, on the other hand, is not so compact, but is soft enough to be cut with a knife. Under the microscope the cementing substance, which in this case is calcium carbonate, has a filmy appearance and incompletely fills the open spaces between the grains of sand. Where the sandstone is very indurated it stands out in bold cliffs, and boulders of considerable erosional resistance cover the slopes. The alternate harder and softer areas give rise to differential weathering and in some places result in deep natural caves. That this formation was built up by a stream is quite certain, for the sand, the irregularity of the bedding planes, the discontinuous layers, the water-worn bones and the posture of the complete skeleton, all show this.

In one of the canyons there appeared to be an irregular line marking the boundary of an unconformity and at the bottom of the *P. lullianus* quarry itself, there was a floor of hard sandstone only a few inches beneath the complete skeleton. There was also other vertebrate material, consisting mostly of teeth and small bones, resting on this floor or only an inch or two above it. The peculiar association of this fragmentary material, most of which was water worn, with the complete skeleton, suggests the secondary deposition of these broken parts along with the original deposit of the whole skeleton. The same torrent which washed out and broke up the other bones, once buried, may have engulfed the colt which is now the type of the new species. There is a strong probability that this less consolidated formation is a channel deposit, resting upon and within the Upper Miocene or Earliest Pliocene, but itself of later age, for we frequently find patches of a later formation occupying the old valley of some prehistoric river. Since the Pliocene is commonly considered a period of uplift and also of semi-arid conditions, there would be few streams and no great amount of stream action; we, therefore, consider this one of the rare deposits representing the period.

*Associated fauna.*—Rhinoceroses are represented by fragments in the quarry and by more complete bones in the neigh-

boring outcrops. They are abundant in the Lower Pliocene but in all probability soon became extinct. At this time they seem to have reached their maximum size and are probably best known by the specimens, from Long Island, Kansas; *Teleoceras fossiger* (Cope) seems very close to the variety with short stout limbs represented in the Oak Creek locality.

Ivory from the main quarry, together with parts of tusks and skeletal material from near-by places, shows the presence of a very large proboscidian in the fauna. It may represent any one of several types of Mastodon, which in the Early Pliocene reached a very great size.

An incomplete skeleton of *Merycodus* sp. was found an eighth of a mile away and about seventy-five feet lower than the stratum bearing the horse skeleton. This genus is well known in the Miocene and Lower Pliocene and is rather common. There is a general resemblance in all these forms except that some are almost twice the size of others. The present specimen is one of the largest known to the writer and is, therefore, assumed to be a very late form. It is more than a third larger than the type of *M. neotatus sabulonis* of Matthew and Cook\* and is twice the size of their smallest specimen: *Merycodus* sp. indesc.; it is also 1/7 larger than the type of *M. osborni* (Matthew). Merriam reports† *Merycodus* from the California Pliocene or Late Miocene, and in size the specimen from the Tejon Hills is quite equal to that from South Dakota.

The absence of *Merycodus* in the Blanco of Texas is taken as an evidence that the formation is distinctly more advanced than most Pliocene deposits. Scott says "these peculiar hypsodont deer persisted even in the Older Pleistocene," but most authors do not credit them with such a long existence. Osborn reports this animal mostly in the Lower Pliocene and it seems quite probable that this was near the close of their career.

The single molar tooth of a grazing camel gives no trustworthy evidence as to the definite age of the formation, for these camels are very abundant in the Upper Miocene and continue on until the Pleistocene.

In this single locality three-toed horses of the *Protohippus* and *Hipparion* type were found, in addition to the new species. Of the true *Protohippus* both large and small species were represented. Three miles from the main quarry, an almost complete specimen was found which resembles *Protohippus placidus*, especially in its size. The association of feet

\* Matthew, W. D., Cook, H. J., Bull. Am. Mus. Nat. Hist., vol. xxvi, pp. 412, 1909.

† Merriam, J. C., Univ. Cal. Publ., Bull. Dept. Geol., vol. viii, No. 13, pp. 287, 1915.



and teeth render it of unusual value for comparative study. *P. placidus* is usually found in the Mioocene, and this small horse, without the malar pit and with semi-functional lateral toes, shows characters seemingly too primitive for the Pliocene period.

The fauna of this Oak Creek formation corresponds closely with that of the Snake Creek Beds of Western Nebraska; the latter, though resembling the Republican River Beds of Western Kansas, show a more modernized type of animal life and are considered by Matthew and Cook to be intermediate between the Blanco of Texas and the Upper Mioocene. The Oak Creek formation, while in some respects like the Etche-goin of California, Middle Pliocene, is not so far advanced and in all probability belongs to the Early Pliocene.

#### IV. *General Conclusions.*

*Pliohippus lullianus*, the earliest one-toed horse now known, is here made the type of a new species. It is tentatively assigned to *Pliohippus* Marsh, awaiting the final settlement of the status of that genus, which, founded upon an imperfect specimen, has been alternately accepted and rejected.

Observations by Merriam, Osborn, Lull and others, point to the protohippine horses as the group from which the modern race was derived, and it is probable that *Pliohippus lullianus* sp. nov. was near if not directly in the ancestral line. Through its unique characters it seems to offer the connecting link between its three-toed ancestors and the monodaetylous *Equus*.

The fauna indicates that the age of the beds, from which the new type came, is Early Pliocene, a period of grass-covered plains. Because the climate was semi-arid and there was little stream action, the deposits of that period are rare and at the present time are nearly always hidden beneath the luxuriant vegetation of the region.

ART. XXXVII.—*The Igneous Geology of Carrizo Mountain, Arizona,\** by WILSON B. EMERY.

DURING the Summer and Fall of 1913, while employed as a field assistant by the United States Geological Survey, the writer had the opportunity of carrying on, under the direction of Professor Herbert E. Gregory, the first detailed geologic investigation ever made of Carrizo Mountain, Arizona. Reconnaissance studies had been previously made by W. H. Holmes in 1875† and in 1909 by Professor Gregory in connection with his work on the Navajo Reservation.‡ During his brief sojourn in the area Professor Gregory noted the main features of the geology and it was because he thought them of sufficient importance to repay detailed examination that the work during the season of 1913 was undertaken by the writer. The results of these studies, in so far as they concern the igneous geology, are here briefly presented.§

*Location.*

Carrizo Mountain is located on the Navajo Indian Reservation in the extreme northeastern corner of Arizona. The area of which it is the central feature, and which is discussed in this paper, lies for the most part within Arizona (see map, fig. 1), but embraces also a strip of country about three miles wide across the border in New Mexico. Rising as it does 2000 to 3000 feet above the surrounding plain (fig. 2), "an igneous island in a sedimentary sea," Carrizo Mountain forms a prominent landmark visible for miles in every direction, except to the south where the view is interrupted by the Boundary Mountains.

*General Features of the Igneous Geology.*

The evidences of igneous activity are now preserved in the Carrizo district in the form of various intrusive bodies, sheets, sills, dikes, and the main large intrusion, a laccolith. It is inferred, however, from the presence of a series of six volcanic plugs just southeast of the mountain that igneous activity was not confined to intrusion but manifested itself as well in extru-

\* Published by permission of the Director of the U. S. Geol. Survey.

† Holmes, W. H., U. S. Geol. and Geog. Survey Terr., embracing Colorado and parts of Adjacent Territory, 1877, pp. 274-276.

‡ Prof. Paper, U. S. Geol. Survey, in preparation.

§ The results of the entire investigation, embodied in a report, constitute the thesis submitted as partial fulfilment of the requirements for the degree of Doctor of Philosophy at Yale University.

FIG. 1.

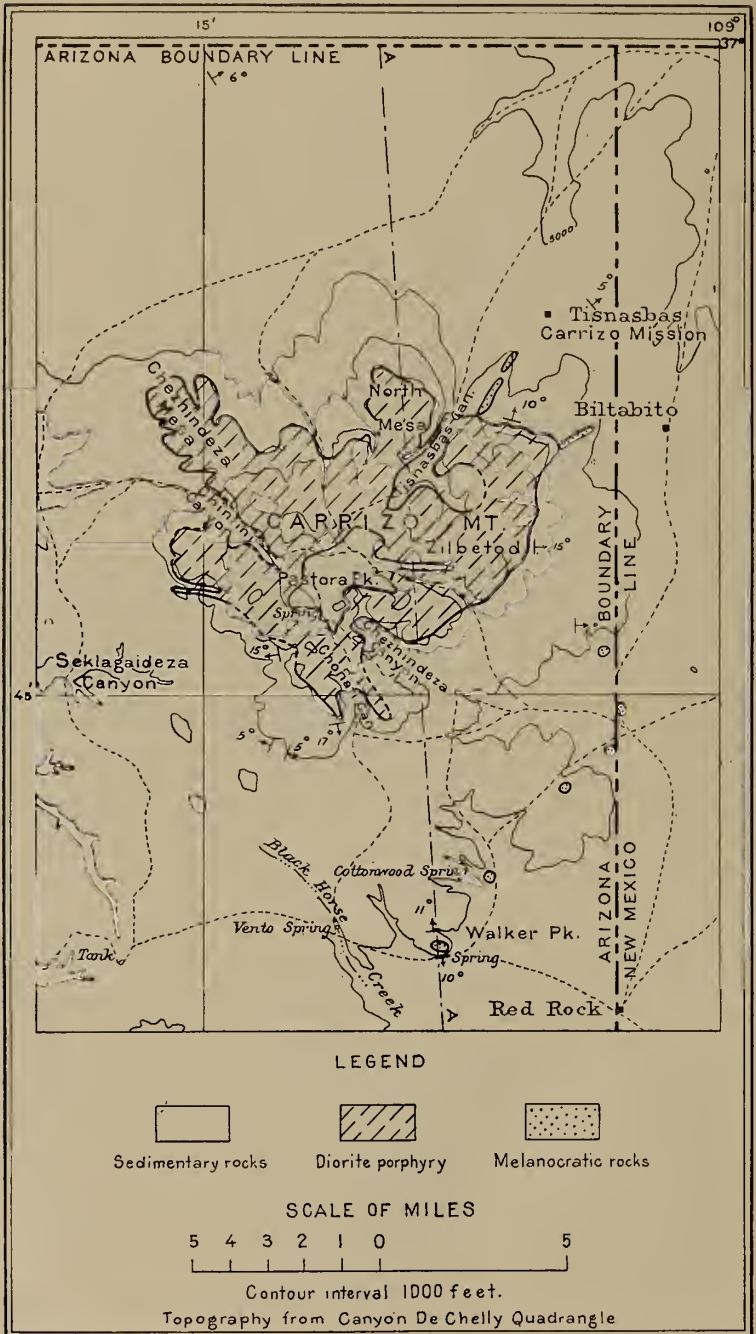


FIG. 1. Geologic map of the Carrizo area.

sion, though all evidence of possible outflows has been completely removed by erosion. The relation of the igneous rock and the surrounding sedimentary beds which range from Triassic to Upper Cretaceous in age is shown on the accompanying map (fig. 1).

*Major intrusion.*—The major intrusion which has produced the marked upturning of the surrounding sedimentary beds is only poorly exposed. There are a number of large outcrops but they are isolated and not traceable, the one into the other, because of the covering of sediments. Consequently the nature of the intrusion is with difficulty ascertained. Indeed, from the appearance of the outcrops, which are in many places very steep-walled, it would seem that there was not one large intrusion but several smaller ones which had united to produce a single result,—domal uplift. There is no reason to doubt that whether of one large intrusion or several smaller ones, the outcrops represent a single period of igneous activity, and that the magma came from one common reservoir.

*Sills and sheets.*—On the north of the mountain and dipping from it at an angle of about  $15^{\circ}$  is an intrusion of sill-like form entirely confined within the base of the Upper Jurassic (?) sediments. This sill, which has been called the Tinasbas sill, from the canyon of that name where it is best exposed, is somewhat thicker at its innermost margin, where it is seen in connection with

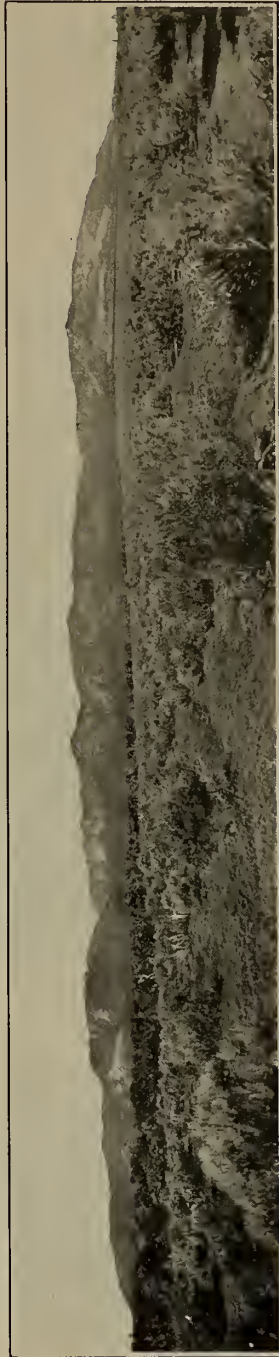


FIG. 2. View of east side of Carrizo Mountain.



its source of supply, than at its outer edge, so that it might be considered a flat laccolith. However, as it is only 300 feet thick at its deepest point, it has been deemed best to call it a sill.

West of North Mesa and between it and Chezhindeza Mesa, there is exposed a mass of igneous material having exactly the same relations to the enclosing beds as the Tisnasbas sill. It is

FIG. 3.



FIG. 3. Holmes Dike.

possible that this is an entirely separate intrusion, but because of the very similar character it is thought to be a portion of the Tisnasbas sill, though the connection is not visible due to the overlying mass of North Mesa.

Intrusive sheets cap both North and Chezhindeza mesas and overlie unconformably sediments of Upper Jurassic (?) age. The sheets evidently are offshoots from the main intrusion and between them and the Tisnasbas sill and its extension the sediments are pinched out. This was noted by Holmes, who says:

“It does not appear to me that the beds of sandstone that occur between the inner mass and the flexed sheets are of uniform thickness. Between the capping of the North Mesa and the inner mass the sandstones are nearly pinched out. They are so obscured by debris that I could not determine their exact relation.”\*

*Dikes.*—The few dikes seen in the Carrizo area, with the exception of that forming Zilbetod peak, are arranged about

FIG. 4.



FIG. 4. Walker Peak, a volcanic neck.

the periphery of the intrusions. Of these, Holmes dike, near the mouth of Tisnasbas Canyon, is among the most prominent. It rises about 200 feet above the creek bed and when seen end on, as in fig. 3, where its continuation northward is not evident, has the appearance of a volcanic plug. Another large dike trends outward from the mountain in the direction of Biltabito store. Other smaller dikes are present both east and west of the mountain and each volcanic plug has an encircling

\* Holmes, W. H., *op. cit.*, p. 275.

group of radiating dikes. In these dikes the rock is soft yet more resistant to erosion than the enclosing sedimentary beds, so that in every case the dike stands up as a wall of greater or less height.

*Volcanic plugs.*—A series of six volcanic plugs is exposed southeast of Carrizo Mountain. When these are joined together they are seen to be arranged on a very flat reversed curve about 20 miles long. Such linear arrangement suggests the presence of a fault as a line of weakness favorable for intrusion, but no movement of that character was recognized. These plugs are rather prominent features of the landscape, standing out dark against the red or light-colored sandstones at their base. They are all of the same character, Walker Peak (fig. 4), the southernmost one, being typical, rising conical at the base but terminated above by cliffs 100 or more feet high.

### *The Petrography of the Intrusions.*

#### Diorite Porphyry.

*Occurrence.*—The central mass of Carrizo Mountain is of diorite porphyry, as are also the sheet-like intrusions associated with it. The porphyry, which is exposed in all the canyons and in many other places on the mountain summits, covers an area of over 100 square miles. Holmes, in speaking of the intrusions and the mountain resulting from them, says

“It is a typical example of the eruptive groups of this part of the Colorado plateau . . . . It has a nucleus of its own, and so far as the surface is concerned is independent of all other eruptive masses. . . . . The trachytes [diorite porphyry of this report] are now found chiefly in contact with the Lower Cretaceous [now referred to the Jurassic] and Jura-Trias rocks, for the reason that the Middle Cretaceous shales, in which a large part of the trachyte was originally deposited, have been completely carried away, leaving only small fragments imbedded in the faces and upper surfaces of the trachyte.”\*

*Macroscopic description.*—In the hand specimen the diorite porphyry shows an abundance of plagioclase phenocrysts and less numerous prisms of hornblende set in a white to grayish, aphanitic groundmass. Quartz phenocrysts are not uncommon. With regard to the megascopic character of the rock Holmes says:

“A specimen of trachyte from West Mesa is found to resemble closely in appearance and composition the trachyte of the other groups of the southwest. It has a bluish white paste, which con-

\*Holmes, W. H., U. S. Geol. and Geog. Survey Terr., embracing parts of Colorado and adjacent territory, 1875, p. 274.

tains the following minerals porphyritically embedded: fine crystals of translucent oligoclase, minute crystals of sanidite, frequently associated with the oligoclase, small crystals of biotite (rare), and a few small enclosures of quartz.”\*

Cross later studied the very specimens collected by Holmes, of which he says:

“Three specimens from the Carrizo Mountains, collected by Holmes, have been examined by the writer. They are all hornblende-porphyrates, almost identical in character with those of the El Late group. There are abundant phenocrysts of black hornblende and plagioclase, 1 to 5 millimeters in length, in an even-grained groundmass, chiefly made up of quartz and orthoclase. Biotite is rare or wanting. Quartz phenocrysts were not seen.”†

Both Holmes and Cross have brought out the similarity of the rocks constituting the numerous laccolithic intrusions of

FIG. 5.

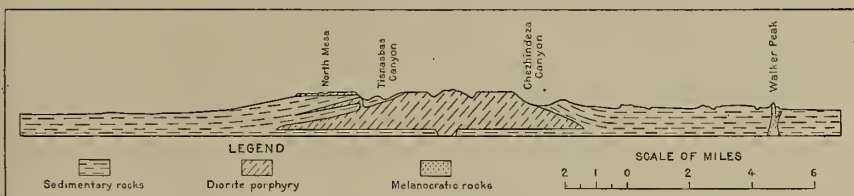


FIG. 5. Structure section across geologic map on line AA.

the Southwest. The writer wishes to further emphasize this similarity. So closely does the description of the rock of the Henry Mountains, given by Cross, correspond to the diorite porphyry of Carrizo Mountain, that his description might be employed here with only minor changes.

*Microscopic description.*—In thin section the rock is seen to consist of phenocrysts of plagioclase and hornblende set in a groundmass of quartz and orthoclase. Phenocrysts of quartz were observed in a number of slides, biotite in one. Iron ore is present in two generations in some places; in all slides it is seen in the groundmass. Apatite is a constant accessory and titanite is not uncommonly present. A few small crystals of zircon were noticed.

Hornblende is of the common, green, strongly pleochroic type. In some places, however, it is rather light in color.

\* Holmes, op. cit., p. 275.

† Cross, Whitman, *The Laccolithic Mountain Groups of Colorado, Utah, and Arizona*, 14th Ann. Rept., U. S. Geol. Survey, Part II, 1895, pp. 210-211.



The extinction angles are slight,  $8^{\circ}$  from the cleavage lines, on the face 010. Twinning parallel to 100 is common. Zonal development is shown in a number of crystals and in some, resorption. Euhedral outlines are well displayed. In some places, the outline is completely preserved by the alteration products; in other places the outline is merely indicated by the few remaining shreds of the unaltered mineral. Alteration to chlorite and calcite, less commonly to epidote, takes place.

The plagioclase shows both Carlsbad and albite twinning and was determined to be an andesine with a composition of about  $Ab_{45}An_{55}$ . Some crystals have a broad tabular outline, others a lathlike development. The feldspar alters most abundantly to kaolin, in less degree to calcite. Quartz when present as a phenocryst is smaller than either the hornblende or the plagioclase. It is of the ordinary type.

Iron ore, as mentioned, is present in places in two generations. As phenocrysts it is observed in places to have a square outline indicating that it is magnetite; elsewhere it is without definite outline and is doubtless, in part, ilmenite. In not a few places it was seen entirely enclosed by the hornblende, indicating its earlier crystallization. It is abundantly concentrated about the borders of the hornblende both within and just without the crystal. As a second generation mineral it is scattered in small grains through the groundmass.

Apatite is present in all sections studied, in some in such large crystals and so abundantly as to almost merit being called a phenocryst. It is of the ordinary type, in long prisms. Titanite is of much less importance as an accessory than apatite, and zircon is of less importance than titanite. Both titanite and zircon are of the usual type.

In the groundmass orthoclase is somewhat more abundant than quartz. Both are developed in very small crystals. In some places, however, the feldspar has a tendency to lathlike development and there it is probably in part plagioclase.

The texture of the rock as a whole is porphyritic. The texture of the groundmass varies from microgranular, where quartz and feldspar are present in about equal amounts, to nearly trachytic, where feldspar is in excess of quartz. In some slides there was observed a tendency toward a micro-poikilitic development, and in one section a microspherulitic texture was noted.

*Hornblendic inclusions in the porphyry.*—There are inclusions of a hornblendic character present in the diorite porphyry. These are ordinarily one or two inches in diameter, but were observed to six inches in length. They are of hornblendic nature so strongly, in places, as to suggest derivation from a hornblende schist, and are in general of very angular outline.

One inclusion, however, in the hand specimen, was seen to fade gradually into the enclosing porphyry. Study of a thin section, containing a portion of both the including and the included rock, revealed the fact that in each there were phenocrysts of similar common green hornblende set in a similar groundmass. The inclusion possessed the characters of the main mass, developed on a smaller scale. This has led the writer to conclude that the inclusions represent portions of the magma, previously solidified, which by later movement came into place in Carrizo Mountain. An occurrence, very similar to this, of hornblende inclusions in diorite porphyry, has been described by Iddings from Electric Peak in Yellowstone National Park.\*

*Classification.*—Holmes was the first to study the rock of the intrusions of Carrizo Mountain. Like his coworkers in the Southwest at that time, he speaks of this rock in the text of his report as a "trachyte."† However in the legend of the geologic map accompanying the reports of the work done by the Hayden Survey in Colorado this same rock is listed as "porphyritic trachyte (hornblendic)."‡ Cross has later had occasion to study the very specimens collected by Holmes from Carrizo Mountain, together with the rocks of other laccolithic intrusions of the Southwest, brought in by the Hayden geologists. He has found that new names must be applied to these rocks, and in speaking of this he says

"In describing these rocks, . . . it will be necessary to use a nomenclature almost entirely different from that adopted by Gilbert, Dutton, Holmes and Peale. That this is true is not a reflection upon these able geologists, for the modern science of petrography was unknown in this country at the time their work in these regions was done. Few of the specimens collected by them had been examined microscopically or chemically when the published reports were written and it is usually stated in those reports that the names used are adopted provisionally."§

Accordingly, in place of Holmes' name, "trachyte," Cross applied the term hornblende porphyrite to the rock of Carrizo Mountain. Since his writing, however, the name porphyrite has itself been abandoned by American petrographers, and this type of rock is now known as diorite porphyry. It should be noted, however, that while the rock is classed as a diorite porphyry, there is in places considerable quartz present.

*Place in the Quantitative Classification.*—A chemical analysis of a rock which, from his description, is thought to be the

\* Iddings, J. P., *The Eruptive Rocks of Electric Peak*, 12th Ann. Rept., U. S. Geol. Survey, Part I, 1890-91, p. 597.

† Holmes, W. H., *op. cit.*

‡ *Geol. and Geog. Atlas of Colorado and portions of adjacent territory*, Hayden, 1877, Sheet XV.

§ Cross, Whitman, *The Laccolithic Mountain Groups of Colorado, Utah, and Arizona*. 14th Ann. Rept., U. S. Geol. Survey, Part II, 1895, p. 175.

typical diorite porphyry of Carrizo Mountain is given by Cross\* and is quoted in the accompanying table. From this analysis the norm and mode have been reckoned, and the rock determined to be a yellowstonose (symbol I, 4, 3, 4) lying almost on the borderline between yellowstonose and tonalose.

Hornblende-porphyrity. Sierra Carrizo.†  
(Analysis, W. F. Hillebrand.)

SiO <sub>2</sub> .....	63·18
TiO <sub>2</sub> .....	·66
Al <sub>2</sub> O <sub>3</sub> .....	16·47
Fe <sub>2</sub> O <sub>3</sub> .....	2·36
FeO .....	2·28
MnO .....	·15
CaO .....	4·77
SrO .....	·09
BaO .....	·15
MgO .....	1·33
K <sub>2</sub> O .....	2·93
Na <sub>2</sub> O .....	4·40
Li <sub>2</sub> O .....	trace
H <sub>2</sub> O 110° + .....	·27
H <sub>2</sub> O 110° - .....	·60
P <sub>2</sub> O <sub>5</sub> .....	·28
CO <sub>2</sub> .....	.....
Total .....	99·86

*Calculation of the Norm of Yellowstonose.*

	Molecular		Or	Ab	An	Di	Hg	Mt	Il	Ap	Q
	Analysis	Ratio									
SiO <sub>2</sub> ---	63·18	1·053	186	426	120	44	21				256
TiO <sub>2</sub> ---	·66	·009							9		
Al <sub>2</sub> O <sub>3</sub> ---	16·47	·162	31	71	60						
Fe <sub>2</sub> O <sub>3</sub> ---	2·36	·015						15			
FeO ---	2·28	·032				5	5	15	9		
MnO ---	·15	·002									
CaO ---	4·77	·086			60	22				6	
SrO ---	·09	·001									
BaO ---	·15	·001									
MgO ---	1·33	·033				17	16				
K <sub>2</sub> O ---	2·93	·031	31								
Na <sub>2</sub> O ---	4·40	·071		71							
Li <sub>2</sub> O ---	tr.										
H <sub>2</sub> O + -	·27										
H <sub>2</sub> O -	·60										
P <sub>2</sub> O <sub>5</sub> ---	·28	·002									
Total	99·86	---	31	71	60	22	21	15	9	2	

\* Cross, Whitman, *The Laccolithic Mountain Groups of Colorado, Utah, and Arizona*, U. S. Geol. Survey, 14th Annual Report, Part II, 1892-1893, p. 227.

† Cross, Whitman, *op. cit.*, p. 227, analysis III, by W. F. Hillebrand.

Q .....	15.36	Q .....	15.36	}	Sal. 86.48
Or .....	17.24	F .....	71.12		
Ab .....	37.20				
An .....	16.68				

Di .....	4.91	P .....	7.17	}	Fem. 12.64
Hy .....	2.26	M .....	4.85		
Mt .....	3.48	A .....	.62		
Il .....	1.37				
Ap .....	.62				

Rest ..... .87

Total ..... 99.99

Class I

Order 4

$$\frac{\text{Sal}}{\text{Fem}} = \frac{86.48}{12.64} > \frac{7}{1} \quad \frac{\text{F}}{\text{Q}} = \frac{71.12}{15.36} < \frac{5}{3} > \frac{7}{1}$$

Persalane

Britannare

Rang 3

Subrang 4

$$\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}^1}{\text{CaO}^1} = \frac{102}{88} < \frac{3}{5} > \frac{5}{3} \quad \frac{\text{K}_2\text{O}^1}{\text{Na}_2\text{O}} = \frac{31}{71} < \frac{3}{5} < \frac{1}{7}$$

Coloradase

Yellowstonose

Symbols I, 4, 3, 4.

*Melanocratic types.*

Two types of melanocratic rocks are present in the dikes and plugs associated with the main intrusions of Carrizo Mountain. In the absence of a chemical analysis it is not thought best to discuss their petrographic character at this time. It may be said, however, that they have been provisionally classified as shonkinite and Carrizo minette, since their mineral character is such as to indicate their relationship to the types shonkinite and minette. Though readily distinguishable under the microscope, these rocks cannot be separated megascopically and so for field purposes may be simply classified as "mica trap."

*Leucocratic type.*

Dacite.

*Occurrence.*—Dacite was noted in only two places in this region. A dike of it is exposed in Seklagaideza Canyon where the trail to the head of that canyon ascends the east wall, and again on the lower trail from this canyon to Red Rock store. Another and smaller dike, thought to be of the same character, is imperfectly exposed on the east of Carrizo Mountain at the mouth of Chezhindeza Canyon.



*Macroscopic description.*—In the hand specimen numerous phenocrysts of a rather pinkish feldspar, quartz, and hornblende are seen set in a light grayish aphanitic groundmass. An occasional phenocryst of iron ore is present.

*Microscopic description.*—Under the microscope the phenocrysts megascopically observed are seen set in a minutely granular groundmass of quartz and feldspar.

Hornblende is idiomorphically developed in long, slender prisms. It is of a somewhat lighter green color than common green hornblende and in places has a distinctly brownish tinge. In it the iron ore is abundantly concentrated. The hornblende is largely altered to chlorite.

Feldspar occurs in two generations. As phenocryst it is present in a few large crystals which show both Carlsbad and albite twinning and have been determined to be andesine with a chemical composition of about  $Ab_{65}An_{35}$ . The feldspar of the groundmass shows albite twinning in places and for many crystals the index of refraction is higher than that of Canada balsam, indicating its plagioclase character. As the feldspar is developed in long, tabular crystals, many of the pieces seen in thin section have a square outline, and as extinction takes place parallel or very nearly parallel to the side this feldspar is thought to be an acid andesine.

Quartz is present in two, and very probably in three generations. It occurs as phenocrysts, in the groundmass, and very likely combined with feldspar in the interstitial glass. As phenocryst the quartz is seen in large rounded forms which exhibit a nearly square cross-fracturing. About these masses the groundmass is much finer grained than elsewhere in the slide and it is supposed that the quartz, partially crystallized before, has been resorbed, thus giving rise to the rounded and embayed outline and a zone of more siliceous character surrounding it.

In the groundmass the quartz is seen to have square outlines and to extinguish diagonally with respect to the side of the square. Quartz of this character, in minute dihexahedrons, has been described by K uch as being very characteristic of certain dacites of the Andes,\* and it is interesting to record that in Carrizo Mountain there is found another example of this somewhat rare mode of occurrence of this mineral.

The texture of this dacite is porphyritic. The groundmass is of microgranular character with a small amount of glass, which very probably consists of uncrystallized quartz and feldspar, filling up the minute interspaces.

\* K uch, Richard, *Geologische Studien in der Republic Colombia*, I, *Petrographie*, 1, Die vulcanischen Gesteine, 1892-93, pp. 68-69.

*Name.*—The mineral character of this rock is so clearly that of a dacite, that, even without chemical analysis, it has been classed as such.

#### *Manner of Intrusion.*

Daly has recently classified all intrusive igneous masses under two main heads, (1) injected and (2) subjacent bodies, according as they come into place either by the injection and consequent uplift of the enclosing strata or by the replacement of these beds. Under the first division are placed sills and laccoliths; under the second, stocks and batholiths.

The uniform character of the diorite porphyry of Carrizo Mountain demonstrates that if, as is possible, the various outcrops of that rock are not portions of one large intrusion, they at least represent upwellings of magma from a single common reservoir. Nowhere were there observed stoped blocks nor was any evidence of assimilation noted, facts which, taken together with the upturning of the beds at the base of the mountain, suggest that intrusion was by injection rather than by a replacement of surrounding beds,—that the intrusion is of the injected rather than of the subjacent type.

It is evident from a study of the writings of Holmes and Peale that they both considered the Carrizo intrusion as belonging to the class of intrusion to which the name laccolith was later applied by Gilbert. Indeed on the geologic sections accompanying the maps of the Hayden Survey, Carrizo Mountain is portrayed in laccolithic form.\* No sedimentary floor is as yet exposed by erosion and that this intrusion is symmetrical and of typically laccolithic shape cannot be assumed. Aside from the irregularity produced by Tinasbas sill and the sheets capping North and Chezlindeza mesas, it seems clear that the intrusion is asymmetrical and has in places broken up through the overlying beds. The porphyry may be seen cutting across the Triassic rocks and the Wingate sandstone (Jurassic) in Tinasbas canyon to supply the material for the Tinasbas sill. It also appears that the igneous mass east of Biltabito Canyon has cut across the Triassic rocks and the Wingate sandstone, and there are probably other transgressions not yet exposed by erosion. Indeed it seems possible that the intrusion consists of several sills with their connecting pipes which have united in producing the effects of laccolithic uplift. Until such facts can be definitely proven, however, it is at least convenient to speak of the intrusion as a laccolith, which form of intrusion to all outward appearances it most closely resembles. (See fig. 5.)

\* Hayden, F. V., U. S. Geol. and Geog. Survey Terr., Atlas of Colorado and portions of adjacent territory, 1877, Sheet XVII, Section 11.

*Depth of Cover.*

The lowest formation observed in contact with the porphyry of Carrizo Mountain is of Triassic age; the highest is the McElmo formation (Jurassic?) within which the Tisnasbas sill is intruded. It is evident from a study of the surrounding region that the Cretaceous sediments were once continuous over the area, but that they were present at the time of intrusion remains to be demonstrated. Indeed the determination of the depth of cover depends upon the age of the sandstone and conglomerate which cap the mountain summit and outcrop for a short distance on the mountain flank south of Chezhindeza Canyon. This sandstone, which is similar both to the Dakota and to certain Tertiary sandstones and whose age cannot be determined because of absence of fossil evidence, rests in angular conformity and apparently without erosional unconformity upon the Triassic rocks. Whether Cretaceous or Tertiary, an erosion cycle is necessary to bring the Triassic into juxtaposition with formations so much higher than it. It is known that in northern Arizona there were such erosion cycles in both pre-Dakota and pre-Tertiary time, so that erosion is of no avail in the age determination of this intrusion. At present it can only be said that if the beds are Tertiary, intrusion took place below a cover of 2000 feet; if the beds are Dakota, beneath a cover of about 5000 feet.

*Age of Intrusion.*

The age of the various laccolithic intrusions of the Southwest has been considered by all students of that region as Tertiary, but so far as the writer has been able to ascertain, little definite evidence of this has been adduced. Were it possible to determine the age of the sandstone capping Carrizo Mountain, the date of intrusion there might be very definitely ascertained. Even in the absence of such proof it is still possible to place the age of the intrusion with much assurance as Tertiary, though not more definitely than that. It is known that there are certain structures of pre-Tertiary age in the area, and that these structures have been magnified by intrusion. Since, then, intrusion is younger than these features, which were probably developed at the end of the Cretaceous, it must have occurred in Tertiary time.

The relative ages of the different intrusions, the main mass, the sills, sheets, volcanic plugs, and dikes cannot be determined as they were not observed cutting each other.

*Contact Metamorphism.*

*Tisnasbas sill.*—There are only a few contacts of the diorite porphyry and the enclosing sedimentary rocks visible in the Carrizo area. The lower contact of the Tisnasbas sill with the

underlying Jurassic (?) sediments is, however, excellently exposed and may be considered typical. Study of a series of thin sections from specimens collected at various distances from this contact revealed a slight increase in the amount of iron oxide in the cement of the sandstone directly at the contact. If, however, one did not know that such an amount of iron oxide was unusual in this sandstone he would not recognize the sandstone as metamorphosed in the least, and, indeed, the amount of metamorphism has been so small that at a distance of three feet from the contact the bed is absolutely normal.

On the mountain summit metamorphism was somewhat more potent inasmuch as the original sandstone has been changed to a resistant quartzite, and this to an unknown though probably not great distance from the contact.

*Sandstone columns at Holmes Dike contact.*—Where melanocratic types of rock have penetrated the sedimentary beds, metamorphism, though not of great importance, is more pronounced than that produced by the porphyry. In the majority of cases a baking of the enclosing sediments has accompanied the intrusion of basic types of rock in this region, but Holmes Dike (fig. 3) has produced certain quartzite columns similar in appearance to those commonly observed in igneous outflows. Study of a thin section of one of these quartzite columns demonstrated the absence of any admixture of igneous material, that the columns consist only of Jurassic sediments altered to quartzite. The columns are of various diameters to one and one-half inches and in length range to three feet, the maximum distance of metamorphic action. Similar, though less perfect, columns were observed by the writer 35 miles west of Carrizo Mountain along the contact of a dike associated with Boundary Butte, Utah; more perfect columns have been noted by Professor Gregory at the northern end of Lukachuka Mountain, Arizona.\*

*Cause of the absence of intense contact metamorphism.*

It is evident from the above discussion that there has been no great amount of contact metamorphism in the Carrizo area, since such effects are commonly not noticeable at a distance of more than three feet from the contact. This phenomenon has previously been recognized by Cross as characteristic of laccolithic intrusions in the southwest and has been attributed by him to the lack of the so-called mineralizing agents, fluorine, chlorine, and superheated steam in the magma.† The absence of intense metamorphism in Carrizo Mountain is believed to be due to this cause.

\*Prof. Paper U. S. Geol. Survey, in preparation.

†Cross, Whitman, Spencer, A. C., Purington, C. W., La Plate folio (No. 60), Geol. Atlas, U. S., U. S. Geol. Survey, 1899, p. 11.



## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *Fluorine in the Animal and Vegetable Kingdoms.*—ARMAND GAUTIER and P. CLAUSMANN, in previous researches, have established the fact that fluorine occurs in all animal tissues, but in two very different proportions and conditions. In tissues of slight vitality, such as epidermis, enamel of teeth, hoofs, hair, etc., fluorine is abundant and may reach 180 milligrams in 100 grams of dry substance, while in the actively vital tissues, such as muscles, glands, etc., there is found scarcely more than from 1 to 4 milligrams of fluorine in the same amount of dry substance. Phosphorus always accompanies it, and, without being proportional to it, increases and diminishes with it. While in the actively vital tissues there are found only about 1 to 4 parts of fluorine with 350 parts of phosphorus, the proportion in the less vital, protective, or ornamental tissues is one part of fluorine to from 3.5 to 5 parts of phosphorus. The latter are practically the proportions under which the two elements exist in the mineral phosphates, hence it appears that they occur in a like combination in these tissues, such as the epidermis, hair, hoofs, feathers, etc. As nothing was previously known about the subject, the authors have made an extensive study of the occurrence of fluorine in plants. It is shown by their results that fluorine exists in all vegetable tissues and that it is always accompanied by phosphorus. Leaves contain the largest amount, from 3 to 14 milligrams of fluorine in 100 grams of dry substance, while grains and other seeds usually contain from 1 to 2 milligrams, and wood contains a somewhat smaller quantity, in the same amount of dry substance. In general, the phosphorus is higher in the vegetable tissues containing the larger amounts of fluorine, but there appears to be no definite relation in any case between the two. The conclusion is reached that the occurrence of fluorine in all parts of animals and vegetables shows that this element, which had been previously supposed to be localized in certain exceptional tissues, is indispensable to the living cell.—*Bulletin*, xix, 140.

H. L. W.

2. *The Qualitative Separation of the Common Metals whose Sulphides are Insoluble in Dilute Acids.*—In order to avoid certain inconveniences connected with the use of the ammonium sulphide separation in the examination of this group of sulphides, M. J. CLARENS has proposed a method by which the metals are precipitated in three successive groups by varying the amount of hydrochloric acid present. The liquid after treatment with hydrochloric acid, and filtration if necessary, is neutralized with ammonia, then one-half its volume of concentrated hydrochloric acid is added and hydrogen sulphide gas is passed into the cold liquid. Copper, mercury, arsenic and antimony are thus precipi-

tated as sulphides, and these are filtered, starting with a dry filter, and washed with a solution of hydrochloric acid of the same strength as was present during the precipitation. In order to precipitate arsenic in the higher state of oxidation the filtrate is heated and hydrogen sulphide is passed again. Then, after filtration if necessary, the liquid is diluted with an equal volume of water, and hydrogen sulphide is passed again. This precipitates the sulphides of tin and bismuth, which are filtered and washed with hydrochloric acid of the proper strength. At last the acid is nearly neutralized and the sulphides of cadmium and lead are precipitated by means of a third treatment with hydrogen sulphide. Directions are given for the examination of each precipitate for the detection of the metals in it. It appears that the method is one which may be conveniently applied in certain practical cases, but for use in laboratories of instruction the necessity of three precipitations by hydrogen sulphide under accurately regulated conditions would seem to make its utility very doubtful.—*Bulletin*, xix, 154. H. L. W.

3. *The Estimation of Vanadic Acid after Reduction by Metallic Silver*.—GRAHAM EDGAR has found that finely divided metallic silver, prepared by precipitation or by igniting the oxide, reduces vanadic acid in hot, dilute sulphuric acid solution to the quadrivalent condition, and that three methods for determining the amount of vanadium present may be based upon the reaction. In the first place, a weighed excess of metallic silver may be used and the loss in weight of the silver shows the amount of vanadium. The second method consists in the titration of the reduced vanadium, which may be accomplished, conveniently and accurately, by means of potassium permanganate solution. The third method consists in determining the amount of silver in solution after the completion of the reaction, for example by titration with a thiocyanate solution. It is interesting to observe that the three methods can be applied, in the order given, to a single portion of a vanadate. The results obtained by the author in his test analyses show an astonishingly close agreement in the three methods not only among themselves but with the known amounts present. It will not be attempted to give full details of the process here, but it may be mentioned that solutions of sodium vanadate containing not far from 0.1% of  $V_2O_5$  were acidified with about 2% of concentrated sulphuric acid, diluted to about 75%, from 1 to 2% of finely divided metallic silver was added and in each case the liquid was boiled for about one-half hour in a small flask. The reduction takes place quantitatively in the presence of hydrochloric acid, but in this case the oxidized silver forms silver chloride, so that the amount of vanadium can be calculated from the gain in weight. It appears to be more accurate, however, to use sulphuric acid solutions free from chlorides.—*Jour. Am. Chem. Soc.*, xxxviii, 1297. H. L. W.

4. *The Density of Radio-Lead from Pure Norwegian Cleveite*.—T. W. RICHARDS and C. WADSWORTH, 3d, have obtained from

Professor Ellen Gleditsch of the University of Kristiania a sample of lead sulphide from carefully selected Norwegian cleveite. The lead of the sample was carefully purified, and four specific gravity determinations made upon a sample of over four grams of the metal gave closely agreeing results averaging 11.273. This specific gravity is lower than 11.289, the density of the Australian radio-lead recently examined by the authors, while the density of ordinary lead is 11.337. It is probable that the Norwegian sample is a nearly pure isotope. The atomic weight of this sample has been determined by the authors, although the details have not yet been published, and it is pointed out as an important fact that the atomic weight, 206.08, divided by the specific gravity gives the atomic volume 18.281, which is practically identical with the atomic volumes of the Australian sample, 18.279 and that of ordinary lead, 18.277, as previously found by the authors.—*Jour. Amer. Chem. Soc.*, xxxviii, 1658. n. l. w.

5. *Theory of the Lead Accumulator.*—The important practical problem of devising a portable dry-cell of the secondary type has been recently attacked by CH. FÉRY. The paper under consideration is preliminary in so far as it deals only with the first logical step in the systematic investigation, that is, a thorough study of the chemical reactions which take place during the acts of charging and discharging lead storage cells. The author first reviews the previous work and thereby shows that the various hypotheses concerning the behavior of the positive plate are so divergent as to leave the whole subject in a state of confusion and uncertainty. In particular he concludes that the theory advanced (about 1882) by Gladstone and Tribe is incorrect. According to this theory, which has received wide acceptance, the process of charging peroxidizes the red-lead at the anode and reduces this compound at the cathode, first to the lower oxide and then to spongy, metallic lead. The discharge may be briefly expressed by the equation  $PbO_2 + 2H_2SO_4 + Pb = 2PbSO_4 + 2H_2O$ , so that *both* plates would be sulphated. (This reaction is called "double sulphating.") On the other hand, there is complete accord with regard to the sulphating of the negative plate, the increase in the mass being accurately proportional to the number of ampere-hours furnished.

The evidence adduced by Féry will now be given in a fairly condensed form. The color of the fully charged positive plate is pure black whereas after discharge this electrode assumes the characteristic brown color exhibited by lead dioxide when chemically prepared. Since, however, the color of a given substance often depends upon its physical condition (fineness of division, etc.), and is therefore not a reliable criterion, the following experimental facts are presented to throw doubt on the sulphating of the positive plate. The active material was removed from the surface of a positive electrode and packed in a porous cup surrounding a sheet of platinum. A plate of zinc constituted the negative electrode, and the cell thus assembled had an E.M.F. of 2.5 volts. Under like conditions lead dioxide chemically derived invariably gave 0.7 volt. A volumetric test was

next applied. A known mass of the positive material (which had been washed and dried) was treated with an excess of a solution of oxalic acid of known volume. The oxalic acid reduced the higher lead oxide and the nitric acid, which was subsequently added, transformed the lead into the nitrate. After all the material had dissolved the excess of oxalic acid was estimated by the aid of a titrated solution of potassium permanganate. Knowing the volume of permanganate required to reduce the same volume of the original solution of oxalic acid, it was a simple matter to calculate the quantity of oxalic acid oxidized by the higher lead oxide. Let  $PbO_x$  = formula of oxide in question,  $p$  = mass of oxide used,  $p'$  = mass of oxalic acid necessary for oxidation, then

$$(x-1)H_2C_2O_4 + PbO_x + 2HNO_3 = 2(x-1)CO_2 + xH_2O + Pb(NO_3)_2$$

$$\text{whence} \quad \frac{207 + 16x}{p} = \frac{90(x-1)}{p'}$$

Experiment gave  $x = 2.3$  so that the required formula for the oxide becomes  $Pb_3O_7$ .

This result is in complete accord with the mutually independent observations of Tennen and Hollar on the electrolytic analysis of solutions of nitrate of lead. In the formation of lead peroxide the ratio  $Pb/PbO_2$  has the observed value 0.853 instead of 0.866, when electrodes of unpolished platinum are used. The smaller number corresponds to the same formula,  $Pb_3O_7$ .

This higher oxide obtained electrolytically was also analyzed by reducing it in a current of hydrogen. This gave  $x = 2.37$ . At the beginning, the reduction is very rapid and the color of the powder changes from *black to brown*; near completion, it is necessary to heat the glass vessel containing the substance. When chemical lead dioxide was subjected to the same treatment it was found that  $x = 1.96$ . This method should have given  $x = 2$ , but a high degree of accuracy was not attempted in the last experiment.

The black substance which would accordingly have the formula  $Pb_3O_7$  is *very unstable*, and the author suggests that the higher oxide which is present in the cells of the positive plate, when completely charged, may be even more rich in oxygen. When placed in a capsule, which was protected from the influence of stray reducing dust, the black powder *gradually turned brown* in the course of a few days, the change of color commencing at the surface. Féry interprets this phenomenon as being due to the spontaneous loss of oxygen and not to an alteration in the physical state of the material.

All the preceding evidence is strengthened by an experiment of another kind. When a positive plate made by Planté's method is discharged by means of a plate of zinc two distinct stages are observed—the one, from 2.5 to 2.3 volts, corresponds to the passage from  $PbO_x$  to  $PbO_2$ ; the other, between 0.7 and 0.3 volts, to the reduction of  $PbO_2$  to the metallic condition. The capacity of the second discharge is about four times greater than that of

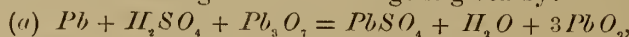


the first, and this leads to  $Pb_2O_6$  as the formula for the higher electrolytic oxide estimated *in situ*.

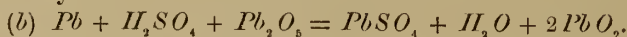
For lack of space we shall pass over the remaining lines of evidence and quote the author's conclusions, which are:

1. The behavior of the lead accumulator while discharging is identical with that of a primary cell with a solid depolarizer, the manganese cell for example; with this difference that the negative electrode gives rise to an insoluble salt.

2. The theory of "double sulphating" is manifestly inexact and the reaction during normal discharge is given by:



or possibly



Formulas (a) and (b) lead to masses of 15 and 10.4 grams of the higher oxide per ampere-hour respectively, the best commercial tests giving values of the same order, namely 12 to 14 for thin plates slowly discharged.

3. The quantity of acid combined during discharge is exactly one-half of that indicated by the theory of "double sulphating."

4. The variations in mass of the positive plate must be very small and in the opposite sense to those predicted by the theory of "double sulphating."

5. The mass of lead to use for the positive electrode must be exactly double that taking part in the reaction at the negative grid if the formula  $Pb_2O_5$  be accepted.

6. When discharged the active material of the positive plate becomes lead dioxide.—*Jour. de Phys.*, Jan.-Feb., 1916, p. 21.

H. S. U.

6. *An Active Modification of Nitrogen.*—In his six earlier papers on this gas R. J. STRUTT has dealt primarily with the properties of active nitrogen when once produced. The seventh contribution, now under consideration, pertains chiefly to the circumstances of its production by the electric discharge.

With this object in view it was necessary to abandon the very efficient but complicated jar discharge and make use of the direct current furnished by three motor-driven magneto generators joined in series. At full speed the output was 15 milliamperes at 5000 volts. The gas used in the experiments was commercial bomb-nitrogen which was kept for a time over phosphorus and then dried by the pentoxide of this element. At least seven different forms of discharge tube were employed in the investigation so that it will not be possible to describe the apparatus in this place. The results obtained may be summarized as follows:

1. The production of active nitrogen in the steady discharge is a maximum near the cathode, it falls to a minimum in the Faraday dark space, and increases again in the positive column until a value is attained which stays constant throughout the remaining length of this column but which is less than that at the cathode.

2. When the amperage is kept unchanged, a much larger quantity of active nitrogen is obtained from the positive column

in a narrow tube than in a wide one. This difference in yield must be connected with the current density rather than with the potential gradients, since the difference between the latter in narrow and wide tubes is insufficient to plausibly account for it.

3. As the length of the positive column traversed by the gas is increased the yield of active nitrogen reaches a limit. This is due to the destructive action of the discharge which, above a certain concentration, nullifies the active modification as fast as it is generated.

4. It has been shown in previous papers that a trace of oxygen (or almost any other admixture) greatly increases the yield of active nitrogen. The amount of oxygen required to bring about this result considerably increases the fall of potential at the cathode, but it does not measurably influence the gradient in the positive column.

5. Active nitrogen can be produced by the spark at atmospheric pressure, but the phenomena are much less brilliant than at low pressures. The destructive influence of the surrounding gas on the active modification is responsible for this difference.

6. The particles scattered from a copper cathode when the uncondensed discharge passes can be made to emit the line spectrum of the metal in a stream of active nitrogen.—*Proc. Roy. Soc.*, vol. xcii (A), p. 438, July, 1916. H. S. U.

7. *The Emission of Electricity from Hot Bodies*; by O. W. RICHARDSON. Pp. vii, 304, with 35 figures. London, 1916 (Longmans, Green and Co.).—This book is the seventh of the series of "Monographs on Physics" edited by J. J. Thomson and Frank Horton. A fair idea of the field covered in the text may be derived from the titles of the chapters, which are: "I. Mainly Considerations of a General Character. II. Theory of the Emission of Electrons from Hot Bodies. III. Temperature Variation of Electron Emission. IV. The Effect of Gases on the Emission of Electrons. V. Energetics of Electron Emission. VI. The Emission of Positive Ions by Hot Metals. VII. The Effect of Gases on the Liberation of Positive Ions by Hot Metals. VIII. The Emission of Ions by Heated Salts, and IX. Ionization and Chemical Action."

Due to the non-existence of a satisfactory and comprehensive theory of conduction for conductors of the metallic type, Richardson has treated the subject of the second chapter in as general a manner as possible, thereby reducing the part played by special theories to a minimum. The last chapter includes a brief account of the results of some experiments recently made by the author with regard to electrons liberated by chemical action. The purely technical side of the general subject has been wisely omitted from the text, but the titles of the most important books and papers relating to this phase are given in the preface. Numerous bibliographical foot-notes facilitate supplementary reading, and the volume closes with both name and subject indices. The high standard set by the preceding numbers of the "Monographs" is fully maintained in the present volume, so that this publication will be found very valuable by students of advanced physics.

## II. GEOLOGY.

1. *La Flora Liásica de la Mixteca Alta*; by G. R. WIELAND. Boletín del Instituto Geológico de México, No. 31. Text of VI + 165 pp. quarto (Mexico, 1914); Atlas of 24 pp. and 50 plates (dated 1916).—This is the first typical North American Liassic flora. It was collected in entirety by the writer in the winter of 1909. Its age was discussed in this Journal for September 1913 (vol. xxxvi, pp. 251–281). Evidently the “Mixteca Alta” of Oaxaca, Guerrero, and Puebla is one of the richest Cycadeoid regions in the world. Neither the Yorkshire coast nor the Gondwanas of India surpass the new Mexican realm in any respect.

The main collections described are from the Barranca Consuelo in the western part of the state of Oaxaca. The section here measured includes 600 meters of plant-beds resting on an eruptive floor, and followed by a marine Jurassic series. The measurements were continued upward through the marine superposition about 375 meters to the base of the Cretaceans. The study of these superposed beds has not been completed by any one and was excluded from the field investigated. Taken as a whole the Consuelo section must always rank as one of the most important type sections of the North American continent.

The plant-beds consist in a much varied succession of shales and sandstones grading into finer conglomerates. Occasionally the finer shales carry coal. In the lower beds seams of a semi-anthracite with a high ash recall the coal of Sutherlandshire, Scotland. An equivalent of the Sonoran Trias was not positively determined, but may occur in the valley of the Rio Nochixtlan. If true Rhætic is present at the base of the Consuelo section the fact was not determined. The section readily divides itself into a lower series 250 meters thick and an upper series 300 meters thick; but no unconformity was observed. In the collections secured the cycads and ferns are relatively modern. The succession of plant types precludes any notable time gap. The Rhætic and the Oolite must afford the extreme boundaries.

The discovery of Cordaites (*Næggerathiopsis*) closely associated with Liassic Cycadeoids (*Otozamites*) was unexpected. The handsome plates of the Atlas show various new Williamsonian fronds and a fine series of fruits. Yet these must be but a mere fraction of the recoverable forms. Of the 70 or more plant types illustrated or described, a considerable number so closely resemble plants of the European Liassic that new varietal names only are attached. It is, however, likely that Professor Nathorst, who takes exception to this method in a recent letter, is justified. He thinks far separated plants nearly always likely to be of different species, while varieties even if present can rarely be determined.

Owing to difficult conditions precluding proof reading, various typographical errors appear in this Bulletin. These should occasion no great inconvenience in its use. They are seldom serious and may readily be excused in this period of nearly universal war. It must be held very creditable to the Mexican Survey to bring out the work at all. May it not be recalled that our own civil war delayed Newberry's record of the San Juan expedition nearly seventeen years?

G. R. W.

2. *Isostasy in the Light of the Planetesimal Theory*; by T. C. CHAMBERLIN. [Note to the Editors of this Journal.]—In the August number of this Journal, "C. S." does me the honor to give an excellent notice of my recent little book on "The Origin of the Earth." There is one sentence in the notice which, though not inaccurate when critically read, will, I fear, give to many readers an erroneous impression, and as the subject to which it relates is one of much importance I beg to add a word to forestall misapprehension. After referring to the view advanced in the book that the earth is segmented into heavy stiff sub-oceanic cones between which lie more irregular, weaker and lighter continental wedges, and that at times of diastrophism these move upon one another along "yield tracts," the review says: "This hypothesis seems to be diametrically opposed to the working hypothesis of isostasy and the latter's postulate that the relief of the earth's surface is compensated for by corresponding variations in surface density which cease at a depth equal to a fiftieth or a hundredth part of the radius of the earth."

It is true that the hypothesis that I have offered departs radically from the *interpretation of the mode* by which isostasy is secured and is at variance with certain limitations that have been assigned the distribution of density in the outer part of the earth which are not thought to have a secure basis, but the view advanced in my book, far from being diametrically opposed to demonstrated or theoretically essential elements of isostasy, expresses its good will toward the doctrine by offering, on its own part, *a new view of the mode by which such approximate isostasy as exists is secured*. This new view is consistent with the growing evidence of a high state of rigidity in the earth. It also postulates an adequate cause for the initiation and maintenance of isostasy through all the geologic ages with an effective residue operative at the present time. In short, the new view endeavors to meet on broad, adequate and lasting grounds what are regarded as the weak points in the doctrine of isostasy as it has heretofore been advocated. The limitations of differences of density in depth are not regarded as having any trustworthy basis, and this view is supported by competent mathematical investigation, the results of which will appear in time. The purpose of this note will be accomplished, if it makes clear that the book in question offers a new line of support for the general doctrine of isostasy and is at variance with current views only on points in respect to which these views are held by some careful students to be weak.



3. *Relations between the Cambrian and Pre-Cambrian formations in the vicinity of Helena, Montana*; by CHARLES D. WALCOTT. *Smithson. Misc. Coll.*, 64, No. 4, 1916, pp. 259-301, pls. 39-44, text figs. 10-13.—When Professor Rothpletz of the University of Munich attended the International Geological Congress in Canada in 1914, he made it a point to visit Helena, Montana, and since then has published his conclusion that the Belt series held by all American geologists to be of pre-Cambrian age is actually of Lower Cambrian time. Such a conclusion from one of Europe's foremost geologists could of course not be neglected, and as Walcott has done more than any other in the interpretation of Proterozoic strata it is but natural that he should reply to Professor Rothpletz' publication. He says: "The Rothpletz failure to find any evidence of an unconformity at the base of the Cambrian is most natural as he unknowingly identified the Cambrian limestones as the pre-Cambrian Helena limestone and hence did not recognize and probably did not see at all the Helena limestone which is beneath the unconformity. . . The Rothpletz view of considering all of the pre-Cambrian sedimentary formations of North America corresponding to the Belt series as of probable Cambrian age is without evidence to support it" (297-298).

Plates 40-43 are splendid illustrations of the very significant unconformities in the Grand Canyon of the Colorado River between the Archeozoic, Proterozoic, and Paleozoic, and nothing of equal grandeur has ever been published before. C. S.

#### OBITUARY.

PROFESSOR CHARLES S. PROSSER, head of the department of geology in Ohio State University and author of many papers and books on geological subjects, died suddenly on September 12 at the age of fifty-six years.

PROFESSOR JOSIAH ROYCE, from 1892 until his recent retirement, professor of philosophy in Harvard University, died on September 14 in his sixty-first year.

PROFESSOR GUSTAV SCHWALBE, the distinguished German anatomist of the University of Strassburg, died in July. His work was concerned particularly with the study of the Lower Paleolithic human remains; it led to the establishment of *Homo neanderthalensis* as a distinct species.

PROFESSOR KARL SCHWARZSCHILD, the eminent German astronomer, has died recently.

PRINCE BORIS GALITZIN, the seismologist and professor of physics in the Imperial Academy of Sciences in Petrograd, died in May last.

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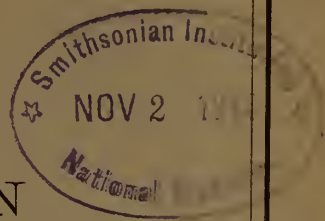
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ART. XXXVIII.—*The Ancestry of Insects with particular references to Chilopods and Trilobites*; by JOHN D. TOTHILL.\*

### *Introduction.*

DATING practically from the publication of Darwin's "Origin of Species," a fund of energy has been directed toward elucidating the probable descent of the various groups of living organisms. In these various groups different hypotheses of derivation have sometimes followed one another in rapid succession. Each in its turn has been of value as a working hypothesis and has often served to elicit new facts that have formed the basis of a supplanting hypothesis.

In the case of the Hexapoda the usual gamut of systems of classification and of genealogy—the one a necessary handmaiden of the other—has been proposed. We owe to the Greek civilization in general and to Aristotle in particular the first attempt to arrange insects in a system of related groups. In the interim between this first attempt (about 300 B. C.) and the more recent one of Handlirsch (1908) there have been many derivations proposed. Of these it is necessary simply to mention one or two of the more interesting. In 1866 Haeckel proposed a genealogical tree deriving the Insecta through the "Tocoptera" which included the "Thysanura," from "Tracheata" which also gave rise to the Arachnids and Myriopods. Three years later Brauer suggested a derivation through the Apterygogenea or wingless insects including Campodea and Thysanura; Brauer's system of classification was based on morphology, metamorphosis, and later on embryology; it was thorough-going and forms the basis of all subsequent systems;

\* Contribution from the Bussey Institution No. 119.

in 1885 it was revised and amplified into a form that has been in general use ever since. Paekard in 1863 and 1870 suggested a derivation through the Apterygogenea (*Lepisma*) from the Myriopods.

Kingsley in 1894 emphasized the close relationship between insects and Chilopods and also the unnaturalness of the old group "Tracheata." In 1903 Carpenter reviewed the whole situation and came to the conclusion that Insects, Chilopods and Diplopods were probably derived independently from Symphyloid stock—a position that in the light of recent data is open to several serious objections.

Each of the various systems proposed has resulted from discoveries in morphology, development, or in paleontology. In recent years discoveries have been made in two directions, each throwing light on the problem of insect genesis. Through the efforts of Barrande, Waleott, Lindström, Beecher, and Raymond, our knowledge of detailed structures and of development in the interesting extinct group Trilobita has been greatly extended. On the other hand, Handlirsch following the trail blazed by Brongniart and Scudder has greatly enriched our knowledge of insect paleontology. In his remarkable book "Die Fossilen Insekten" there is proposed a new system of classification based, as was Brauer's, on development, morphology, and particularly on paleontology. There is also proposed a heterodox ancestry in which the Hexapods are derived not in the usual way through the Apterygogenea from terrestrial tracheate myriopod-like animals but directly from trilobites. This derivation is accepted without reserve by Schuehert (1915) in his exceedingly illuminating Text Book of Geology, and it has also been accepted by Ruedemann (1916). While it is suggestive and very helpful it is open to certain objections and the time seems, therefore, opportune to once more review the whole question of insect genesis. The object of the paper will be largely achieved if it succeeds only in stimulating the search for further facts.

#### *An examination of the available data.*

In tracing the lineage of any complex of related organisms the first point is of course to discover the most generalized members of the group. In the insects these have been sought in both the wingless Apterygogenea and in the winged Pterygogenea. In the case of the former it will serve the present purpose to recall some of the salient features in a few characteristic examples. In *Lepisma saccharina* (fig. 1, A and B), the mouthparts are greatly specialized by reduction, the eyes are also reduced; on the other hand the primitive number of





Examples could be multiplied but sufficient has been said to indicate that the Apterygogenea occasionally preserve even in the adult condition primitive 'ancestral' characters, such as the tritocerebral and abdominal appendages, structures that have almost or completely disappeared in the Pterygogenea. In this sense they are more generalized than any other living insects. Enough has also been said to indicate on the other hand that the Apterygogenea are highly specialized animals as indicated by the frequent reduction of mouthparts, visual organs, tracheae, etc.; and by the development of peculiar structures such as the caudal "spring" and the collophore. Handlirsch points out that the absence of wings does not necessarily represent a primitive condition, but that these insects may have once possessed wings and lost them as a result of taking up their abode in the peculiar environment in which they now live. In cave insects, such as ants, and in parasitic insects (especially of fur- or hair-bearing vertebrates), such as the fleas and lice, reduction or loss of wings is extremely common. Be this as it may, the various specializations found in the group seem to make it certain that it is not in the direct line of descent of the great Pterygogenea complex.

Turning to the Pterygogenea, the remarkable findings of Handlirsch from the Pennsylvanian rocks engendered a new point of view concerning the most generalized insect. *Stenodictya* (fig. 2) is typical of these ancient insects and I will confine my remarks to it. It is a large insect with well-differentiated head, thorax and abdomen; with all abdominal segments and with well-developed cerci. The wings are of peculiar interest in that the venation is practically that of the "hypothetical wing" long since suggested by Comstock and Needham. The organs of flight are also of interest in that a small pair is developed on the prothorax and because all the abdominal segments show lateral wing-like outpushings. This seems to indicate the method of origin of wings and does away with the necessity of deriving the winged insects from the Apterygogenea.

In a word the Palæodictyoptera as illustrated by *Stenodictya* appear to represent the ancient stock from which the present Pterygogenea complex has been derived.

If this inference is correct then the problem resolves itself into discovering an ancestor for the Palæodictyoptera. Before developing the problem, however, it may be pointed out that the abdominal appendages on the *Stenodictya* larva (fig. 2, B) figured seductively by Handlirsch opposite a figure of a trilobite with the same sort of appendages are of doubtful phylogenetic significance. The insect was aquatic in its early stages and yet most of the Pennsylvanian insects were terrestrial. In

recent aquatic insects such as *Sialis* and *Sisyra* there are serially arranged jointed appendages functioning as gills, but all such structures in recent insects are shown by embryology to be secondarily acquired. It seems fairly certain that the similar structures in *Stenodictya* are secondarily derived and that insects were originally terrestrial; in this case the structures would have no phylogenetic significance.

Returning to our problem, it may be of interest to construct from the available data a hypothetical ancestor for the Ptery-

FIG. 2.

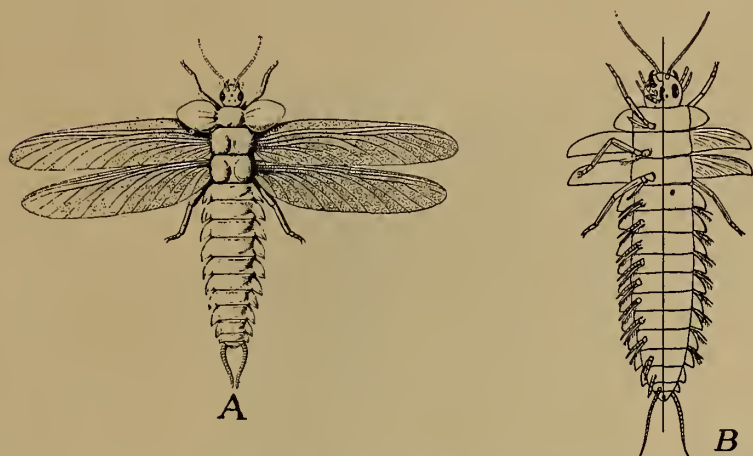


FIG. 2. A. *Stenodictya* (Palæodictyoptera), one of the most generalized of all Pterygonea. (After Handlirsch.)

B. Larva of *Stenodictya*. The abdominal appendages are probably secondary. (After Handlirsch.)

gonea. As wings seem to have arisen in the Palæodictyoptera the ancestor would have no wings and consequently the thoracic segments would be no larger than the abdominal. The result would be an animal with head and trunk, the latter with 14 segments (fig. 3). The habit must have been predaceous which would imply a short straight alimentary tract.

Turning to the structure of the nervous system, one of the most conservative of morphological structures and consequently one of the most useful for phylogenetic purposes, embryology of recent forms (Viallanes, Wheeler) shows that there are six neuromers in the head, a brain triad and a gnathal triad, and that a pair of ganglia connected by commissures follow in each segment. Cephalization would be less marked than in recent insects. The nervous system is indicated in the diagram (fig. 3, B).

In insect embryos one of the most universal and striking features is the early development and final disappearance of paired appendages on the abdominal segments. Graber, Wheeler, Heymons and others have figured these structures in numerous insects; I find they occur also in *Paratenodera* (fig. 4), *Chauliodes*, *Ranatra* and *Polistes*. The only possible interpretation seems to be that these rudiments represent a condition of serial polyphy in ancestral forms. This condition is therefore represented in the diagram.

FIG. 3.

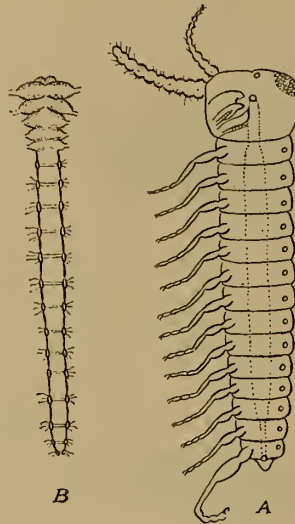


FIG. 3. Generalized hypothetical ancestor of Pterygoinea. (Original.)

In figure 4 it can be seen that the tracheæ have already invaginated—i. e. the spiracles are plainly visible. These invaginations occur generally in insects at an extremely early stage, in fact immediately after the appearance of the appendages. This seems to indicate that they are ancient structures and that the immediate wingless forbears of insects were tracheate and therefore terrestrial. The hypothetical ancestor may, therefore, be supplied with tracheal invaginations—at least ten pairs as in insects, and probably fourteen.

There remains the head. I cannot discuss the question of head segmentation at this time, interesting though it is. Viallanes, Wheeler and Heymons are agreed that the insect head is composed of six segments and these investigators have paid particular attention to the development of the brain. Folsom

(1900), working with the tiny embryo of *Anurida*, supposes there are seven segments; the presence of the extra pair of appendages described has not been verified, and seems to be extremely doubtful. Janet (1899), arguing from adult anatomy, supposes there are seven segments; the evidence is not at all convincing. In the diagram I have, therefore, indicated six head segments.

The rudiments of the maxillæ in insects are characteristically paired on each side and possibly indicate a biramous condition

FIG. 4.



FIG. 4. Germ band of *Paratenodera sinensis*, a Chinese mantid, showing the rudiments of abdominal appendages, and the spiracles. (Original.)

of all the ancestral appendages. The evidence, however, only points directly to the biramous condition of the first and second maxillæ.

The hypothetical ancestor being now visualized (fig. 3), the next problem is to search for such an animal in the various kindred groups of which we have knowledge.

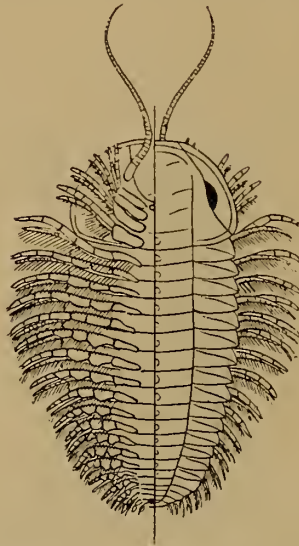
The Arachnoidea are by general consent considered to be specialized in their own particular direction and may be passed by in silence.

One of the most interesting of all groups is that of the Trilobites. In early Cambrian times they were already greatly differentiated and dominated the life of the oceans, thus occupying the ecological position that the fish do to-day. Some were very small, some more than a foot long; some lived in deep waters, some in shallow; some were bottom feeders and others pelagic. In Ordovician times the group reached its climax both in the number of species and in diversity of form.



With the differentiation and multiplication of fish in the Silurian epoch there was initiated the beginning of the end of trilobites and the number of species fell away rapidly. There was a slight expansion in the Devonian and as in the preceding age there was a marked tendency toward the development of (to us) curiously bizarre and ornamented forms. There followed a rapid decline and the group became extinct with the

FIG. 5.

FIG. 5. The trilobite *Triarthrus beckii*. (From Handlirsch after Beecher.)

passing of Paleozoic time. More than 2000 species have been described and this can represent but a fraction of the total.

It is a source of surprise that a group showing such collective vitality should have given rise to no terrestrial forms as have the Annelida, Malacostraca, Arachnoidea, Gastropoda, and Vertebrata. Handlirsch indeed takes exception to this view and derives a number of groups directly or indirectly from these ancient crustaceans. As insects are numbered among these the similarities may be examined somewhat closely.

In *Triarthrus beckii* (fig. 5), studied with such signal success by Beecher, there are two regions, head and trunk. On the twenty or so trunk segments are serially homologous biramous jointed appendages. The head carries five pairs of appendages, thus indicating *at least* five segments.

The trilobite head problem here suggests itself. Beecher

('96) supposes that the head of *Triarthrus* is made up of at least six segments and possibly of seven; Jaeckel ('01) finds at least six head segments in a series of trilobites and supposes a total of eight. These findings cannot be taken too seriously for the reason that the developing trilobite brain has not been examined—and it is in the ontogeny of the head that the key to the same problem in other groups (Arachnida, Hexapoda, Vertebrata) has been found. They are, however, highly suggestive and it is probable that trilobites had at least as many head segments as insects, perhaps the same number.

Returning to *Triarthrus*, the long antennæ are instructive as are also the compound eyes.

FIG. 6.

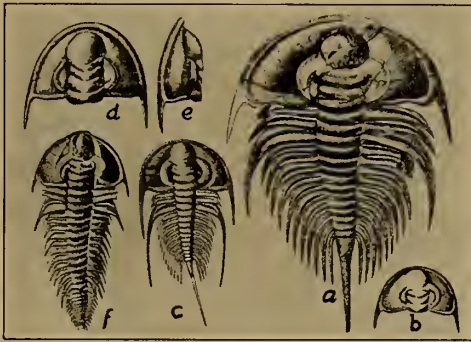


FIG. 6. a, b, *Olenellus thompsoni*; c-e, *O. gilberti*; f, *Mesonacis vermontana*. Showing specialization of first three post-cephalic segments. (From Grabau and Shiner, after Walcott.)

Lindström (1901) among others has paid special attention to the eyes of trilobites and finds at least three kinds—isolated eyes or ocelli, aggregate eyes of biconvex lenses, and compound eyes. The three kinds of insect eyes are roughly comparable and it is conceivable that they may have been derived from those of trilobites.

In *Olenellus* (fig. 6) there is a regional specialization of the first three post-cephalic segments. In many trilobites, such as *Albertella*, *Ceraurus*, there is a tendency toward specialization of the caudal extremity by the formation of caudal spines; in *Neolenus serratus*, whose appendages have been recently discovered by Walcott on specimens from the Burgess shale (Middle Cambrian), there are jointed caudal rami strongly suggestive of insect cerci.

In some respects, therefore, the trilobites, especially such generalized forms as *Mesonacis* (fig. 6) and *Paradoxides*, fulfill the requirements of our hypothetical insect ancestor. The absence of spiracles and the general lack of strong convincing evidence of close relationship indicates, however, that if a relationship exists, as seems quite likely, it is scarcely as close as supposed by Handlirsch. I will return to the group later.

FIG. 7.

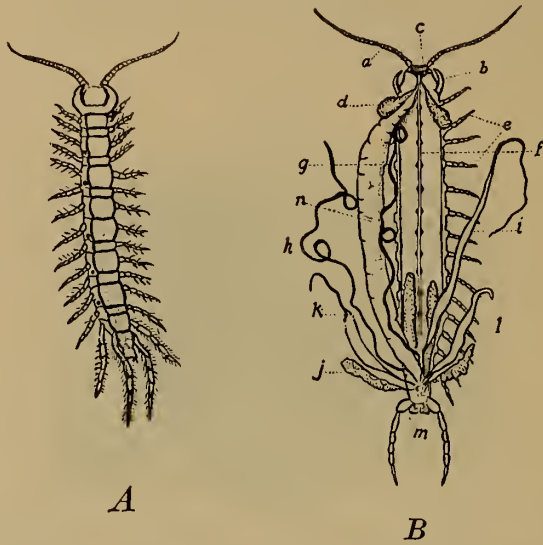


FIG. 7. A, *Lithobius* adult. A representative chilopod. (After Koch.)  
 B, *Lithobius*; a, Antennæ; b, Maxillipedes; c, Brain; d, Salivary glands;  
 e, Legs; f, Ventral nervous system; g and h, Malpighian tubes; i, Vesicula  
 seminalis; j and k, Accessory glands. (After Vogt and Yung.)

The Progoneata, characterized by the Diplopoda, are by general agreement of myriapod students less closely related to the Opisthgoneata (Chilopoda) than they are to insects. They throw little or no light upon the present discussion.

Turning to the Chilopoda, there are no fossil forms yet known that throw much light upon their lineage, even *Palæocampa* is distinctly disappointing. Recent forms are, however, plentiful and illuminating. A dissection of *Scolopendra* shows that the nervous system is almost identical with that in generalized insects. In *Lithobius* (fig. 7, A and B) the number of trunk segments is reduced to 16 (compare fig. 3); a tracheal system histologically identical with that of insects is well developed; also the last pair of legs is larger than the

others and suggest the insect cerci. The problem of head segmentation has been studied by Heymons for *Scolopendra* and the head is composed of six segments as in insects. I find the same condition in *Scolopendra*, *Linotenia* and *Cryptops*. In all these forms the mandibles and two pairs of maxillæ correspond to those in the Pterygonea and the maxillæ are biramous. The whole group exhibits the condition of serial polyphyly so characteristic in insect embryos. Several kinds of eyes are also found in the group (although reduced by reason of cave habits) and from these it would seem an easy transition to the eyes of insects. Embryological development is also remarkably similar in the two groups but that of Chilopods is in several important respects less specialized.

In short the Chilopods are unquestionably very intimately related to the Pterygonea, as Kingsley, Korschelt and Heider, Heymons and others have pointed out. An ancient Chilopod showing no specialization of the maxilliped would have looked suspiciously like fig. 3 and would have fulfilled the specifications better and more closely than any trilobite known at the present time.

#### *The Ancestry of the Opisthogoneata.*

If, as seems probable, the Pterygonea arose from an ancient Chilopod stock it may be interesting to speculate concerning the ancestry of Chilopods. The primitively biramous condition of appendages is suggested by the embryonic condition of the two pairs of maxillæ and of the maxillipedes, also by the slight thickenings at the base of all the embryonic trunk appendages in *Scolopendra*, *Cryptops* and *Linotenia*. The spiracles develop early but perhaps not quite as early as in insects—the point needs reinvestigation. In embryos of the same forms also, as pointed out by Heymons for *Scolopendra*, there are rudiments of two pairs of antennæ.

The extremely interesting and anomalous *Onychophora* invite at least inspection in this connection. Many investigators have supposed that this group, represented by the single genus *Peripatus*, is related to the tracheate arthropods because of the paired appendages and tracheæ. As Handlirsch points out, however, the tracheæ are in position and histological structure utterly unlike those of Chilopods and Hexapods. It may be recalled that tracheæ also occur in many terrestrial Arachnoidea and in some half dozen or so genera of Isopod crustaceans. In these latter cases the tracheæ have clearly arisen independently and there seems good reason for supposing an independent derivation in the case of *Peripatus*. The peculiar fleshy legs and the nervous system are also very



unlike the corresponding structures in Chilopods or insects. It seems therefore less of a mental effort to regard these animals as an independent offshoot from Polychæte annelids than to regard them as a direct bridge between Annelids and Chilopods.

Returning to the Trilobites, practically all that was said concerning the similarities between generalized trilobites and Pterygogenea would apply with even greater force to Chilopods. Regional divisions of head and trunk, polypody, head segmentation, antennæ, eyes and cerci all suggest affinities.

If in Cambrian times an adventurous species of the Mesonacidæ had left its marine surroundings to discover the terrestrial world, it seems a fair guess that gills would have been exchanged for lungs or tracheæ. With no further change than the loss of gills and acquisition of tracheæ (a change actually accomplished in the Isopoda and certain Arachnoidea) our bold adventurer would now resemble in many fundamental respects a generalized Chilopod.

The lack of knowledge concerning the trilobite head and the all-important nervous system preclude the possibility of attaching more than suggestive value to a trilobite derivation of the Chilopods. With the present lack of data, however, this derivation seems at least as logical as any of the various ones suggested.

#### *Conclusion.*

In conclusion a survey of the available data shows that the Pterygogenea are closely related to Chilopods and were quite possibly derived from an ancient stock in which the maxillipedes were not developed as jaws. Also that the Chilopods were in turn very likely, though by no means certainly, derived as Handlirsch suggests, from ancient generalized trilobites.

The probability of this derivation is increased by comparing the manner of development in each group. In the trilobites Barrande, Beecher, and others have shown that practically all the segments were added after the egg stage; in the Chilopods, Zograv, Voerhoff, and Heymons have shown that most of the specialization by addition of segments takes place during the egg stage; in the Hexapods numerous investigations have shown the segments arise only during the egg stage. This brief series exemplifies one of the most fundamental changes that has been undergone in the entire history of animals.

From the ethological point of view also this series represents a transition from predaceous marine animals, to predaceous terrestrial wingless forms, to predaceous terrestrial winged animals.

From the point of view of vertical distribution a glance at figure 8 shows the possibility of the derivations suggested. Trilobites were well differentiated at the base of the Cambrian series and reached their maximum deployment in Ordovician waters; they disappeared toward the end of Paleozoic time. The Chilopoda are known from Pennsylvanian rocks through

FIG. 8.

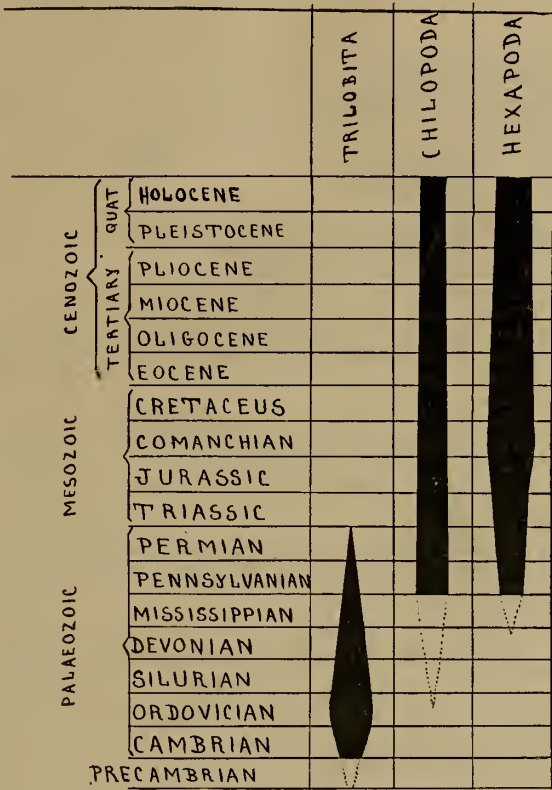


FIG. 8. Vertical distribution of trilobites, centipedes and insects. (Original.)

the discovery of *Palæocampa*. As this is clearly a highly specialized form (in virtue of the elaborate system of macrochætæ and the small number of segments) it seems probable that the group was highly differentiated in Pennsylvanian times and that it arose in much earlier Paleozoic times. Many insects are known from the Pennsylvanian rocks; it seems

clear that they reached their stage of maximum deployment in the Mesozoic era and that they are now in a condition of decline.

I wish finally to express my appreciation of the kindly help and criticism given during the preparation of this paper by Dr. Percy E. Raymond in the field of palaeontology; by Dr. R. V. Chamberlain in connection with Chilopod structures and embryology; and by Dr. Wm. M. Wheeler in the field of insect embryology.

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ART. XXXIX.—*Some Characters of the Apical End of Pseudorthoceras knoxense McChesney*; by GEORGE H. GIRTY.\* With Plate I.

SPECIMENS showing the apical end of uncoiled cephalopods are as a rule very rare. It is then somewhat in the nature of an exception that the apical end of *Pseudorthoceras knoxense* is not uncommonly preserved. The specimens that I have heretofore examined, however, show very little save that instead of tapering regularly, or if not regularly at least symmetrically, to a point, they are obliquely truncated so that the apex is not central but lies almost in the periphery.

There have recently come into my hands two specimens which show characters that have not previously been observed. Though the characters are not new to the group as a whole, but on the contrary are in accord with those of the few types on which Hyatt and others have made observations, they nevertheless seem deserving of record. These specimens were found weathered out of shale and they have had the original shell replaced by pyrite, a form of preservation particularly favorable to the retention of the finer surface structures of fossils. They were collected from the Des Moines group of the Pennsylvanian series near Des Moines, Iowa, and were sent to me by Mr. G. A. Larson, of whose generosity I avail myself of this occasion to make recognition.

The better of the two specimens shows the usual oblique truncation, the end being compressed so that a section across it

\* Published by permission of the Director of the U. S. Geological Survey.



would be elliptical. It is ornamented near the apex by very fine, transverse and longitudinal striæ which become finer and fainter above, so that all except the embryonic portion appears almost absolutely smooth. One side of the shell (that on which the apex lies) is marked toward the end by what may be a sort of cicatrice. This structure is a minute ridge defined on each side by a depression or sulcus, both ridge and sulci dying out distally and losing themselves within a short distance in the general curvature of the shell. Proximally the ridge is strongly prominent, its end forming the apex of the specimen. It thus resembles a minute rod projecting through the shell and ending abruptly. Under strong magnification it seems to show a very fine, longitudinal groove or slit. From what has been said it will be apparent that these structures are developed on the non-truncated side of the apex. The rest of the apical portion shows little besides the sculpture, which is, however, more or less modified in harmony with the configuration; the annular markings are not parallel but converge toward the straight side, thus apparently rounding over the end, and the longitudinal lines also are somewhat curved. A stria distinctly larger than the rest passes down the center of the straight side, in line with the ridge of the cicatrice.

The second specimen is less regular and less clear than the other. The end has a crumpled look and is bent over so that the apex projects beyond the plane of that side. A cicatrice (a short raised line) is apparently present but it is oblique. The concentric striæ, rather more irregular and remote than in the other specimen, can be distinctly seen, but the fine, longitudinal markings are so extremely faint as to be doubtful. I believe that they are really indicated. Their faintness, however, can hardly be ascribed to abrasion, for the other superficial characters appear to be obscured little, if at all.

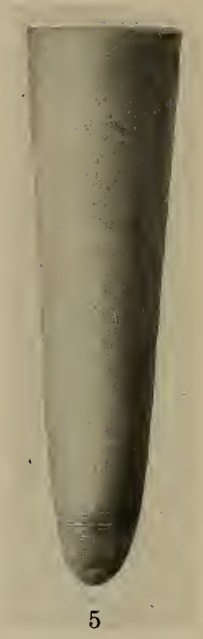
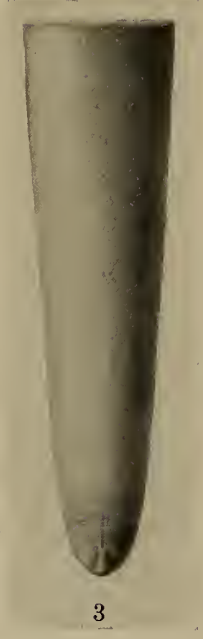
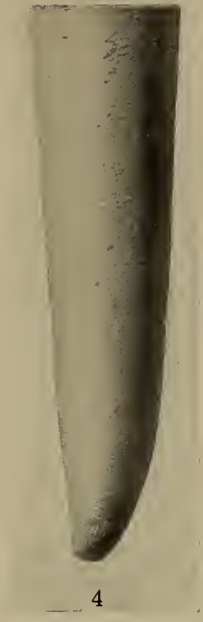
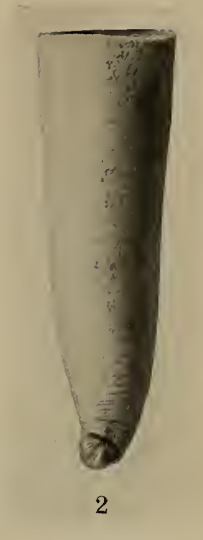
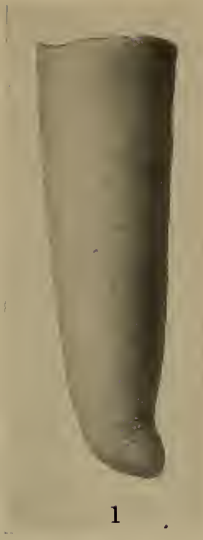
#### DESCRIPTION OF PLATE I.

*Pseudorthoceras knowense* McChesney.

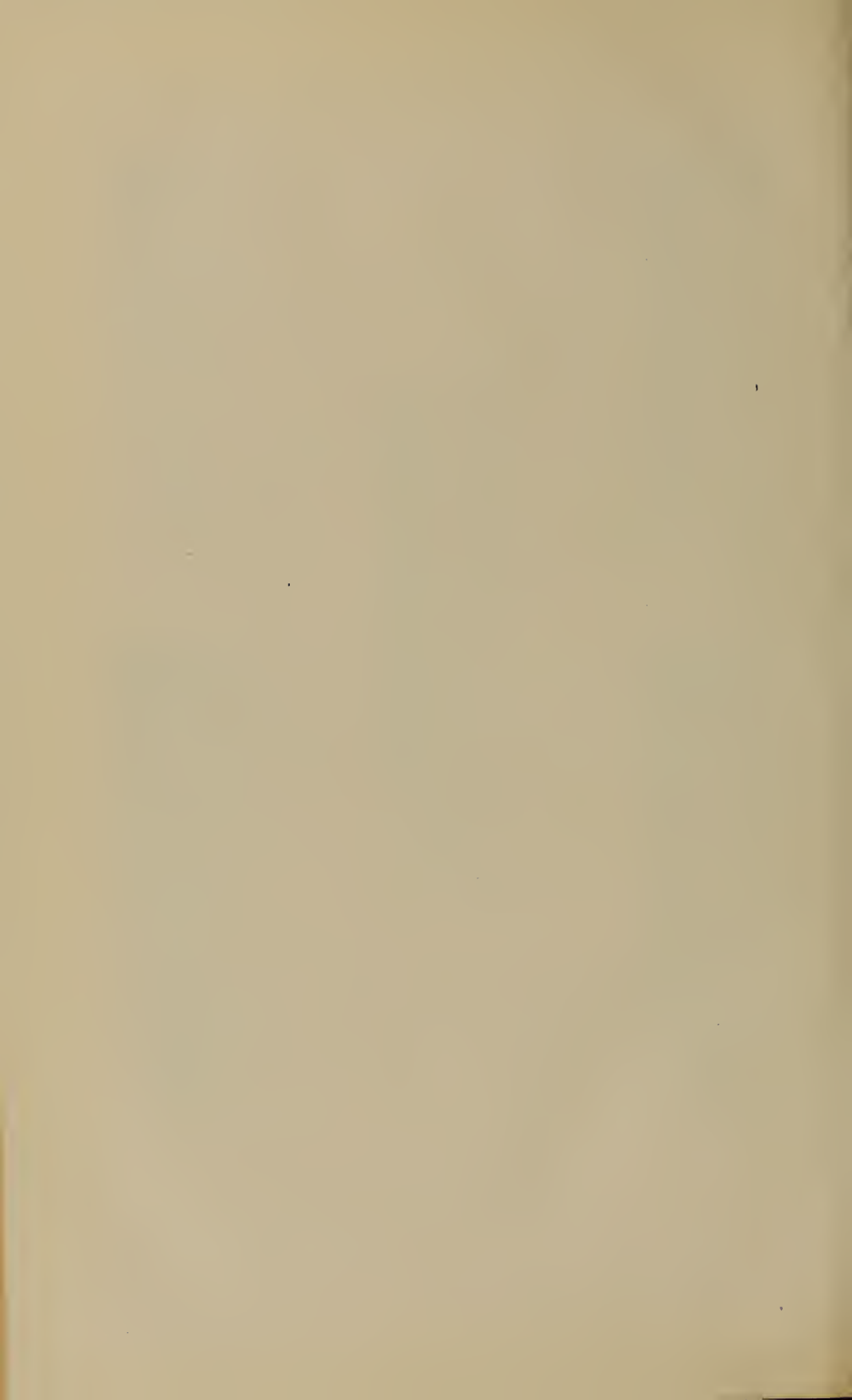
FIGS. 1 and 2. Two views of a specimen that has the end distorted. This specimen does not show the longitudinal lines of the other, and the transverse lines are farther apart.  $\times 10$ .

FIGS. 3, 4, and 5. Three views of a symmetrical specimen. The very fine cancellating sculpture is confined to the apical portion. Figure 3 shows the straight side and figure 5 the curved side of the specimen as presented by figure 4.  $\times 10$ .

Both specimens were obtained in the Des Moines group near Des Moines, Iowa.



*Pseudorthoceras knoxense* McChesney.



ART. XL.—*On the Electrolysis and Purification of Gallium*; by HORACE S. UHLER and PHILIP E. BROWNING.

[Contribution from the Sloane Physical and the Kent Chemical Laboratories of Yale University.]

DURING the process of separating metallic gallium from an alkaline solution by electrolysis it was noticed that black coral-like deposits sometimes formed around the cathode instead of the bright liquid globules which were expected. Since we have not found any mention of "trees" in the literature of gallium and since one of us has determined a sufficient condition for their production, it seems desirable to present a brief account of these interesting structures.\*

The electrolyte used was obtained in the following manner. The leady residue† was shaved into small pieces with an ordinary iron ice-plane and dissolved in a solution made from equal volumes of water and strong nitric acid. On cooling, most of the lead crystallized out as the nitrate. Concentrated sulphuric acid was then added to the filtrate and the resulting liquid was evaporated nearly to dryness. The insoluble lead sulphate was removed by filtration after the addition of water. Silver was next precipitated as the chloride by treating the filtrate with hydrochloric acid. By adding an excess of ammonia to the filtrate the hydroxides of gallium and indium were thrown down while most of the copper and zinc compounds were kept in solution. When working with large masses of material it was found necessary to repeat the last operation in order to effect a satisfactory purification of the hydroxides of gallium and indium. Finally, these hydroxides were separated from each other by taking advantage of the facts that indium hydroxide is insoluble in a solution of sodium hydroxide whereas gallium hydroxide is readily soluble in an excess of caustic soda. The filtrate thus obtained constituted the electrolyte used in the cells. With regard to the chemical processes just outlined, it may be remarked that each step was checked spectroscopically and found to produce satisfactory and efficient separations.

The electrolytic cells consisted of the following assemblage of very simple parts. The vessel containing the liquid was an ordinary glass crystallizing dish 10<sup>cms</sup> in diameter and 6.3<sup>cms</sup> deep. The anode was a thin rectangular sheet of platinum foil, the edges of the submerged portion being 5.5<sup>cms</sup> horizontally and 3.5<sup>cms</sup> vertically. The cathode consisted of a platinum wire sealed into a glass tube with about 2<sup>cms</sup> projecting at the lower end. This design usually enabled the gallium to

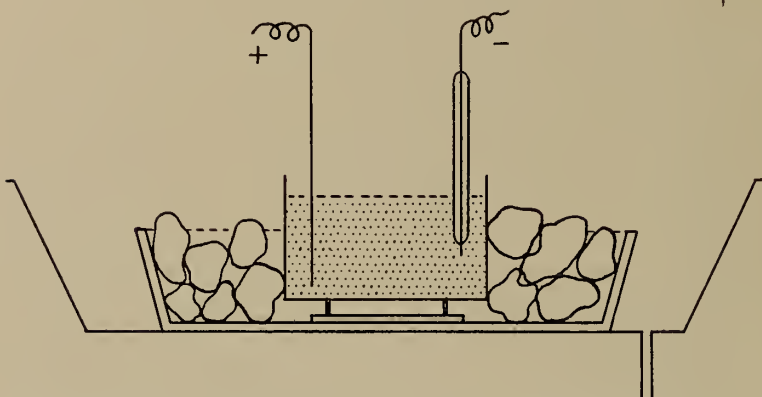
\* The configuration of the gallium trees closely resembles that of certain arborescent forms of native copper, the similarity being very striking in the case of a specimen from Bisbee, Arizona.

† This Journal, vol. xli, p. 351, April, 1916.



deposit as liquid globules which eventually fell automatically into a small glass spoon kept vertically below the cathode. A sectional view of a cell is shown to scale in figure 1. This diagram also indicates the additional convenient accessories employed in the production of trees. It was found that trees were invariably formed at about  $0^{\circ}\text{C}$ ., hence the statement that the figure is intended to suggest ice in a porcelain developing tray with the crystallizing dish supported on the four feet of an inverted brass stool, affords an adequate explanation.

FIG. 1.

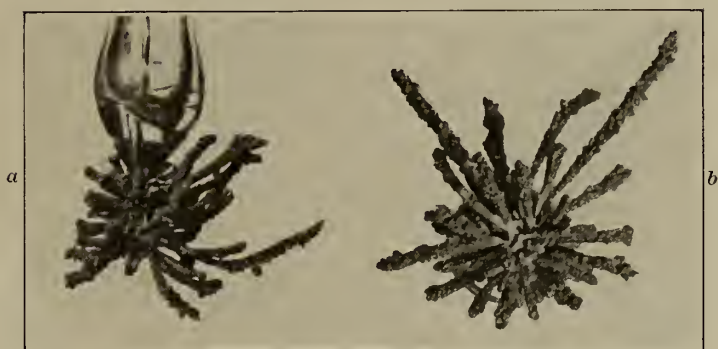


The current used was about 0.28 ampere giving a mean current density of 0.007 and 6 amperes per square centimeter at the anode and cathode respectively. These means are, of course, extremely rough since the distribution of electricity was far from uniform, especially at the cathode tip.

Since the melting point of gallium is about  $30^{\circ}\text{C}$ . it may occur to the reader to look upon the scheme of cooling the electrolyte as a perfectly obvious procedure for the production of trees. The necessary condition for the formation of these solid structures is, however, not as simple as might be expected at first thought. With three cells in series and at room temperature ( $23^{\circ}\text{C}$ .) it sometimes happened that one or two of the cathodes would continue to present liquid globules while the remaining cells or cell respectively would give the solid phase. Stroking a globule with a fragment of solid gallium often started the growth of a tree, but not invariably. The deposition of a tree at room temperature seems to depend upon a number of factors, such as the alkalinity of the electrolyte, the curvature of the surface of the liquid globule, etc. These idiosyncrasies are on a par with the predisposition to pro-

longed undercooling which metallic gallium ordinarily shows. Although we do not know the necessary conditions for the generation of trees we have never failed to produce them at will by cooling the electrolyte in an ice bath. If the solution is at room temperature and a liquid globule is growing, the change to the solid phase may be brought about gradually by placing ice in the tray and slowly cooling the liquid, whereas if the solution and electrodes are at  $0^{\circ}$  C. before and after the

FIG. 2.

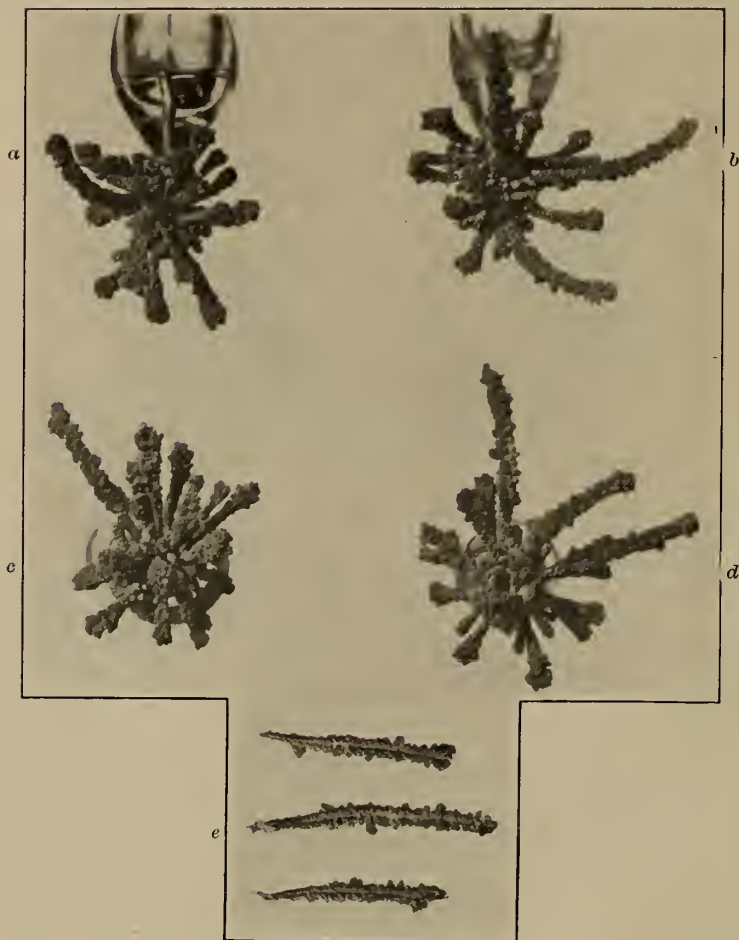


current is started the deposit will be solid from the very beginning.

A fairly complete idea of the appearance of the trees may be derived from the associated figures which were obtained by first photographing the objects natural size with a long focus Dallmeyer "Rapid Rectilinear" portrait lens stopped down to "U. S. 100" and then enlarging the negatives nearly two-fold. Figures 2*a*, 3*a*, and 3*b* show certain trees when the line of sight was horizontal, while 2*b*, 3*c*, and 3*d* give the respective aspects of the same trees when viewed from below, that is, when looking vertically upward along the axes of the cathodes. The three photographs first mentioned illustrate the fact that the branches of the trees are concave on the upper side. Figures 2*a* and 2*b* pertain to a tree which was formed with only one cathode in the solution. The two longest branches in 2*b* were directed approximately toward the outer edges of the anode, as was often found to be the case for a single cathode. Figure 3 represents two trees which were deposited simultaneously on two cathodes joined in parallel. In 3*a* and 3*b* the trees appear as seen from the center of the submerged portion of the anode, the plane containing the vertical axes of the cathodes being normal to the line of sight. For 3*c* and 3*d*

the relative position of the anode was such that if it were drawn on the page it would be represented by a straight line parallel to the upper edge of the sheet and cutting across the tops of figures 3*a* and 3*b*. Figure 3*e* shows the upper sur-

FIG. 3.



faces of three of the large branches broken from the pair of trees. These surfaces always have a medial groove apparently caused by the convection currents of hydrogen bubbles which stream upward in sheets from the outer edges of each branch.

The fully-developed branches are invariably thinnest at the point of attachment to the "trunk" and grow more massive at the outer or free ends. (In figure 3e the tips of the wires—on which the branches were mounted for convenience in photographing—can be seen at the free ends of the branches and should not be confused with the details of the gallium structure.)

The growth of a tree takes place in the following stages. It begins as a spherical ball which appears to be perfectly smooth at first but which becomes visibly rough as the diameter increases. These rugosities develop into sharp points which eventually build up a configuration similar to the outside of a chestnut burr. After this the characteristics of a figure of revolution are gradually lost as certain branches grow more rapidly than others. In general, the branches of young trees are thin and pointed while those of more mature trees are bludgeon-shaped as shown in figure 3. Under the given experimental conditions about 20 hours were required to deposit the structures reproduced in the photographs. When the cathode consists of a bare platinum wire which projects 6 or 8 millimeters below the free surface of the electrolyte, the trees develop relatively broad leaves instead of roughly cylindrical branches. These leaves are approximately horizontal and are piled up one above another over the entire length of the submerged portion of the wire.

Passing from geometrical to physical and chemical properties, the following facts may merit recording. The material of the trees is hard and strong like the solid phase derived in any other manner. Hence the trees are stable, permanent structures so long as they are kept at a temperature ten degrees, more or less, below the melting point. For this reason, as well as on account of their general appearance and ease of control during development, the gallium trees would afford a more interesting and instructive lecture experiment than the classic lead ones. Throughout the period of electrolytic deposition the trees are intensely black. This color is largely superficial, for when the branches and trunk are cut to pieces, the freshly exposed surfaces have either the dull appearance of slightly tarnished lead or the characteristic silver luster of clean gallium. After removal from the electrolyte and drying, the branches become partially covered with gray and white patches, as may be seen in the photographs. Three trees which had been kept under water for over a month and then allowed to dry were chiefly grayish black. The ends of their branches, however, had turned brown and a pure white powder completely filled the spaces on the undersides of the trees where the branches joined the trunk. The color changes



are probably closely related to the following phenomena. As soon as the current is interrupted the trees react on the electrolyte and give off gas bubbles copiously. When kept in ice water they evolve a little gas for a day or two, the rate of reaction decreasing as the time of immersion increases. The evolution is more rapid in water at 23° C. When a tree (of any previous history) is plunged into boiling water a relatively large amount of gas is suddenly liberated with a hissing sound as the parts of the structure coalesce into a mixture of bright liquid globules and the colored compounds.

The metal deposited in the liquid state has properties similar to those of the trees. When a globule is allowed to remain in the electrolyte (in the spoon) for ten or more hours the surface loses its high reflecting power and becomes coated with a blackish skin. The brilliant gallium shot (conveniently obtained by dropping a fresh globule into cold water and then hastening solidification by kneading the molten metal with a thin glass rod which has previously become contaminated with the solid phase) gradually acquire a dark coating when kept in air, water, ethyl alcohol, and kerosene. It was also observed that some gas was evolved in each of the liquids, especially in distilled water. In fact, on one occasion the cork stopper of a vial, which had contained a pile of shot under water for several days, was blown several feet upward by the pressure of the gradually accumulated gas. The predisposition of the metal to acquire a dark surface may be greatly diminished by first removing the black substance with dilute nitric acid (or otherwise) and then agitating the liquid gallium in four or more changes of boiling water. The metal thus cleansed partially crystallizes (sometimes with edges more than 1<sup>cm</sup> long) when converted into the solid phase and only shows a slight gray hue after a month's exposure to ordinary air. Since it was not the object of this investigation to identify the black, brown, and white compounds mentioned above we are not prepared at present to give a complete explanation of the reactions involved; nevertheless, it seems probable that the colored compounds correspond to different degrees of oxidation and that sodium and water play important parts in the observed phenomena.

During the process of electrolyzing (at room temperature) the alkaline solution of gallium a white, flocculent substance often appears in the liquid, especially in the immediate vicinity of the surface of the anode facing the cathode. When the electrolyte used is the liquid first decanted the white material sometimes forms in relatively large quantities on the anode from which it eventually peels off and forms a talus at the bottom of the dish. A sample of this substance was collected,

washed with distilled water, and tested both chemically and spectroscopically. All the evidence thus obtained favored the belief that the compound is gallium hydroxide. In this connection, it may be remarked that an apparently identical material is produced by bubbling carbon dioxide through a solution of gallium in sodium hydroxide. The formation of the white substance at the anode is doubtless due to the decrease in concentration of the sodium solvent in this region. This decrease may be brought about both by the absorption of carbon dioxide from the air and by the ionic redistribution involved in the passage of the electric current. Obviously the electrolyte may be cleared up by adding caustic soda.

Attention may now be directed to figure 4 which not only illustrates the last paragraphs both of the present article and of our preceding paper (*loc. cit.*) but it also constitutes the only reproduction of the complete arc spectrum of gallium which we have seen. Figure 4*a* shows the spectrum of the mother liquor of the caesium-gallium alum mentioned below. The purification produced by ten crystallizations of the alum is made evident by figure 4*b*. The spectrum of a specimen of electrolytic gallium (not heated in hydrogen) is given in figure 4*c*. Spectrogram 4*d* pertains to the gallium-indium alloy obtained by a sweating process. The following table of wave-lengths (International System) will assist in the identification of the most prominent lines. The bands and faint lines due to the carbon arc and to slight impurities are not tabulated. The numbers indicating lines belonging to the first order of the concave grating have no accents. Lines of the second and third order are designated respectively by single and double accents. *H* = "head" of gallium band. *n* = new (see previous paper). *R* = widely reversed throughout entire length of arc. *r* = reversed chiefly near positive electrode. Lack of space precluded numbering the strong zinc lines shown in figure 4*d* between 19' and 21'. Their wave-lengths are 4680.138, 4722.164, and 4810.534. In figure 4*a* the principal caesium lines ( $\lambda\lambda 4555.34$  and  $4593.21$ ) may be readily seen on the less refrangible side of the very intense indium line,  $\lambda 4511.37$ .

As already stated in our previous paper,\* a fairly satisfactory separation of gallium and indium may be obtained by the action of sodium hydroxide upon the hydroxides of the elements, as recommended by Lecoq de Boisbaudran. Another method† described by the same investigator, the crystallization of the ammonium alums in 70 per cent ethyl alcohol, proves also good, a very few crystallizations giving a gallium product showing only spectroscopic traces of indium, zinc, copper, and lead.

\* This Journal, vol. xli, p. 351, April, 1916.

† Compt. rend. (Paris), xcv, 410.

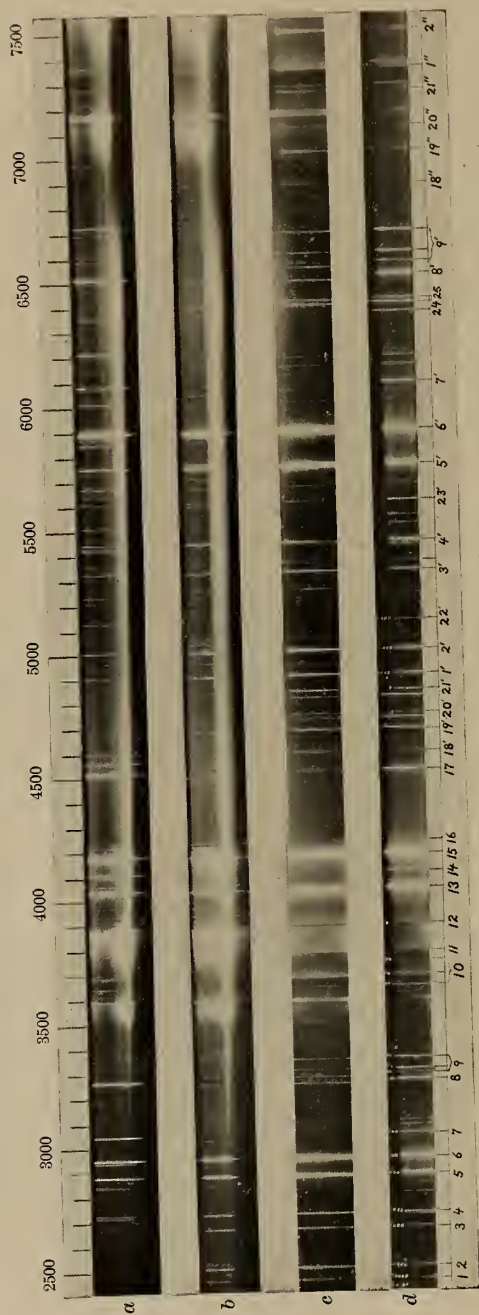


FIG. 4.

<i>Gallium.</i>		<i>Lead.</i>	
18', 18"	2294 <i>n, R.</i>	23'	2802·01
19', 19"	2338 <i>n, R.</i>		3639·57
20', 20"	2371 <i>n, r.</i>	10	3683·47
21', 21"	2418 <i>n, r.</i>		3740·00
1, 1', 1"	2450·10 <i>R.</i>		
2, 2', 2"	2500·18 <i>R.</i>		<i>Zinc.</i>
3, 3'	2659·84 <i>r.</i>	23'	2800·9
4, 4'	2719·66 <i>r.</i>		{ 3282·28
5, 5'	2874·24 <i>R.</i>		{ 3302·56 }
6, 6'	2943·66 <i>R.</i>	9, 9'	{ 3302·91 }
11	3778 <i>n, II.</i>		{ 3344·99 }
12	3889 <i>n, H.</i>		{ 3345·51 }
13	4033·03 <i>R.</i>	24	6362·346
15	4172·05 <i>R.</i>		
—	{ 5353·81		<i>Calcium.</i>
	{ 5359·8	16	4226·72
	{ 6396·84		
25	{ 6413·74		
 <i>Indium.</i>			
22'	2560·22		
7, 7'	3039·36 <i>r.</i>		
8, 8'	3256·03 <i>r.</i>		
14	4101·82		
17	4511·37		

The reasonably complete separation obtained by the fractional crystallization of the ammonium alums of gallium and indium from water solution, as previously described,\* suggested the substitution of caesium for ammonium. Accordingly, a portion of a gallium-indium alloy weighing 2·3 grms., and containing 10 per cent of indium, small amounts of zinc and lead, and traces of copper, was converted into the sulphates, and a calculated amount of caesium sulphate was added. The caesium-gallium alum crystallized readily,† and after ten crystallizations a spectroscopic examination of the product showed practically pure gallium; the indium, zinc, copper, and lead having been almost entirely removed (fig. 4*b*). The mother liquor gave evidence of a considerable amount of indium and also indubitable evidence of the presence of zinc and lead, showing that indium, zinc, and lead may be removed from gallium by this method (fig. 4*a*).

The examination of some gallium deposited electrolytically from an alkaline solution showed the presence of traces of zinc (fig. 4*c*), and the following process was tried to separate the zinc: a weighed porcelain boat containing 0·15 grms. of the element was placed in a combustion tube so connected with a

\* This Journal, vol. xli, p. 351, April, 1916.

† These crystals lend themselves well to a microchemical test for gallium.



hydrogen generator that the hydrogen was dried by passing through strong sulphuric acid. While the current of hydrogen was passing through the tube the full heat of the Bunsen burner was applied directly under the boat, and the heating was continued until no further sublimate appeared. This was determined by moving the boat from time to time and examining the tube above it. The boat and its contents were then allowed to cool in the current of hydrogen, and when cool were removed and weighed. A loss of 0.0008 gm. was observed, and the contents of the boat, tested spectroscopically, did not give the slightest trace of the strongest zinc lines. The amount of sublimate in this experiment was too small to be removed for examination, but a much larger sample of the metal, similarly treated, gave a sublimate which proved when examined spectroscopically to be chiefly zinc.

Yale University, New Haven, Conn., August, 1916.

ART. XII.—*A Pleistocene Locality on Mt. Desert Island, Maine*; by DWIGHT BLANEY and F. B. LOOMIS.

ON the southern end of Mt. Desert Island, Maine, at the head of Goose Cove, there occurs a deposit of Pleistocene clays which has never been described. The bed is so peculiarly rich in well-preserved fossils that it should be a frequented locality for the study of postglacial marine remains. It has a further interest because on the other side of the island in Frenchman's Bay, only about ten miles away, a careful study of the marine fauna has been made for a period of many years, so that an opportunity is presented for an unusually interesting comparison of these two faunas, both the Pleistocene and the recent faunas having lived under approximately the same bottom conditions, except as to the matter of temperature.

The clays form a bed from below the low-tide level to about twenty feet above high tide, making a bank which blocks the head of the cove, and especially along its lower portions is well exposed. In the shallow water of the cove many of the shells may be found washed out, but most of the fossils will not stand such rough treatment as the weathering by the sea imposes. The clay is fairly soft and as the fossils nearly fill it, collecting is rapid work. We found it convenient to collect the larger shells on the spot and carry home blocks of clay, from which after drying the delicate and smaller shells could be easily washed out. The abundance of the material may be judged from the fact that in two to three hours we collected over three hundred shells.

The following is a list of the shells taken from this locality, with comments as to the abundance of the fossils in the clay, and in Frenchman's Bay, some ten miles away:

	Goose Cove	Frenchman's Bay
1. <i>Pecten islandicus</i> , Müller	The most abundant and well preserved form.	Very rare, only dead shells ever found.
2. <i>Mytilus edulis</i> , Linne	Very abundant but poorly preserved, crumbling easily.	Very abundant.
3. <i>Modiolus modiolus</i> , Linne	Rather rare and of small size.	Very abundant.
4. <i>Nucula tenuis</i> , Montagu	Rare.	Common.
5. <i>Leda minuta</i> , Müller	Fairly common.	Not found.
6. <i>Leda pernula</i> , Müller	Not common.	Not found.
7. <i>Astarte elliptica</i> , Brown	Very abundant.	Not found.
8. <i>Astarte laurentiana</i> , Lyell	Common.	Not found.

	Goose Cove	Frenchman's Bay
9. <i>Cardium pinnulatum</i> , Courad	Not common.	Very common.
10. <i>Serripes groenlandicus</i> , Gmelin	Fairly common.	Rare.
11. <i>Macoma calcarea</i> , Gmelin	Very abundant.	Common.
12. <i>Mya arenaria</i> , Linne	Rare.	Very abundant.
13. <i>Mya truncata</i> , var. <i>uddevallensis</i>	Very abundant.	Never dredged alive.
14. <i>Saxicava arctica</i> , Linne	One double valved specimen.	Very common.
15. <i>Bela turricula</i> , Montagu	Rare.	Very common.
16. <i>Buccinum undulatum</i> , Linne	Common.	Common.
17. <i>Fusus</i> ( <i>Chrysodomus</i> ) <i>decemcostatus</i> , Say	Rare.	Very common.
18. <i>Fusus</i> ( <i>Sipho</i> ) <i>pygmaeus</i> , Gould	A fragment.	Very common.
19. <i>Trichotropis borealis</i> , Sowerby	Rather rare.	Common.
20. <i>Aporrhais occidentalis</i> , Beck	Rare.	Not common.
21. <i>Lunatia groenlandica</i> , Beck	Common.	Not common.
22. <i>Lepeta caeca</i> , Müller	Fairly common.	Very common.
23. <i>Margarita cinerea</i> , Couthouy	Fairly common.	Common.
24. <i>Rhynchonella psittacea</i> , Gmelin	Two valves.	Not found.
25. <i>Terebratella spitzberg-</i> <i>ensis</i> (?), Davidson	One fragment.	Not found.

✓ Beside the above these clays contain a series of barnacles, and Bryozoa, but we did not collect these in quantities sufficient to be significant.

The species most abundant in these Pleistocene clays, like *P. islandicus*, the *Ledas*, *Astartes*, *Mya truncata*, *Rhynchonella* and *Macoma calcarea*, are now either wanting or extremely rare in Frenchman's Bay, but are the common forms of the Labrador coast. This whole Pleistocene fauna with much the same relative abundance in the different species is the typical fauna of the Labrador waters. The conditions under which the Pleistocene fauna lived and those of the Labrador waters of to-day would seem to be much the same, and the sole cause of the transfer of this fauna from Maine to Labrador has been temperature. As the Pleistocene fauna moved north, a more southern fauna has taken its place.

If the Pleistocene fauna of Maine and the recent fauna of

Labrador to-day were both preserved as fossil faunas, the temptation would be very strong to identify them as of the same age, which indicates some of the difficulties in the way of synchronizing two extinct faunas, when the time element separating them is not very great. In this case the constant element has been temperature.

The clays at Goose Cove, Mt. Desert Island, would usually be designated as Leda Clays, but it should also be noted that they contain *Saxicava*, which in Canada belong to a later phase. The mingling of Leda faunas and *Saxicava* faunas is characteristic of the deposits in Maine.

In general the Goose Cove fauna resembles most closely the fauna found in New Brunswick and described by Matthew. It is also very similar to the fauna found at Portland, Me., but differs from both of these in many fundamental respects. From the collections made at Saco, Me., and at Gardiner, Me., the Goose Cove fauna differs even more widely, though it would be expected to resemble them more closely. The presence of *Modiolus modiolus* in abundance, of *Trichotropis*, of the *Ledas*, and *Astartes*, of *Rhynchonella psitticea* and *Terebratella* make a surprising close affinity to the fauna found at Montreal where these forms are distinctive, and occur in about the same relative abundance as at Goose Cove.

For the most important literature see the following, which contain all the minor references :

Dawson, J. W., Canadian Ice Age, 1894.

Packard, A. S., Glacial Phenomena of Labrador and Maine, Memoirs Boston Soc. Nat. Hist., vol. 1, pp. 210-303, 1865.

Stone, G. H., The Glacial Gravels of Maine, U. S. Geol. Survey, Monograph 34, 1899.

Amherst, Mass.



ART. XLII.—*Methods in Reversed and Non-reversed Spectrum Interferometry*; by CARL BARUS.\*

1. *Introductory*.—Thus far it had been impossible to use the fringes individually, because of the tremor of the apparatus. It is therefore desirable to endeavor to obviate this annoyance, if possible, and the end would appear to be most easily obtainable if the distances are made smaller. At the same time the results for small distances will be interesting for this very reason, in contrast to the long distance methods (meters).

Furthermore, the development of different methods, with a consideration of the peculiarities of each, will constitute an essential contribution to the theory of the phenomena. For from this, the degree of importance which is to be attached to the original diffraction at the slit of the collimator (i. e., the limiting angle at the slit, within which diffracted rays must lie to be subsequently capable of interference, whether reversed or inverted) will appear in its relations to the total dispersion of the system. The slit, however fine, is still a wavefront of finite breadth.

2. *Apparatus*.—In the first experiments, the device with two identical reflecting gratings,  $GG'$ , fig. 1, was firmly mounted on a massive spectrometer, the four mirrors  $m$ ,  $n$ ,  $M$ ,  $N$ , being specially attached. White light received from the collimator,  $L$ , after two dispersions, was viewed at the telescope  $T$ . Both gratings were on a slide  $ss$ , enlarged in fig. 2, set in the direction  $LT$  of the previous figure. The carriage,  $c$ , fig. 2, was provided with universal joints ( $a$  with a vertical axis,  $b$  and  $e$  with horizontal axes normal to each other), while the swivelling of the grating  $G$  was controlled by set screws at  $d$ , relative to the axle at  $e$ .

Unfortunately the displacement of the mirror  $M$  (on a micrometer) passes the corresponding pencil across the face of the grating  $G'$  and thus virtually includes a fore and aft motion of the latter. Thus the fringes pass, with rotation, from very fine hairlike striations, through a horizontal maximum of coarseness, back to vertical lines again, when homogeneous light and a wide slit are employed. The annoyances due to tremor, however, were not overcome. Moreover there is difficulty in obtaining Fraunhofer lines normal to the longitudinal axis of the spectrum. This method was, therefore, abandoned.

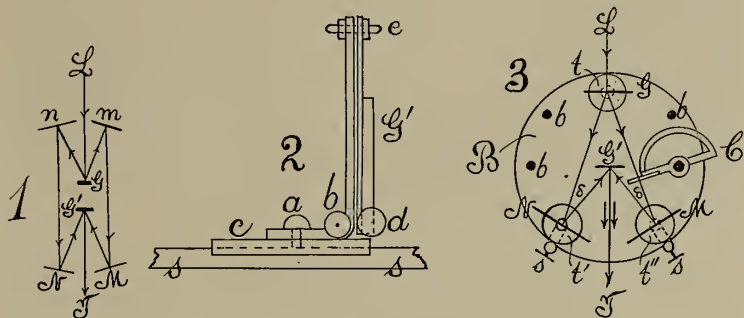
The design shown in fig. 3, with a transmitting grating at  $G$  (grating space  $D = 352 \times 10^{-6}$  cm.) and a stronger reflecting grating at  $G'$  ( $D = 200 \times 10^{-6}$  cm.), was next tested,  $M$

\*Abridged from a Report to the Carnegie Institution of Washington, D. C.

being the micrometer mirror. The mean distance of  $M$  from  $N$  was about  $15\text{cm}$ , from  $MN$  to  $G'$  about  $10\text{cm}$  and to  $G$   $40\text{cm}$ . Later these distances were enlarged. First order spectra were used and the fringes obtained easily and brilliantly, particularly with mercury light, in both green and yellow. They rotated as above, admitted a displacement  $M$  of about  $1\text{cm}$ . But they were still too mobile to be used individually.

The same design, fig. 3, was now mounted on a round heavy block of cast iron,  $B$ ,  $30\text{cm}$  in diameter, and  $4\text{cm}$  thick, the distance  $G$  to  $MN$  being about  $20\text{cm}$ . A number of screw sockets  $b, b, \dots$ , were drilled into  $B$  on the right and left, for mounting subsidiary apparatus.  $G'$  as before was on the universal slide

FIGS. 1, 2, 3.



(fig. 2), movable in the direction  $LT$ . The tablets,  $t, t'$ , etc., of  $G, M, N$ , and  $G'$  were mounted tentatively on standards of gas pipe  $1.6\text{cm}$  in external diameter and  $6\text{cm}$  long. Slight pressure by the finger tips showed a passage of several fringes across the field, but the fringes were stationary in the absence of manual interferences and in spite of all laboratory tremors. A parallel arm of the same pipe was therefore firmly attached to the stem of  $N$  and  $M$ , each arm terminating in a fine horizontal set screw,  $s, s$ , below, adapted to push against the rim of the iron block. In this way adequately stationary conditions and an elastic fine adjustment for superposed longitudinal spectrum axes were both secured with advantage. It was now possible to manipulate the micrometer at  $M$  by hand; but a glass plate compensator,  $C$ , rotated by a tangent screw over a graduated arc was also convenient. Later other types were attached, including an air compensator, in which path difference was secured by exhausting the air within a closed pipe provided with glass plate ends. These contrivances were eventually superfluous, however, as it was found that on redne-

ing the rotation of the micrometer screw, the latter could be used at once.

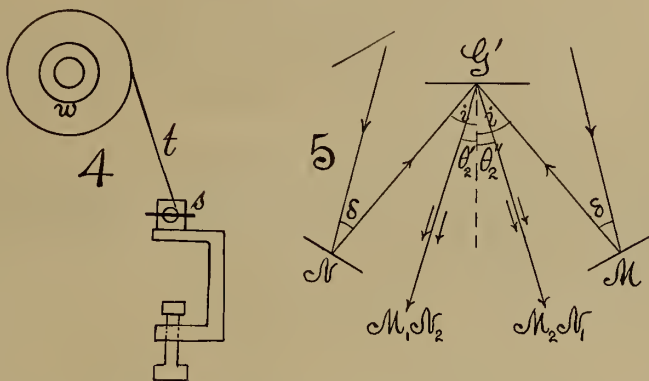
In case of homogeneous light and a wide slit, fringes were visible in an ordinary telescope for a play of over  $2^{\text{cm}}$  of the micrometer screw, passing however between extremes of fineness. The slit images are not of equal breadth, if first and second order spectra are superposed, but if the longitudinal axes are coincident any position of the narrow image within the broader produces a wide vertical strip of fringes, usually more or less horizontal. They are very easily found. The sodium flame is too feeble for use. The mercury arc is unfortunately too flickering, so that the fringes jump about and are useless for measurement. Excellently sharp quiet fringes are obtained with sunlight (white), in which the cross hatched interference pattern is nearly linear at the line of symmetry of the reversed spectra. The fringes climb very decisively up and down this line with the motion of the micrometer, reduced as suggested. The electric arc or a Nernst filament are equally available as a source of light. Finally by suitably rotating the grating  $G'$  on the axis  $e$ , by aid of the set of screws  $d$ , fringes whose distance apart is over  $\frac{1}{3}$  of the width of the telescope field may be obtained, quite sharply. As this distance represents but  $30 \times 10^{-6}$  em., there is no difficulty of realizing  $10^{-6}$  em., in case of these long fringes.

3. *Measurements. First and second order spectra.*—The steadiness of the fringes even in an agitated location induced me to make a few measurements for orientation. Accordingly the Fraunhofer micrometer, reading to  $10^{-4}$  em., was provided at its screw head with a light wooden wheel,  $w$ , fig. 4, about  $10^{\text{cm}}$  in diameter and 3 millimeters thick. A groove was cut in the circumference of the wheel, so that a silk thread,  $t$ , could be wrapped around it. The other end of the thread was wound around a brass screw,  $s$ , about 6 millimeters in diameter, turning in a nut, preferably of fiber, which was fastened to the edge of the table by a small brass clamp. In this way it was possible to control the motion of individual fringes crossing a fiducial line in the field of the telescope. This simple device worked surprisingly well, a smoothly running micrometer being presupposed. In fact, it was possible to set a fringe to a few millionths of a centimeter. Later the micrometer head was grooved and a finer turning screw suitably attached to the base,  $B$ , of the apparatus.

The fringes should be widened as far as convenient, by rotating the grating on the axle  $e$ , fig. 2, by aid of the set screws,  $d$ . In this case they climb up or down the transverse strip, as  $s$  in fig. 4 is slowly rotated. Fringes moving horizontally are not serviceable, because they are too near together.

It is not difficult to obtain the single vertical line (which shifts laterally), black or bright, on suitable rotation about  $e$ . On either side of this transitional adjustment the fringes move vertically (climb or fall) in opposite directions, for the same micrometer displacement. The arrow-shaped forms are also often satisfactory, and may be obtained by adjusting the two bright patches on the reflecting grating into coincidence, by the eye, in the absence of the telescope. The grating  $G'$  is

FIGS. 4, 5.



moved fore and aft for this purpose on the slide,  $s$ , fig. 2, until the two bright strips become one.

In making the first adjustment, I incidentally combined the first order spectrum from  $N$ , with the second order spectrum from  $M$ , as shown in fig. 5, under the impression that the wider  $D$  groups from the latter were due to slight curvatures of mirrors. The fringes were nevertheless easily found and showed no anomalies, except that observation had to be made near  $M$  or  $N$ .

It appears from fig. 5 that the equations for this case imply

$$\begin{aligned} \sin i + \sin \theta_2'' &= 2\lambda / D_2 \\ \sin i - \sin \theta_2' &= \lambda / D_2 \end{aligned}$$

where the angles  $i$  and  $\theta$  are equal ( $\theta_2' = \theta_2''$ ). Thus  $\sin i = 3\lambda / 2D_2$  and  $\sin \theta = \lambda / 2D_2$ ,  $D_2$  being the grating constant ( $D_2 = 200 \times 10^{-6}$  cm).

$$\begin{aligned} \text{Hence } \sin i &= .4420, \sin \theta_2 = .1423 \\ i &= 26^\circ 14', \theta_2 = 8^\circ 11'. \end{aligned}$$

while from the first grating,  $D_1 = 350 \times 10^{-6}$  cm.,

$$\begin{aligned} \theta_1 &= 9^\circ 38'; \text{ whence } \sigma = i + \theta_1 = 35^\circ 52' \\ \delta &= i - \theta = 16^\circ 36' \end{aligned}$$



Trial readings of the micrometer for a passage of 20 fringes each were made without special precautions and showed (omitting the data) an average of  $10^{-6} \times 30.1^{\text{cm}}$  per fringe. As the line of symmetry lay very near the two  $D_1, D_2$  doublets, this is obviously an approach to half a wave length. For accurate work  $D_1, D_2$  and  $D', D'$ , should be superposed, in which case the fringes would lie between and actually correspond to their mean wave length.

A number of measurements, like the above, were now made with different types of fringes, and the average values successively taken from 3 or 4 batches of 30 fringes each.

The results were less decided when long fringes were used. The final mean value of the 10 sets was  $\delta e \times 10^6 = 30.19^{\text{cm}}$  per fringe. Actual or approximate coincidence of the  $D$  lines made no appreciable difference.

In the following results the reflection from the mirror  $M$ , fig. 5, was used in the first order and from  $N$  in the second order after leaving  $G'$ . Observations were made near  $N$ , fig. 5. The displacement corresponding to 80 fringes was successively taken.

The mean value

$$10^6 \delta e = 30.0^{\text{cm}}$$

agrees with the above.

Similar trial observations (combined first order from  $N$  and second order from  $M$ ) were made with red light near the  $C$  line in series of six with a mean value  $\delta e \times 10^6 = 34.0^{\text{cm}}$ .

Again near the  $b$  line (green) giving  $\delta e \times 10^6 = 27.5^{\text{cm}}$  per fringe. These should therefore be distributed in terms of wave length and they are as nearly as may be expected in the ratio in question, seeing that the total displacement for 60 fringes does not exceed  $.004^{\text{cm}}$ . For accurate data it would be necessary to count many hundreds of fringes, and to correct the  $\delta e$  values by multiplying by  $\sec(\theta_2 - \theta_1) / 2$ . I have not done this as the red and green fringes are not so distinctly seen as the yellow.

4. *Continued. First order spectra.*—The apparatus was now readjusted in such a way that first order spectra were available from both mirrors. This puts the grating  $G'$ , fig. 3, at a greater distance from the line  $M$  and  $N$  than before, for the angle  $\theta_2$  is smaller. A series of trial results were investigated in the same manner as above, the mean values from four successive pairs of eighty fringes, each being taken in three repetitions. They gave an average value of  $\delta e \times 10^6 = 29.25^{\text{cm}}$ , somewhat smaller than half a wave length of the  $D$  light used. Unfortunately the screw at  $s$  (fig. 4) here worked jerkily, to which the low value is probably due.

In this case  $\sin \theta_1 = \lambda / D_1$ , where  $D_1 = 352 \times 10^{-6}$  cm. or  $\theta_1 = 9^\circ 38'$ ; and  $\sin \theta_2 = \lambda / D_2$ , where  $D_2 = 200 \times 10^{-6}$  cm. or  $\theta_2 = 17^\circ 9'$ , whence

$$\sigma = 26^\circ 47' \text{ and } \delta = 7^\circ 31'.$$

In a later series of experiments, the play of the screw,  $s$ , was improved, so that it ran more smoothly. The following values were found in two repetitions, from four pairs of 80 fringes each :

$$\delta e \times 10^6 = 30.1, \quad 30.0^{\text{cm}},$$

and in five pairs of 100 fringes each,  $\delta e \times 10^6 = 29.5^{\text{cm}}$ .

If the mean value of these data is compounded with the above mean, the average is

$$\delta e \times 10^6 = 29.56^{\text{cm}}.$$

5. *Continued. Second order spectra.*—The same phenomenon was not sought in the two second order spectra from  $G'$ . Magnificent arrows were obtained, useful throughout about 5 millimeters of the micrometer screw, after which they lost clearness. This limited range could no doubt be immensely increased if optical plate glass were employed in place of the ordinary plate used. The data for pairs of observations, including 60 or 80 fringes, gave (5 repetitions) a mean value of  $\delta e \times 10^6 = 30.5^{\text{cm}}$ . In the last two measurements the sodium doublets coincided.

In this case  $\sin \theta_2'' = 2\lambda / D_2$ , where  $D_2 = 200 \times 10^{-6}$  cm. and  $D_1 = 352 \times 10^{-6}$  cm. (first grating). Thus

$$\sigma = 45^\circ 44', \quad \delta = 26^\circ 28'.$$

If the above mean data are summarized the results appear as follows ( $\lambda = 58.93 \times 10^{-6}$  cm.):

- $G$  1st order,  $G'$  1st order, mean  $\delta e \times 10^6 = 29.56^{\text{cm}}$
- $G$  1st order,  $G'$  1st and 2d order, mean  $\delta e \times 10^6 = 30.2$
- $G$  1st order,  $G'$  2nd order, mean  $\delta e \times 10^6 = 30.5$ .

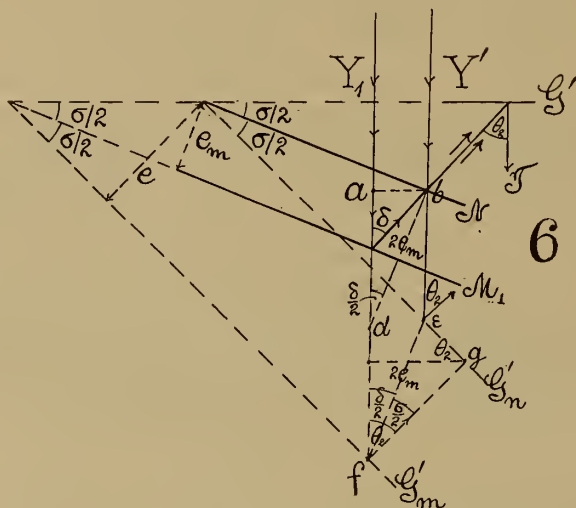
If computed as  $\delta e = \lambda / 2 \cos \delta/2$ , these become

$\delta e \times 10^6 = 29.53^{\text{cm}}$	Diff.....	+ .03 <sup>cm</sup>
29.78		+ .42
30.27		+ .23

The maximum error of  $4 \times 10^{-7}$  cm. is equivalent to but a little over 1 per cent of the distance between fringes, and it would be idle to suppose that the apparatus, fig. 4, could be set more accurately. In fact, the largest error occurs in the second set which were first made and in which the play of the apparatus, fig. 4, was inadequately smooth.

6. *Theory.*—Hence the theory\* of the apparatus (fig. 6) may be regarded as justified. Here the rays  $Y_1$  and  $Y'$  come from the first grating ( $G$  transmitting) and after reflection from the opaque mirrors  $M$  and  $N$  (the former on a micrometer) impinge on the second reflecting grating  $G'$ , with a smaller grating space, and thereafter interfere along the line  $T$ , entering the telescope. To treat the case the mirrors  $M$ , etc., may be rotated on the axis  $T$  normal to  $G'$  in the position  $M_1$ .  $G'_n$  and  $G'_m$  show the reflections of  $G'$  in the mirrors  $N_1$  and  $M_1$ . We thus have a case resembling the interferences of thin plates

FIG. 6.



and if  $e_m$  is the normal distance apart of the mirrors  $M_1$  and  $N_1$ , the displacement  $\Delta e_m$  per fringe is given by

$$\lambda = 2\Delta e_m \cos \delta / 2$$

where  $\delta$  is the angle between the rays incident and reflected at the mirrors. This is the equation used above. If the mirrors and the reflections of the gratings  $G'$  make angles  $\sigma/2$  and  $\sigma$  with  $G'$ , the actual lengths of the rays (prolonged) before meeting to interfere, terminate in  $\epsilon$  and  $f$  respectively. Let the image of  $G'$  be at a normal distance  $e$  apart. Then  $e = 2e_m \cos \sigma/2$ , for the figure  $fdbe$  is a parallelogram. If the distance  $\epsilon g$  is called  $C$  we may also write

$$\lambda = e \cos \theta_2 + C \sin \theta_2$$

since  $C = 2e_m \sin \sigma/2$  and the angle of diffraction  $\theta_2 = (\sigma + \delta)/2$ .

\* This Journal, xlii, pp. 63-73, 1916; cf. § 3.

7. *Compensator Measurements.*—A. With the object of testing the interferometer under a variety of conditions, measurements were made with a number of different compensators and the experience obtained may be briefly given here. The first of these was a very sharp wedge, such as may be obtained from ordinary plate glass. The piece selected, cut from an old mirror, on being calipered showed the following dimensions :

Length,  $5^{\text{cm}}$  ; thickness at ends,  $\cdot 375$  and  $\cdot 367^{\text{cm}}$ .

Hence the angle of the wedge is  $a = \cdot 0016$  radians or about  $\cdot 1^{\circ}$ . No difficulty is experienced from the deviation of the rays for so small an angle, though sometimes the fringes are unequal and the lines presumably curved. This wedge was attached to a Fraunhofer micrometer, moving horizontally parallel to the wedge, and the normality of the rays passing through the glass was found by rotating it around an axis perpendicular to the rays, until the direction of motion of the fringes was reversed. In view of the small angle  $a$  and the micrometric displacement, it was easy to count single fringes, or fractions as far as about  $1/30$  of a fringe, even though the beam traversed the glass twice. In the first experiments the data of the horizontal displacement,  $r$ , of the wedge, were found for successions of seven fringes. From the mean value of 8 such sets,  $r = \cdot 2008^{\text{cm}}$  and the displacement per fringe would be  $\delta r = \cdot 0287^{\text{cm}}$ .

In another series made with care as to the normal adjustment, the horizontal displacement,  $r$ , of the wedge for successions of 11 parallel fringes was taken. Again omitting the individual data, the mean displacement was found to be  $r = \cdot 3014^{\text{cm}}$ , whence per fringe,

$$\delta r = \cdot 0274^{\text{cm}}.$$

This difference from the preceding result shows that extreme care must be taken in placement.

If  $x$  be the distance from apex of the wedge, its thickness is  $e = xa$ , or per fringe  $\delta e = a\delta x = a\delta r$ . The index of refraction was found to be  $\mu = 1\cdot 526$  by total reflection. Thus without correcting for dispersion,

$$2(\mu - 1) \delta e = \lambda$$

and with the above values

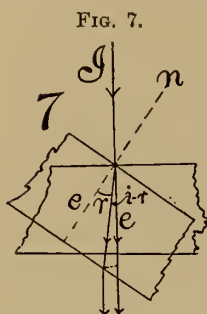
$$a = \frac{10^{-5} \times 5\cdot 893}{2 \times 526 \times \cdot 028} = \cdot 0020 \text{ radians.}$$

This is larger than the calipered value, because the rays go



through the wedge twice obliquely. The reduction, however, would here be too complicated, but will be treated later. The method is interesting as allowing of the complete control of a single fringe; i. e. the equivalent of  $30 \times 10^{-6}$  cm. As this corresponds to  $\cdot 028^{\text{cm}}$  on the micrometer, the displacement  $\delta x = \cdot 001$  is equivalent to  $10^{-6}$  cm. Furthermore the method presents an expeditious means of finding  $a = \lambda/2(\mu - 1)\delta x$  when  $a$  is very small.

B. In the next place the revolving compensator, *C*, fig. 3, was employed. This also proved to be an admirable device for controlling the fringes, and it was much more rapid than the preceding. Unfortunately the computation is inconvenient as the normal position cannot be ascertained with sufficient accuracy. To find it, the plate was revolved until the fringes changed their direction of motion. This is an indication of the insertion of the minimum thickness of glass, but is not sharp enough for precision. Hence on repetition the data are not liable to be coincident. Mean values are given,  $i$  denoting the angle of incidence.



Same plate as in the preceding work,  $e = \cdot 370^{\text{cm}}$ .

No. of fringes passing:	0	10	20	30	40	50
Mean $i$ :	$0^{\circ}$	$5\cdot 4^{\circ}$	$7\cdot 8^{\circ}$	$9\cdot 5^{\circ}$	$11\cdot 0^{\circ}$	$12\cdot 3^{\circ}$

Another somewhat better and thicker plate was now inserted with the following mean results. Thickness  $e = \cdot 489^{\text{cm}}$ .

No. of fringes passing:	0	10	20	30	40
Mean $i$ :	$0^{\circ}$	$5\cdot 2^{\circ}$	$6\cdot 8^{\circ}$	$8\cdot 3^{\circ}$	$9\cdot 6^{\circ}$

The reason for the large discrepancies found is not clear to me, even in consideration of the wedge-shaped plates. The mean of the results may, however, be used for computation.

The path increment introduced by the glass of thickness  $e = \cdot 489^{\text{cm}}$  and index of refraction  $\mu = 1\cdot 526$ , at an angle of incidence  $i$  and refraction  $r$  for  $n$  fringes, beginning at  $i = 0$  may be written (see fig. 7, where  $I$  is the incident ray)

$$n\lambda = e\mu \left( \frac{1}{\cos r} - 1 \right) - e \left( \frac{\cos(i-r)}{\cos r} - 1 \right)$$

This is a cumbersome equation. If the angles  $i$  are small, the cosines may be expanded and then approximately since  $i = \mu r$  nearly,

$$n\lambda = e(\mu - 1) i^2 / 2\mu.$$

Thus for the second set (mean)

$r = 3.6^\circ$	$4.8^\circ$	$5.9^\circ$	$6.8^\circ$
$10^5 \lambda = 6.7$	$6.4$	$6.9$	$6.5^{\text{cm}}$

The wave-length thus comes out very much too large, but in consideration of the inadequacy of the fiducial position,  $i = 0^\circ$ , this is not unexpected. Thus the probable values of  $i$  (computed from  $\lambda$  correct) agree with some of the individual series. In addition to this the effect of slightly wedge-shaped plates, etc., can not be ignored. For the first set (mean values), the results are similar.

C. An air compensator was now installed consisting of a tube  $e = 15^{\text{cm}}$  long and about  $2^{\text{cm}}$  in diameter, closed with glass plates. The fringes were easily found, and sharp. Unfortunately the pump was not quite tight, so that on breaking the count of fringes at low pressures, it was difficult to state when the conditions had become isothermal. Hence the following results are rough :

	Temp. $19.7.$								
No. of fringes,	0	30	67	0	30	70	0	40	68
Exhausted to ( $p$ ),	$75.1$	$41.8$	$0$	$75.1$	$43.0$	$0$	$75.1$	$32.1$	$0^{\text{cm}}$
$dp/dn,$	---	$11.1$	$11.1$	---	$10.7$	$10.6$	---	$10.7$	$11.2$
$\lambda \times 10^6,$	---	$59.7$	$60.6$	---	$57.6$	$57.1$	---	$57.8$	$60.0^{\text{cm}}$

the mean value thus appears as  $\lambda = 10^{-6} \times 5.88$  for sodium light. The equations used are (1)  $n\lambda = e(\mu - 1)$  where  $n$  is the number of fringes counted,  $e$  the tube length and  $\mu$  the index of refraction of air. Again

$$p = C(\mu - 1)\vartheta \tag{2}$$

where  $p$  is the pressure,  $\vartheta$  the absolute temperature and the constant  $C$  computed from normal conditions ( $76^{\text{cm}}$  and  $0^\circ \text{C}$ ) is (Mascart's values)  $C = 952.6$ . Hence

$$\lambda = \frac{e}{C} \frac{p}{n\vartheta} = \frac{e}{C} \frac{dp}{d(n\vartheta)} = \frac{e}{C\vartheta} \frac{dp}{dn} \tag{3}$$

when  $\vartheta$  is constant. It is this assumption which is not quite guaranteed above. To obviate this in the following experiments, the total number of fringes were counted from exhaustion to plenum. Their number was definite to the fraction of a fringe.

	Temp. $19.3^\circ \text{C}.$ ; $e = 15^{\text{cm}}$					
No. of fringes,	0	$69.5$	0	$69.5$	0	$69.5$
Exhausted to ( $p$ ),	$75.8$	$0$	$75.8$	$0$	$75.8$	$0^{\text{cm}}$
$dp/dn,$	---	$1.090$	---	$1.090$	---	$1.090$
$\lambda \times 10^6,$	---	$58.8$	---	$58.8$	---	$58.8$

These results are correct to  $\frac{1}{2}$  per cent and are as close as the estimation of  $p$ ,  $c$ ,  $\theta$ , and fractions of a fringe will warrant. If results of precision were aimed at, a long tube should of course be used. What was particularly marked in these experiments was the motion of fringes in the passage from any approximately adiabatic to isothermal conditions and on approaching a plenum of air.

Since the refraction depends on density there should not, apparently, be any motion at all; but the thin tube is always more nearly isothermal than the much larger barrel of the air pump. As a consequence there is residual expansion from the former to the latter.

D. The behavior of an old Babinet compensator, placed nearly normal to one of the beams (see fig. 3), was peculiar,

FIG. 8.



though the fringes were clear and easily controlled. The dimensions of the right-handed quartz wedge were roughly calipered and found to be: Length  $4.2^{\text{cm}}$ , thickness at ends,  $1.017$  and  $0.934^{\text{cm}}$ . Thus there is a grade of  $.083/4.2 = .0193$ , or something over  $1^\circ$  of arc. An up and down displacement of  $2.5^{\text{cm}}$  of this wedge was available behind the stationary counteracting left-handed wedge.

The fringes were not uniform and they required an inclination to the vertical of the rulings of the grating  $G'$ . The fringes were evidently curved lines, intersected by the vertical strip within which they are visible. Consequently they appeared as in fig. 8, with linear elements in the middle, shortening into dots at either end of the strip. On motion of the compensator wedge, they moved toward or from the center of symmetry, as is also indicated in the figure. Tiled fringes were frequent. The most interesting feature however, was their alternate appearance and evanescence, in *cycles*. While the wedge was moved over  $2.5^{\text{cm}}$  of its length, 7 of these cycles appeared and vanished, each consisting of about 36 to 40 fringes. The disappearance was not always quite complete, but the fringes could *not be restored* by any adjustment for coincidence of spectra.

An attempt was made to find the angle of the quartz wedge by the first method. Data,  $.0023$ ,  $.0024$ ,  $.0024^{\text{cm}}$ , were found for the displacement of the micrometer per fringe. Hence (apart from dispersion)

$$\alpha = \frac{10^{-5} \times 5.893}{2 \times .5442 \times .0024} = .022 \text{ radians}$$

which as in the glass plate is again above the calipered value.

In another somewhat thinner Babinet compensator, the constants were: Length, 3.35<sup>cm</sup>, thickness, small end .494<sup>cm</sup>, large end .496<sup>cm</sup>; the prism angle is  $a = .062/3.35 = .0185$  radians, also about 1°.

In this case there was no periodic phenomenon, but in its place the degree of longitudinal coincidence of the axes of the two spectra continually changed. The fringes at once sharpened, however, on readjustment of either mirror, indicating a continuous small change of deviation, due to curvature, probably, in the quartz wedge. In the preceding periodic case, no readjustment of deviation sufficed to restore the fringes. The wedge was now detached and used alone. In spite of the relatively large angle (1°), no difficulty was experienced in adjusting or controlling the fringes; but the face curvature just suggested appeared as before, so that readjustment for varying wedge angle was required from time to time.

8. *Micrometer displacement of the second grating.*—In the preceding paper\* it was shown that if the angle between the gratings  $G$  and  $G'$  is  $\phi$  and the angle between the mirrors  $M$  and  $N$  (which in a symmetrical adjustment would be  $180^\circ - (\theta_1 + \theta_2)$ ,  $\theta_1$  and  $\theta_2$  being the angle of diffraction at  $G$  and  $G'$  for normal incidence at  $G$ ) is decreased by  $\alpha$ , so that the adjustment is non-symmetrical, then the displacement  $\delta e$  of the grating  $G'$ , per fringe, will be very nearly

$$\delta e = \frac{\lambda \cos^2 \theta_2}{2(\alpha - \phi) \sin \theta_2}$$

if  $\alpha$  and  $\phi$  are small. Here  $\alpha$  is effectively the angle between the mirrors  $M$  and  $N$ ; since, if  $M$  is rotated  $180^\circ$  on the line of symmetry (normal to the grating  $G$ ), the two mirrors would intersect at an angle  $\alpha$ . The result of fore and aft motion thus depends on the angle  $\alpha - \phi$ , and if  $\alpha = \phi$ ,  $\delta e = \infty$ , per fringe; i. e. fore and aft motion would produce no result. This is necessarily the case when but a single grating is used, as in the earlier methods. In the case of two gratings, however, it is not only difficult to make a perfectly symmetrical adjustment of mirrors and grating, but it would not be of any special advantage. Hence the fore and aft displacement  $e$  of the grating  $G'$  will probably be accompanied by a slow motion of the fringes, from which the angle  $\alpha - \phi$  may be computed.

The following experiments were made with the grating  $G'$  on a micrometer slide, moving normally to the face of the grating. With the mirrors, etc., placed so that optical paths were nearly equal, the adjustment screws on  $M$  and  $N$  sufficed to bring the fringes strongly into view. Successions of 3 and

\* This Journal, xlii, p. 71, 1916, §4.



of 4 fringes were tested, as these required an adequately large displacement of the micrometer, which was moved both forward and backward. The results (omitting details) were :

	No. of fringes	Mean $\delta e$ displacement per fringe
(increasing) . . . . .	3	·0088 <sup>cm</sup>
(increasing) . . . . .	4	·0080 <sup>cm</sup>
(decreasing) . . . . .	4	·0073 <sup>cm</sup>

The mean of the three results is  $\delta e = \cdot 008^{\text{cm}}$  per fringe. The individual data were not smooth, because the micrometer placed between the mirrors  $M$  and  $N$ , is in an inconvenient position for manipulation. The different sets of values, moreover, correspond to different adjustments and therefore to slightly different values of  $\alpha - \phi$ . As an order of values only is wanted, it was not considered worth while to remedy the deficiencies.

In accordance with the equation given, if  $\delta e = \cdot 008^{\text{cm}}$ ,  $\lambda = 58\cdot 9 \times 10^{-6}$  cm.,  $\theta_2 = 20^\circ$  be inserted,

$$\alpha - \phi = \frac{\lambda \cos^2 \theta_2}{2\delta e \sin \theta_2} = \cdot 0095 \text{ radians} = 54^\circ.$$

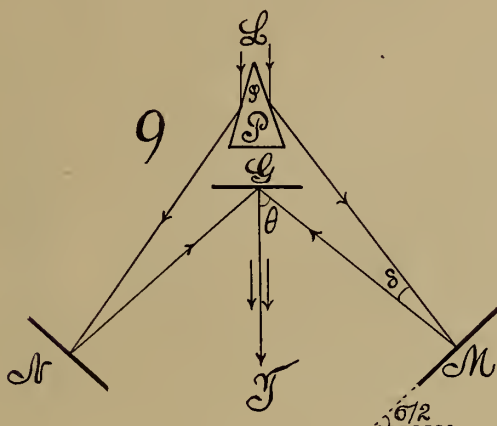
The adjustment is thus about half a degree out of symmetry, a result which in case of improvised apparatus is inevitable and moreover without significance in the precision of the method.

9. *Prism Method. Reflection.*—The grating  $G$  was now removed and replaced by a silvered prism (as shown in fig. 9). A small prism angle,  $\phi$ , is essential ( $\phi = 18^\circ$ , about), as a large divergence of rays would not be accommodated on the interferometer, fig. 3. The fringes were found without difficulty, in the second order, the arc lamp being used. They are also easily distorted, if the edge of the prism is not parallel to the rulings of the grating. In such a case the symmetrical arrow-shaped forms become one-sided and, as it were, curved or faintly fringed beyond the limits of the strip. To get the best adjustment, the lamp should shed about the same amount of undeviated light from both faces of the prism, on a screen temporarily placed behind it. The illuminated strips on the grating must coincide to the eye, while making the fore and aft adjustment. Finally the grating is to be slowly rotated on the axis normal to itself, until fringes of satisfactory shape and size appear. Naturally this is done through the telescope and a readjustment of the longitudinal axes of the spectra is necessary after each step of rotation. Fringes so obtained are as good as those obtained by any other method.

The range within which the fringes are sharp is small, not

exceeding 2 millimeters of displacement of the micrometer mirror,  $M$ . A partial reason for this will appear from fig. 9 and results from the fact that the illumination on the grating due to  $M$ , moves laterally across the stationary strip due to  $N$ . Clearly if the latter is also on a micrometer, it might, in turn, be displaced in the opposite direction to  $M$  and restore the fringes to full brilliancy. The range in this case may be in-

FIG. 9.



creased, till either illuminated strip gets beyond the edges of the grating.

If the prism angle is  $\phi$  and the angle of diffraction for normal incidence is  $\theta$ , the angle,  $\delta$ , between the incident and reflected ray at  $M$  is

$$\delta = \theta - \phi$$

Thus  $e \tan \delta/2$  is the displacement of the strip of light on the mirror  $M$ , if  $e$  is the normal displacement of the latter. Hence the corresponding displacement,  $x$ , on the grating is  $x = 2e \sin (\delta/2)/\cos \theta$ .

If  $b$  be the distance from the prism to the light spot reflected on  $M$ , and  $c$  the distance from there to the bright spot on the grating,  $\phi$  may be computed as

$$\sin \phi = \frac{2\lambda c}{b}$$

for the spectra are in the second order.

The data are :

$$10^6 \lambda = 58.93 \text{ cm} ; b = 38.0 \text{ cm} ; c = 20.4 \text{ cm} ; D = 200 \times 10^{-6} \text{ cm}.$$

Whence

$$\phi = 18^\circ 13', \theta = 36^\circ 6', \delta = 17^\circ 54',$$

and

$$x = \frac{.50 \times .1556}{.808} = .096^{\text{cm}}$$

if  $e = .25^{\text{cm}}$ , as found. Thus the rays of the same origin, or rays capable of interfering, are found in a vertical strip on the grating not more than 1 millimeter wide. It is interesting to note that the fringes vanish by becoming coarser and wider corresponding to the narrowing of effective edges in contact.

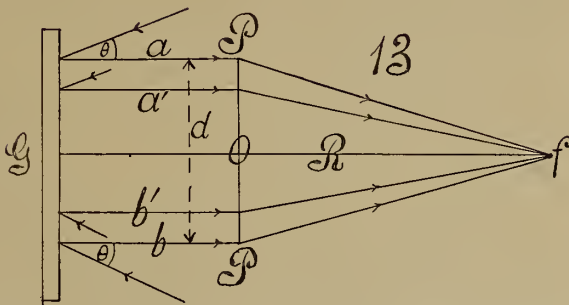
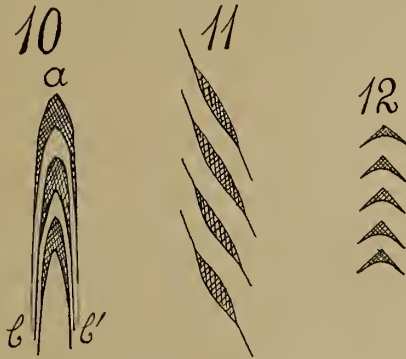
The attempt to produce these fringes with homogeneous (sodium) light and a wide slit again failed, although much time was spent in the endeavor. Even with a narrow slit and accentuated sodium lines (impregnated arc), the phenomenon may be produced between the doublets, however close together, but it fails to appear with the same adjustment when two corresponding lines coincide. I was only able to produce it in a continuous spectrum between the two doublets, and with a fine slit. It is important to ascertain the reason.

Both mirrors,  $M$  and  $N$ , are now placed on micrometers moving nearly normal to their faces. Beginning with a coincidence of the illuminated strips on the grating, the  $M$  micrometer was moved until the fringes disappeared. The  $N$  micrometer was then moved in the same direction, until the reappearing fringes passed through an optimum and finally vanished, in turn. Thereafter the  $M$  micrometer was displaced again, always in the given direction and the same cycle repeated; etc. It was possible to pass through about 8 cycles with each micrometer, before the illumination reached the edge of the grating, each cycle corresponding to a displacement of about 2 millimeters for a single mirror; but a total displacement of  $2.5^{\text{cm}}$  was registered which would obviously have been increased much further if the grating had been wider. The following data gives a concrete example:

Position of $N$	Advance of $N$	Remarks	Position of $N$	Advance of $N$	Remarks
$2.42^{\text{cm}}$	----	} Broad arrows $M$ advanced	$1.75^{\text{cm}}$	----	} Vertical lines $M$ advanced
$2.20$	----		$1.54$	----	
----	$.22^{\text{cm}}$		----	$.21^{\text{cm}}$	
$2.20$	----	} Narrow arrows $M$ advanced	$1.54$	----	} Vertical lines $M$ advanced
$1.98$	----		$1.37$	----	
----	$.24$		----	$1.7$	
$1.98$	----	} Upright lines inclination changed $M$ advanced	etc.		
$1.75$	----				
----	$.23$				

As both mirrors move in the same direction, the two illuminated strips on the grating gradually separate, until they are quite distinct. Meanwhile the fringes pass from the original sagittate forms to very fine hairlike striations, with rotation. Whereas the part of the spectrum within which the former occur is less than the distance apart of the sodium lines (doublets), the hairlines are visible within a strip of spectrum many times as broad as the sodium doublet. Ten such lines

FIGS. 10, 11, 12, 13.



may be visible. In good adjustments the sagittate forms are seen to be a nest of very eccentric, identical hyperbolas, as in fig. 10, arranged or strung on the same major axis. The vertices,  $a$ , are therefore thick and pronounced, but taper rapidly down into hairlines,  $b$ ,  $b'$ , on both sides. Frequently but half of the coarse vertices,  $a$ , abundantly fringed on one side,  $b$  or  $b'$ , appear. Nevertheless this does not seem to be an exhaustive description of the phenomena, for it is not uncommon, when partial hyperbolas appear, to find the striations (which are always faint) in the same direction on both sides, as in fig. 11; i. e. the striations are apt to be nonsymmetrical on the two sides, as if they constituted a second diffraction



phenomenon superimposed on the first phenomenon. Roof-shaped forms, fig. 12, strongly dotted, are also common, often irregularly awned.

Figure 13 may be consulted to further elucidate the subjects under consideration.  $G$  is the grating,  $PP'$  the principal plane of the objective of the telescope,  $a$  and  $b$  are two rays interfering at the focus  $f$ , and leaving the grating parallel and symmetrically placed to the axial ray  $of$ . The passage of the coarse sagittate phenomena into the hairlike striations, as  $a$  and  $b$  move farther apart, may then be accounted for in accordance with the general theory of diffraction; i. e. if the distance apart of  $a$  and  $b$  is  $d$  and the principal focal distance  $of$  is  $R$ ,

$$\frac{\lambda}{d} = \frac{z}{R}$$

where  $z$  is the distance between the two fringes of wavelength  $\lambda$ . Hence  $z$  will increase as  $d$  decreases, agreeing with the effect of fore and aft motion, or with the effect of simultaneous, large ( $2.5^{\text{cm}}$ ) displacement of both mirrors, neither of which destroys the symmetry of the interfering rays.

The motion of a single mirror,  $M$  or  $N$ , for instance, does destroy the symmetry, and it was shown in §8 that the limiting range of displacement of  $.25^{\text{cm}}$  moves either  $a$  or  $b$ ,  $.096^{\text{cm}}$  out of symmetry. The interferences thus vanish without much changing in form or size, and vanish in all focal planes.

The breadth of the blades of light  $aa'$  and  $bb'$ , figure 13, capable of interfering is thus  $x$  on the grating and

$$x \cos \theta = .096 \times .808 = .078^{\text{cm}}$$

normally. Since the rays are parallel after leaving the collimator, this would be about half the breadth of the effective beam on the objective of this apparatus. Thus  $2 \times .0776 = .155^{\text{cm}}$ , increased by the width of the refracting edge of the prism is the width of the strip of white light, which after separation by the knife edge of the prism, furnishes the two component beams which potentially interfere on recombination. It is reasonable to suppose that the elements of these beams come from a common source and that the width in question is produced by the diffraction of the slit.

This datum is more appropriately reduced to the angle at the slit,  $\alpha$ , within which the rays, capable of interfering with each other after the interferometer cleavage, lie. As the collimator used was  $l = 22^{\text{cm}}$  from slit to lens,

$$\alpha = 2x \cos \theta / l = .155 / 22 = .0070.$$

Hence the angular width of the wedge of white light, with its apex at the slit of the collimator and containing all the rays which can mutually interfere, is about  $.007$  radians, or less than half a degree of arc. One would infer that a long ( $l$ ) collimator

(i. e., one with weak objective) is advantageous, as the blade of parallel rays issuing is proportionately wide and the range of displacement at  $M$  or  $N$ , larger. Similarly divergence subsequently imparted by dispersion (prism, grating), before the rays reach the mirrors,  $M$ ,  $N$ , should have the same effect. The results obtained for dispersion bear this out, but not those for a long collimator. Moreover the width of the slit, so long as the Fraunhofer lines do not vanish, is of no consequence. It thus seems tenable (to be carefully investigated below), that the positive effect of dispersion has a deeper significance, bearing directly on the structure of the interfering wave trains: i. e., the length of the coördinated, uniform wave train is greater, as the dispersion to which the wave train has been subjected is greater. Two parts of it will therefore fit over a correspondingly longer range of path difference.

A number of other results point in the same direction. Thus I may instance the impossibility of obtaining fringes with homogeneous light and a wide slit, whereas two identical sodium lines ( $D_1$  and  $D_1'$ ), superposed, show the interferences strongly. The lines actually become helical in shape and much broader. The range of displacement of  $N$  may be decreased from  $\cdot 25^{\text{cm}}$  to  $\cdot 10^{\text{cm}}$ , by narrowing the beam emerging from the collimator with a slotted screen, while the fringes themselves are coarsened by this process. With the screen removed the fringes are not only sharper and finer, but apparently they may be seen to slowly move laterally across the fiducial sodium lines. This is in accord with the increased range of displacement of the mirror. The observation, however, is complicated by the fact that the sodium doublets are not quite in the same focal plane. The fringes must, in a reduced case, lie midway between them, in the line of symmetry of the spectra.

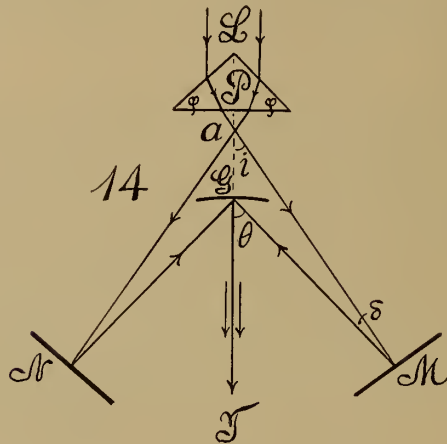
10. *Prismatic Refraction, with grating.*—The method indicated in fig. 14 was next tested for small distances and the experiments begun in the third order of spectra of the grating  $G$ . The refracting prism,  $P$ , was a small right-angled sample, with faces only about  $1^{\text{cm}}$  square; but it sufficed very well. Its distance from the grating being about  $13^{\text{cm}}$ , and the illuminated spots on the mirrors  $18\cdot 8^{\text{cm}}$  apart, the mirrors were nearly normal to each other. In fact, as  $\theta$  in the third order is about  $62^\circ$  and  $i'$  about  $28^\circ$ ,  $\delta = 34^\circ$  and  $\sigma = 90^\circ$ .

Hence on displacing the micrometer mirrors,  $M$  or  $N$ , the illuminating strips move relatively rapidly across the face of the grating,  $G$ . Nevertheless the fringes are easily found and controlled. Their range of visibility is larger than in the cases of the preceding paragraph. They remain in view for normal displacement of  $M$  of 3 to 4 millimeters, passing from hairlike

striations, through sharp arrows, back to the hairlike forms. The range has thus been increased by the dispersion. The arrows are of the slender type, with re-entrant sides and part of the outline accentuated.

In the second order of spectra from  $G$ , the phenomena were much the same, but far more brilliant. The arrows were now evenly wedge-shaped and very slender. The fringes entered as nearly vertical hairlike striations and after passing the optimum vanished as inflated arrows. The range of visibility

FIG. 14.



was as before about 3.5 millimeters so that the change of order has not had any further marked effect, such as might be anticipated. As in the preceding paragraph, if the impinging collimated beam is narrowed, the range of visibility decreases; in fact the arrows themselves are reduced to slightly oblique lines. Within the limits given the fringes are well adapted for interferometry.

First order spectra are not available because of the large value of  $i'$  in the case of the right-angled prism.

Taking the results of the last two paragraphs together, the increase of the range of displacement is due to the dispersion of the prism. The breadth of the pencil, diffracted at the slit, after leaving the collimator and prism, increases. It was shown in the earlier report that inversion of spectra on a longitudinal axis does not preclude the possibility of interference. Taken as a whole therefore, the present results have a direct bearing on Huyghen's principle.

[TO BE CONTINUED.]

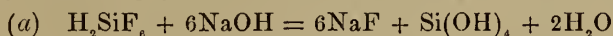
ART. XLIII.—*A Study of the Separation of Hydrofluoric Acid and Fluosilicic Acid*; by J. G. DINWIDDIE.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxxxiii.]

THE work to be described in this article was done with a view towards finding some satisfactory method for the analysis of a solution containing both hydrofluoric and fluosilicic acid.

The importance of an accurate method for this determination lies in the fact that commercial hydrofluoric acid very often contains as an impurity fluosilicic acid, which is of no use in etching, and which is a nuisance in analytical work. The value of a solution of hydrofluoric acid is obtained often by direct titration with alkali using phenolphthalein as indicator. Under these conditions each molecule of fluosilicic acid,  $\text{H}_2\text{SiF}_6$ , requires six molecules of alkali for neutralization and, therefore, will be counted as six molecules of hydrofluoric acid.

Almost the only attempt to discriminate between these two acids when present together has been made by Katz,\* who titrates first in water solution and then in alcoholic solution together with potassium chloride in order to get a differential equation. The reaction in water solution is



and in 50 per cent alcoholic-potassium-chloride solution,



The hydrofluoric acid requires the same quantity of alkali for neutralization whether titrated in water or in alcohol solution, while the fluosilicic acid requires one-third of the alkali in alcoholic-potassium-chloride solution that it does in water solution.

Were there no complications in the above reactions, the calculation of the results would be as follows:—

Let  $x$  be the volume of alkali required for neutralizing the hydrofluoric acid, and let  $y$  be that required by the fluosilicic acid in the alcoholic solution. Then  $3y$  will be required by the fluosilicic acid in water solution.

$$\begin{aligned} \text{Then, } x + 3y &= \text{cc. req. in water titration} = a \\ x + y &= \text{cc. req. in alcohol titration} = b \end{aligned}$$

$$\therefore 2y = (a - b)$$

Thus the difference between the amount of alkali required for the water and for the alcohol titration is equivalent to two-thirds the amount which would be required for the fluosilicic acid alone in water solution.

\*Katz, *Chemiker Zeitung*, xxviii, 356 and 387, 1904.



In testing this method on a mixture of known concentration, Katz finds that the alcoholic-potassium-chloride titration requires considerably less than the theoretical amount of alkali. He explains this result by assuming that some of the free hydrofluoric acid is absorbed by the precipitated potassium fluosilicate and is thus kept from being neutralized. Using normal and twice-normal alkali for titrations, he gets results which tend to indicate that, for very small amounts of fluosilicic acid, each molecule carries down with it one molecule of hydrofluoric acid, while for larger amounts three molecules carry down two of hydrofluoric acid.

On this basis he makes out a sliding factor to be used according to the relative proportions of the two acids present. For the fluosilicic acid content, if the difference between the water and the alcoholic titration is

5% or less of the water titration,	multiply it by (.0576),
5-10% of the water titration,	multiply it by (.058-.0595),
10-12% " " " " " " " "	(.06-.061),
over 12% " " " " " " " "	(.0617).

These factors are calculated on the basis of 2 N alkali.

Since Katz uses twice-normal alkali, and uses only from three to eight cubic centimeters in a number of the titrations, there is ample room for very large percentage errors.

Before attempting to go farther, it was thought advisable to repeat some of Katz's work as well as to compare the titration of pure fluosilicic acid in water and in alcoholic-potassium-chloride solution.

For a comparison of the two titrations of the pure acid, three samples were used: No. 1 was made by suitable dilution of Baker and Adamson's commercial fluosilicic acid; Nos. 2 and 3 were made by treating silica and calcium fluoride with concentrated sulphuric acid, passing the evolved silicon tetrafluoride through a double coil of glass tube (water-cooled) and then into water where the fluoride of silicon was decomposed into fluosilicic acid and silica.

The following table shows the results of these titrations:

TABLE I.

Alkali used was approx. 0.33 normal NaOH.

	$\text{H}_2\text{SiF}_6$ gm. of solution	NaOH req. (in alcohol) cc.	NaOH req. (in water) cc.	NaOH req. (cc. per gram)
No. 1	7.6774		42.1	5.48
	6.6227		36.3	5.481
	8.5302	15.9		1.864
	8.4770	15.7		1.852

		cc. of solution.			
No. 2	{	10		35.78	
		10		35.79	
		10		35.80	
		10		35.80	
		10	12.27		
		10	12.30		
		H <sub>2</sub> SiF <sub>6</sub>	NaOH req.	NaOH req.	NaOH req.
		cc. of solution	(in alcohol)	(in water)	(cc. per gram)
			cc.	cc.	
No. 3	{	10		38.23	
		10		38.30	
		10		38.15	
		10	13.18		
		10	13.20		
		30	39.85		

With each of the three samples, the alcoholic titration requires from one to three per cent more than one-third of that required in the water titration.

This result might be explained in either of two ways: that the fluosilicic acid, as sold commercially and as made in the Penfield-Offermann method for determining fluorine, may always contain small amounts of free hydrofluoric acid, or the solubility of potassium fluosilicate may be sufficient to allow it to be appreciably acted upon by the alkali used. The latter of these two explanations seems more plausible; for when the end-point has been reached, as shown by the pink of the phenolphthalein, the color fades out upon short standing, and continues to disappear after successive additions of alkali sufficient to bring back the pink. Upon heating the mixture, the hydrolysis goes much farther and practically all of the potassium fluosilicate is converted to fluoride and silica.

To test Katz's theory of the absorption of hydrofluoric acid by potassium fluosilicate, 10<sup>cc</sup> portions of fluosilicic acid were mixed with varying amounts of hydrofluoric acid and these mixtures were titrated, after addition of alcohol and potassium chloride, with approximately 0.3 normal sodium hydroxide. Since the amount of alkali required for each acid separately was known, it was easy to calculate what the mixture should require, were there no complications. These results are shown in Table II.

The fluosilicic acid used required for 10<sup>cc</sup> in alcohol, 10.77<sup>cc</sup> of standard alkali. Upon addition of increasing amounts of hydrofluoric acid, that unaccounted for seems to reach a maximum which is equivalent to approximately 1.3<sup>cc</sup> of the

TABLE II.

H <sub>2</sub> SiF <sub>6</sub> used cc. of solution	HF used gram. of solution	KCl added gram.	NaOH req. cc.	"NaOH theory cc.	Diff. cc.
10	4·8818	3	19·91	21·07	1·16
10	5·6151	1	21·49	22·62	1·13
10	10·2629	1	31·12	32·42	1·30
10	12·2639	1	35·37	36·65	1·28
10	16·3859	1	44·01	45·34	1·33

alkali used. This would give a ratio of absorption of one molecule of HF for about  $\frac{1}{4}$  of H<sub>2</sub>SiF<sub>6</sub> instead of a ratio of 1:1 as Katz\* found under these conditions.

If the precipitate of potassium fluosilicate formed in the presence of free hydrofluoric acid consisted entirely of potassium fluosilicate and of free hydrofluoric acid which it absorbed, then by determining the potassium in it, a measure of the fluosilicic acid originally present would be obtained. Or if a known amount of potassium chloride were added for precipitation and that remaining in the filtrate determined, the difference would be that which was used up in forming potassium fluosilicate. For this purpose a standard solution was made of which 10<sup>cc</sup> contained 0·5090 grams of potassium chloride. Table III gives the results of precipitating potassium fluosilicate from a solution of fluosilicic acid with and without hydrofluoric acid being present.

TABLE III.

KCl used gram.	H <sub>2</sub> SiF <sub>6</sub> used gram.	KCl in filtrate gram.	HF used gram. of solution	K <sub>2</sub> SiF <sub>6</sub> prec. gram.	KCl equiv. of K <sub>2</sub> SiF <sub>6</sub> gram.	H <sub>2</sub> SiF <sub>6</sub> equiv. filtering and decomp.	KCl by Total KCl.
<i>a.</i> 0·5090	0·2634	0·2381 calc.	--	0·4006	0·27085	0·2622	----
<i>b.</i> 0·5090	0·2634	0·2422	--	0·3979	0·2687	0·2601	---- ·5110
<i>c.</i> 0·5090	0·2634	0·2414	--	0·3991	0·2695	0·2609	---- ·5109
<i>d.</i> 0·5090	0·2634	0·2258 calc.	10	0·4196 calc.	0·2832 calc.	0·2748	---- ·5073
<i>e.</i> 0·5090	0·2634	0·2288	10	0·4169 calc.	0·2824	0·2725	·2785

It will be seen that *a*, *b*, and *c*, each give a precipitate equivalent to a little less than the theoretical value for fluosilicic acid. This would be expected on account of the appreciable solubility of potassium fluosilicate.

In *d* and *e*, where about 10 grams of hydrofluoric acid were added, in each case the filtrate contained considerably less of potassium chloride than would have been the case if no potassium had been used up except by fluosilicic acid in form-

\* P. 422.

ing potassium fluosilicate. In *e* the precipitate weighed four or five per cent too much. It was decomposed by ammonia and the solution was filtered to get rid of asbestos and then acidified with hydrochloric acid and evaporated. The residue was heated with hydrochloric acid to drive off all silica and fluorine and to convert the entire residue to potassium chloride. The residue of potassium chloride so obtained was found to weigh several per cent more than if the potassium had been present in the precipitate only as potassium fluosilicate.

The precipitate of potassium fluosilicate formed in the presence of free hydrofluoric acid contains an excess of potassium salt as well as free hydrofluoric acid, and it is evident that the fluosilicic acid in a mixture of the two acids cannot be estimated by determining the potassium in the precipitate or in the filtrate.

Since the fluosilicic acid carries down with it free hydrofluoric acid and fluorides when it is precipitated in the presence of these, it was determined, if possible, to precipitate the hydrofluoric acid as some insoluble fluoride, and, having thus removed it from the solution, to determine the fluosilicic acid remaining.

Accordingly, to a mixture of fluosilicic and hydrofluoric acids was added a neutral solution of calcium chloride sufficient to precipitate as calcium fluoride all of the fluorine present as hydrofluoric acid. Next was added potassium chloride sufficient to form with the fluosilicic acid, potassium fluosilicate, and to the mixture was added alcohol to make the final solution consist of 50 per cent alcohol. The precipitate obtained under these conditions was found very difficult to filter, so the mixture was made up to a definite volume and after allowing to settle the clear supernatant liquid was decanted through a dry filter. Aliquot parts of the total volume were then titrated with standard alkali.

If all of the hydrofluoric acid were actually precipitated as calcium fluoride and all of the fluosilicic acid as potassium fluosilicate, then for each molecule of HF originally present there should be in the filtrate one molecule of hydrochloric acid, and for each molecule of fluosilicic acid two molecules of HCl, according to the reactions,



Upon titration of this filtrate, therefore, the alkali required should be equal to that which would be required in water solution for the hydrofluoric acid originally present, plus one-third of that for the fluosilicic acid originally present. Thus the difference between the original water titration and the titration



of this filtrate should be just two-thirds of the alkali required in the reaction,



and so the amount of fluosilicic acid could be calculated.

Titration made in this manner all tended to run low to about the same extent as those made after simply adding potassium chloride and alcohol to the mixture of the two acids. The explanation of this is probably that an insoluble compound of potassium fluosilicate and hydrofluoric acid is formed even in the presence of soluble calcium chloride.

In a second series of experiments, to a solution of the mixed acids calcium chloride was first added, and to an aliquot part of the clear liquid was added potassium sulphate and alcohol. The potassium ion should form potassium fluosilicate, and the sulphate ion calcium sulphate which with 50 per cent alcohol is sufficiently insoluble not to decompose the potassium fluosilicate when the solution is made neutral with alkali. The results here were low to about the same extent as in the former series of experiments.

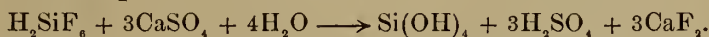
This method of making a mixture containing a precipitate up to a definite volume and using an aliquot part of the clear liquid is not to be recommended unless the precipitate is very small and it is impossible to filter and wash it; therefore, other insoluble fluorides such as lead fluoride were tried, but the precipitates were just as hard to filter and no better results were obtained.

Since other methods failed, and since calcium fluoride seemed to be more suitable for the removal of fluorine than other fluorides because of its greater insolubility, it was determined to find some method of precipitating this compound in a form capable of being filtered.

The expedient of Rose, which is to precipitate calcium carbonate together with calcium fluoride, was obviously of no value since the carbonate would decompose the fluosilicate and form calcium fluoride. Calcium sulphate, while being rather insoluble in water, is more soluble than calcium fluoride. Therefore it was thought that if an excess of pure powdered calcium sulphate were added to a solution of sodium fluoride the more insoluble calcium fluoride would continue to form at the expense of the sulphate until all of the fluoride was precipitated as calcium fluoride. There should then remain a precipitate of calcium fluoride mixed with the excess of calcium sulphate.

Upon trial, the precipitate formed in the above manner by the use of calcium sulphate was found to be quite easy to filter and wash, obtaining clear filtrates. A solution containing

hydrofluoric acid and fluosilicic acid was now treated with calcium sulphate, and, after stirring well and allowing to stand, the precipitate was filtered and washed. To the filtrate was added alcohol and potassium chloride, and then the free acid was neutralized with standard sodium hydroxide. The results here were low, just as in the previous attempts, and the explanation is very probably that calcium fluoride is sufficiently soluble in the free acid present to dissolve partially and to form in the filtrate free hydrofluoric acid upon addition of the alcohol and this would then be absorbed by the potassium fluosilicate. If sodium acetate is added in order to decrease the acidity of the solution before addition of calcium sulphate, then the filtrate continues to require alkali very much beyond the amount required by theory. It is probable that in very weakly acid solutions the calcium sulphate acts on the fluosilicic acid to form calcium fluoride, and this would account for the excess of alkali required as follows :

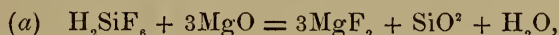


Finally the method of Stolba\* for determining the water of crystallization in crystallized fluosilicates was tried. This method was to heat a weighed amount of the material, e. g.  $\text{CuSiF}_6 \cdot \text{XH}_2\text{O}$  with a weighed amount of magnesium oxide. The reaction is as follows :

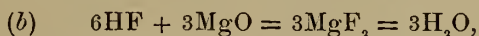


and the loss in weight, therefore, represents the water of crystallization.

To a known weight of magnesium oxide in a platinum crucible was added a solution containing a known amount of fluosilicic acid and the mixture was well-stirred. The reaction should be



and upon evaporating to dryness and heating to redness, there should remain (according to Stolba) only  $3\text{MgF}_2 + \text{SiO}^2$ . With the same weight of fluorine in the form of hydrofluoric acid only  $3\text{MgF}_2$  would remain according to the equation



knowing the total amount of fluorine that in the form of hydrofluoric acid and of fluosilicic acid in a mixture could be calculated by the increase in weight of the magnesium oxide used. However, upon heating the mixture formed as in equation (a) to a temperature somewhat below redness, the increase in weight was considerably more than required by theory,

\* Stolba, *Jour. prakt. Chem.*, cii, 2.

showing that all of the water had not been driven off. Upon increasing the heat until a low red was reached, there was a continued decrease until the loss in weight was much greater than that required to account for the loss of water. Therefore, it was found that this method is of no use for distinguishing between hydrofluoric and fluosilicic acids, and its value in determining the water of crystallization as given by Stolba is, at least, very doubtful.

For the determination of fluorine in soluble fluorides, Greef\* takes advantage of the fact that ferric chloride forms with sodium fluoride an insoluble complex fluoride,  $\text{FeF}_3 \cdot 3\text{NaF}$ , which does not give a red color with potassium sulphocyanide. By addition of a large amount of sodium chloride, the complex fluoride is made sufficiently insoluble, and the end-point of the reaction is obtained by adding 5 cm<sup>3</sup> of a 5 per cent solution of potassium sulphocyanide and 20° of a mixture of equal parts of alcohol and ether. When ferric chloride has been added in quantity sufficient to form the sodium-iron-fluoride, the next drop after vigorous shaking gives a pink color to the alcohol ether layer. Knowing the concentration of the ferric chloride, the amount of fluoride taking part in the reaction is readily calculated according to the equation



The results of this method are quite accurate provided that care is used in detecting the first permanent pink, that conditions of concentration of the different titrations are uniform, and that the solution of the fluoride as well as the ferric chloride standard be strictly neutral.

Since the presence of free acid causes a marked shifting of the end-point of this reaction, it was thought worth while to make a series of titrations, varying the amount of free hydrochloric acid in order to ascertain the effect on the quantity of ferric chloride necessary to give a permanent pink. Table IV gives the results of these titrations.

From the results as shown in this table, it can be seen that very small amounts of free acid cause a relatively large decrease in the quantity of ferric chloride solution required. Thus in a volume of approximately fifteen cubic centimeters only 0.1° of normal hydrochloric acid causes a decrease of nearly four per cent in the result, while as much as 2° causes a difference of almost 50 per cent. In numbers 12 and 13 a small amount of acid was added and then the solution was neutralized before titration just to ascertain how accurate the determination could be made when the solution was acid to begin

\* Greef, *Berichte*, xlv, 251, 1913; see also Guyot, *Comptes Rendus*, lxxi, 274, 1870.

TABLE IV.

No.	NaF cc.	NaCl gram.	KSCu cc. 5%	N.HCl cc.	FeCl <sub>3</sub> sol. cc.
1.	10	10	5	0·0	11·50
2.	10	10	5	0·0	11·55
3.	10	10	5	0·0	11·53
4.	10	10	5	0·1	11·11
5.	10	10	5	0·2	10·63
6.	10	10	5	0·4	10·10
7.	10	10	5	0·6	9·66
8.	10	10	5	0·8	8·88
9.	10	10	5	1·0	8·39
10.	10	10	5	2·0	5·90
11.	10	10	5	4·0	3·45 (?)
12.	10	10	5	1 <sup>cc</sup> (then neutralize)	11·65
13.	10	10	5	5 <sup>cc</sup> “	11·50
14.	20	20	10	0·0	23·12
15.	20	20	10	0·0	23·14

with. The results show that with proper care a solution of alkali fluoride can be obtained nearly enough neutral to give quite an accurate determination.

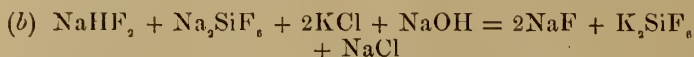
Greef claims that by the use of the ferric chloride method he can estimate the amount of sodium hydrogen fluoride which is present in a mixture containing sodium fluosilicate. Greef's directions for this determination are as follows: "Titrate a weighed portion of the mixture in hot water solution with standard sodium hydroxide using phenolphthalein as indicator. In this now neutral solution, determine the total fluorine by titration with standard ferric chloride solution as described above. Dissolve another portion of the mixture in a small volume of water and, after addition of alcohol until the concentration is approximately 50 per cent in alcohol, add about one gram of potassium chloride and titrate with the standard sodium hydroxide until neutral to phenolphthalein." In calculating the results from data obtained by following the above directions, Greef assumes that the alkali used in the alcoholic titration is a measure of the total free hydrofluoric acid in the mixture and that in the water titration for each equivalent of sodium hydrogen fluoride, one equivalent of alkali is required, while for each equivalent of sodium fluosilicate four equivalents of the alkali are used. From the total fluorine as found by the ferric chloride titration and from the results obtained in the water and in the alcohol titration, Greef calculates the content of the original material in sodium fluosilicate, sodium fluoride and sodium hydrogen fluoride according to the following equations:



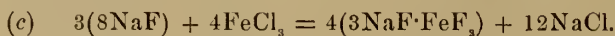
In the water titration :



and in the alcoholic titrations :



and the ferric chloride titration for total fluorine :



If there were no complications, it is easily seen that the alkali used in equation (b) would be equivalent to the sodium hydrogen fluoride present, while that used in (a) less that used in (b) would be a measure of the sodium fluosilicate present.

However, as has been shown by Katz\* and also in the present paper, when a mixture of free hydrofluoric acid and of fluosilicic acid or sodium fluosilicate is titrated in alcoholic potassium chloride solution, a marked absorption of free acid takes place. On this account the titration as in (b) can not be a measure of all the sodium hydrogen fluoride present in such a mixture as that described by Greef.

\* Katz, *Chemiker Zeitung*, xxviii, 356, 387, 1904.

## SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. *The Occurrence of Germanium in Zinc Materials.*—The presence of small quantities of the very rare metal germanium in zinc ores has been observed spectroscopically in several instances, but in most cases the amounts present were too small to serve as practical sources of the element. G. H. BUCHANAN, of the New Jersey Zinc Company, has announced that in some material at his disposal germanium was found in sufficient quantity to be readily detected by the ordinary chemical reagents. The material is a by-product from a Wisconsin blende, but its exact nature is not disclosed at present. The presence of an unusual element had been indicated in the course of analysis, and it was found to give in acid solutions a sulphide soluble in ammonium sulphide. Then several portions of one hundred grams each of the material were treated with concentrated hydrochloric acid and the resulting solutions were distilled to about one-half volume in the presence of a current of chlorine to keep the arsenic in the pentavalent state. The distillate contained the unusual element. Upon

dilution with a small amount of water this liquid gave with hydrogen sulphide a white flocculent precipitate. If, however, the distillate was greatly diluted the precipitation was slow and incomplete, but in this case the addition of strong hydrochloric acid caused an immediate precipitation. The white sulphide was soluble in ammonia and in alkaline sulphide solution. Upon ignition the sulphide gave a white oxide. It was found further that the element gave a sparingly soluble double potassium fluoride. These reactions agree with the properties ascribed by Winkler to germanium. Two portions of the sulphide were collected on a Gooch filter, dried at  $110^{\circ}$  and weighed, then after conversion to oxide by ignition it was found that the ratio  $\text{GeO}_2 : \text{GeS}_2$  was 0.749 and 0.744, whereas the theoretical ratio for the atomic weight 72.5 is 0.766. An approximate determination of the  $\text{GeO}_2$  in the material used gave 0.25 per cent. Several zinc ores were tested for germanium by the chemical method that has been mentioned. Joplin ore and some Mexican ores gave positive tests, but the amounts were very much smaller than that in the Wisconsin material. The Franklin ores gave negative results. A spectroscopic examination of the product by Dr. K. Burns of the U. S. Bureau of Standards indicated that germanium was the principal constituent while zinc was absent, lead weak, silicon present, tin fairly strong, copper present (?), cadmium trace, gallium present and indium trace. This occurrence of germanium is very interesting and it leads to the hope that a practical source of this exceedingly rare element has now been found.—*Jour. Indus. and Eng. Chem.*, viii, 585. H. L. W.

2. *A New Volumetric Method for Cobalt.*—W. D. ENGLE and R. G. GUSTAVSON have devised a method for the determination of cobalt, which can be applied in the presence of nickel and gives excellent results according to the test analyses of the authors. To apply the method the metals of the copper and iron groups and also manganese are first removed by suitable methods. The solution may contain, besides cobalt, nickel, zinc and the metals of the alkalis and alkaline earths, but must be free from any substance that will liberate iodine from potassium iodide in acid solution. This solution having a volume of about  $100^{\circ}\text{C}$  is made acid with dilute sulphuric acid, using about  $5^{\circ}\text{C}$  in excess, and 1 or 2 g. of dry sodium perborate are added. After agitation and solution of the perborate, sodium hydroxide is added to strong alkaline reaction and the mixture is boiled for 10 minutes to decompose the excess of perborate. This operation precipitates cobaltic hydroxide,  $\text{Co}(\text{OH})_3$ , while nickel does not form a higher oxide. The solution is now cooled to room temperature and, after 1 g. of potassium iodide has been added, the solution is acidified with dilute sulphuric acid and, after the precipitate has dissolved, the liberated iodine is titrated with standard sodium thiosulphate solution. The theoretical value of this solution, based upon standardization with potassium dichromate, was found to agree very closely with the value obtained by standardizing

with a known amount of a cobalt compound by following the described analytical process.—*Jour. Indus. and Eng. Chem.*, viii, 901.

H. L. W.

3. *The Determination of Aluminium as Oxide.*—WILLIAM BLUM of the U. S. Bureau of Standards has made an extensive study of this commonly used method. The novel feature of the procedure recommended consists in adding a few drops of an alcoholic solution of methyl red (0.2 per cent), heating just to boiling, and adding ammonia drop by drop until the color changes to a distinct yellow, then boiling for one or two minutes and filtering immediately. It is claimed that calcium and barium, if present, do not form carbonates with the carbon dioxide of the air under these conditions. Attention is called to the well known advantage of the presence of ammonium chloride when the precipitation is made, and washing with a 2 per cent solution of ammonium chloride is recommended. Ignition of the oxide in a platinum crucible over the blast lamp for about five minutes is advised. Attention is called to the importance of keeping the crucible closely covered while cooling and weighing, and the importance of weighing very rapidly, but the suspicion arises that at the Bureau of Standards they have been following the bad practice of trying to weigh warm crucibles; for the following suggestive statement is made: "Tests at this Bureau have shown that in common with most substances capable of absorbing moisture (even those not intrinsically hygroscopic) recently ignited  $Al_2O_3$  absorbs within the first ten minutes' exposure to the atmosphere a large proportion of the water which it will absorb in twenty-four hours." It is well known to experienced chemists that a slightly warm crucible, when placed upon the balance pan, shows a deficiency in weight on account of the ascending current of air produced, and that it then requires something like ten minutes for the crucible to cool sufficiently to show its true weight. It is advisable either to supply the desiccator with a thermometer, or to touch the face with the crucible before weighing, to make sure that it is cold.—*Jour. Amer. Chem. Soc.*, xxxviii, 1282.

H. L. W.

4. *Ozone, Its Manufacture, Properties, and Uses*; by A. VOSMAER, 8vo, pp. 197. New York, 1916 (D. Van Nostrand Company).—Part I of this book, comprising only 18 pages, deals with the early history, constitution, nature, occurrence, and properties of ozone, and the tests for it. The second part presents an extensive discussion of the manufacture of the substance, while the third part is devoted to its uses, and the last part gives a list of the United States patents, and an extensive bibliography. There are 75 illustrations and diagrams. The author has had a long period of experience with ozone in Holland, and is thus able to give much interesting information. Some of the apparatus and methods described are of his own invention, but it appears that he gives proper credit to other methods than his own, and that he has endeavored to treat the subject from a scientific stand-

point. There is much praise of the application of ozone to the purification of water supplies as practiced in Europe, and this application is strongly urged for this country, where at present it appears to be comparatively neglected. The view that minute quantities of ozone in the air make it agreeable and healthful for inhalation is advocated, and the use of the substance for the purification of air is recommended.

H. L. W.

5. *A Theory of Color Vision.*—At the present time there is no generally accepted theory of color vision, and there is considerable divergence of opinion as to the tests which should be applied for color-blindness. Consequently the new point of view proposed by R. A. HOUSTON may be appropriately outlined in this place. The author first shows that the Young-Helmholtz theory, which accounts very well for the phenomena of color mixing, involves a certain amount of arbitrariness and does not demonstrate the existence of three primary color sensations. The paper is divided into two parts: the first, which deals with the retinal process, applies principles already more or less familiar; but the second part, which relates to the cerebral process, uses an idea quite original in its application to color vision.

(a) The first step in the argument consists in assuming that there exist in the eye a very great number of vibrators, with a free period in the green, and that these execute forced vibrations under the influence of light waves. The amplitude of the forced vibrations is a maximum when the free period of the vibrators coincides with the period of the incident light. When formulated mathematically this hypothesis leads to a visibility curve which is similar to the one obtained experimentally by H. E. Ives. These graphs suggest probability curves, for each has a single maximum ordinate (in the green) and bends down toward the axis of wave-lengths on both sides (red and violet). To conform to Fechner's law the additional assumption is made that, when  $E^2$  acquires a small increment, the increase in the energy absorbed is proportional to  $d(E^2)/E^2$ , where  $E \cos \omega t$  represents the force per unit mass exerted on a typical vibrator by the light wave. This assumption implies that some of the vibrators cease to act when  $E^2$  is increased. "When the energy of a vibrator reaches a critical value, the force attaching the vibrator to its center snaps, the latter then ceases to absorb light energy, and a chemical change takes place. This critical value is not the same for all the vibrators, but varies from vibrator to vibrator. We may identify the chemical change with the bleaching of the visual purple, but this identification is not necessary to the explanation." When  $E$  is kept constant the same identical vibrators do not remain in action all the time for there are two processes going on in opposite directions which balance one another, visual purple being bleached and constantly restored. When  $E$  increases, the point of equilibrium is shifted. Owing to the bleaching and restoration of the visual purple the vibrators must be assumed to be in a perpetual state of agitation. Their free vibrations are continually being renewed.



The Purkinje effect may also be accounted for along the same general lines. This effect consists in the horizontal contraction of the visibility curve and in the shifting of its maximum toward the limiting wave-length  $0.50\mu$ , as the intensity of the light decreases to a very small value. Instead of supposing that the rods in the retina are chiefly responsible for vision at low intensities and the cones for vision at high intensities, it is only necessary to assume that the vibrators have different free periods and that the number  $0.55\mu$  (which was substituted for a symbol  $a$  in calculating the first approximation to Ives' curve) is a mean value. In other words, the visibility curve is the resultant of a very large number of elementary curves of the same type and not of three curves which would correspond to the hypothesis of three independent primary sensations.

(b) Since it is not possible to give briefly an adequate account of the general theory of the cerebral process, a few sentences from the original paper, which contain the kernel of the matter, will now be quoted. "We suppose the vibrators to set up waves in the nerves and that the nerves carry these waves to the brain. The analogue of the telephone may be useful in this respect; the vibrators may be likened to the diaphragm and the nerve to the telephone wire. There is, however, one important difference. When a musical note is sung into the telephone it is transmitted correctly along the wire and reproduced at the other end, because the diaphragm reproduces accurately the sound wave. It is fundamental to the theory given here that the vibrator does not reproduce the light wave accurately, owing to its being subject to too many disturbing influences. No matter how monochromatic the incident wave is, the wave transmitted along the nerve is not monochromatic. It is as if the diaphragm in the transmitter were subject to disturbing influences of such a nature that the person at the other end hears a medley of musical notes over a range of half an octave on each side of the notes originally sung into the transmitter."

Houstoun takes a slightly asymmetric curve of the same general shape as a probability curve as typical of the distribution of energy over the range of wave-lengths set up in the nerve by monochromatic stimulation. The area under the curve gives the luminosity of the impression, the position of the maximum, the hue, and the narrowness of the curve the degree of saturation. The phenomena of color mixing are readily reproduced theoretically by drawing energy curves corresponding to the objective constituents of the incident light and then constructing the resultant curve. For example, we may plot one sensation curve for lithium red and another for thallium green and then add the ordinates, the abscissas being proportional to the wave-lengths. Finally, following Dr. Edridge-Green, the author explains the apparent trichromatism of our ordinary visual sensations on the ground that the color-perceiving center in the brain is not sufficiently developed to discriminate between the character of

adjacent curves. "Two curves must be widely different in shape and position, before the colour-perceiving center can detect the difference. A curve has an infinite number of points on it. The colour-perceiving center is so badly developed that, as far as it is concerned, the curve is sufficiently specified by three points on it, provided that these points are distributed over the spectrum. We can therefore represent our energy curve by three points."—*Proc. Roy. Soc.*, vol. xcii (A), p. 424, July 1916.

H. S. U.

6. *On the Auditory Sense.*—An interesting and doubtless important contribution to our knowledge of the sense of hearing has recently been made by M. MARAGE. The paper in question is the result of a careful scientific study of the various phases of deafness arising from certain kinds of injuries suffered by the French soldiers in the present war. The author divides the causes of the special sorts of deafness, with which he is primarily concerned, into two classes: (a) a fragment of an ordinary shell or a rifle ball strikes the skull at a point more or less remote from the ear in such a manner as not to produce any direct lesion of the brain. The shock always gives rise to general headaches, buzzing, partial loss of memory, lowering of audition, and slight trembling of the members. (b) A shell of the largest caliber explodes in the immediate vicinity (from 1 to 4 meters) of a soldier. No apparent wound exists, but the symptoms just specified are met with in an exaggerated degree. Loss of consciousness lasts from a few hours to six days; very violent pains in the frontal region persist for several months; very pronounced buzzing which gradually disappears; complete loss of memory; absolute or nearly complete deafness (sometimes the patient hears but does not understand); violent trembling, especially of the upper portions of the body; and sometimes total deaf-muteness.

The apparatus used is a motor-driven siren designed to produce the sounds *ou*, *o*, *a*, *é*, and *i*. The intensity of the vowel sounds emitted can be estimated from the indications of a pressure gauge. From a statistical study of numerous cases Marage has established the fact that there are four and only four curves corresponding to the various types of partial deafness. Two curves are associated with injuries to the middle ear, and two pertain to lesions of the internal ear and to the auditory centers. These graphs are plotted with the vowels equally spaced as abscissas and with the corresponding least intensities audible as ordinates. The manner of examining a patient seems quite simple since it consists in sounding one vowel at a time while increasing the intensity until the subject indicates that he just begins to hear the note. The manometer is, of course, hidden from the view of the person under examination. The next day, or even a few minutes later, the process is repeated. An honest patient always reproduces the first set of data, whereas a simulator of partial deafness can never remember the intensities of all the five notes specified by him in the first test as inferior limits of hearing. A case of

feigned total deafness can be readily detected by increasing the air pressure to such an extent that the subject can no longer endure the intense sounds emitted by the siren.

From the point of view of the physicist the most important conclusion drawn by the author is that "The theory of Helmholtz is insufficient for the explanation of the different kinds of deafness: it seems that the auditory centers, situated in the interior of the brain, have a preponderating importance for the differentiation and interpretation of the various vibrations which can influence the ear."

An interesting corollary is deduced from the fact that the curves corresponding to injuries to the inner ear and to the nerve centers have absolute minima. In one curve, for example, deafness is absolute for  $a$  and  $i$ , but not for  $ou$ ,  $o$  and  $\acute{e}$ . These curves pertain to cases of deaf-muteness, and the author explains, in the following manner, the fact that normal parents may produce deaf and dumb children. "During the period of gestation the mother has a fall or receives a mechanical shock which seems unimportant. The shock is transmitted integrally by the intermediary of the amniotic liquid to the entire surface of the brain of the fetus which is not protected by an ossified cranium; a cerebral agitation is set up which is much feebler than that caused by a projectile, but which, acting upon a far more delicate nervous system, produces analogous lesions and effects." That deaf-mute parents may have normal offspring is consistent with this view which does not involve the hypothesis of hereditary influence.—*Jour. de Phys.*, vol. vi, Jan.-Feb., 1916, p. 29. H. S. U.

7. *Concise Technical Physics*; by J. LORING ARNOLD. Pp. viii, 275, with 294 figures. New York, 1916 (McGraw Hill Book Co.).—This book is intended primarily for use in the first course of theoretical physics in schools of engineering, and its differentiating characteristic is extreme brevity. The author says: "This book is intentionally laconic." "It contains nothing but what can be required of every student." "It lays particular stress upon fundamental conceptions, to the exclusion of too much detail." "The book aims to give a thorough and comprehensive basis on which to build further knowledge in each department of the subject."

The chief branches of physics are taken up in the following order, which differs somewhat from the usual sequence: kinematics and mechanics of solids (67 pages), mechanics of fluids (20), sound (23), heat (28), light (44), magnetism and static electricity (18), and current electricity (67). With few exceptions, the text is as accurate as is consistent with its condensation, the line diagrams are numerous and clear cut, and about eighty problems are suggested for solution. In the subject of light both the ray and wave-front methods are used in the derivation of the formulas. The only feature of the book which may be annoying to a student who is acquainted with other texts on physics is that the typographical errors are concentrated in the names of

eminent scientists. For example, we find: Bjerknes, Clerc Maxwell, Helmholtz, Melda, Michaelson, Rhumkorff, etc. U. S. U.

8. *A Text-Book of Physics, Fourth Edition*; edited by A. W. DUFF. Pp. xiv, 692; 609 figures and 279 problems. Philadelphia, 1916 (P. Blakiston's Son & Co.).—A careful comparison of the latest edition of this work with the third (see vol. xxxiv, page 483) shows that the text has been thoroughly revised. The method of presentation has been simplified and clarified in many places, especially in the paragraphs relating to the dynamics of rotation. The symbolization has also been improved; for example,  $u$  is replaced by  $v_0$  in the case of initial velocity. A new part on Sound has been written, especial attention being paid to the recent investigations of Miller, Sabine, and others. Typographical errors have been eliminated as far as possible. It is thus evident that the fourth edition shows appreciable improvement over the third and that it is a thoroughly reliable and well-balanced text-book. U. S. U.

## II. GEOLOGY.

1. *Expedition to the Baltic provinces of Russia and Scandinavia, 1914. Part 1.—The correlation of the Ordovician strata of the Baltic basin with those of eastern North America*; by PERCY E. RAYMOND. Bull. Museum Comp. Zoölogy, vol. lvi, No. 3, Shaler Memorial Series No. 2, 1916, pp. 179-286, pls. 1-8. *Part 2.—The Silurian and high Ordovician strata of Esthonia, Russia and their faunas*; and *Part 3.—An interpretation of the Silurian section of Gotland*; by W. H. TWENHOFEL. *Ibid.*, vol. lvi, No. 4, Shaler Memorial Series No. 3, 1916, pp. 289-354, pls. 1-5, text fig. 1.—These important and far-reaching correlation papers comparing the Ordovician and Silurian of Esthonia, Sweden, and Norway with those of North America, give much more detail than any others in the English language. The Ordovician begins with the Dictyonema beds, for earlier there had been elevation (warping) and erosion throughout the area studied. The formations which immediately succeed the basal ones are correlated by Raymond with the American Beekmantown, and in this he is in harmony with the European stratigraphers, but differs from the conclusions of some American geologists. In correlation, Raymond places main reliance on the graptolites, though he remarks, "If there were no other evidence than that afforded by the time of the first appearance of certain genera in Russia and America, it might well happen that the Walchow and Kunda formations [the basal Ordovician of Esthonia] might be correlated with the Chazy, but I do not see that they could be correlated with any younger strata" (268). Since the reviewer's visit to Esthonia in 1903, it has always seemed to him that the faunal development of these formations, especially as shown in the brachiopods, was rather that of the Chazy than the



Beekmantown, for the latter series has but few of these shells, whereas there is an abundance in the former and its equivalent, the Stones River series. On the other hand, the *Ceratopyge* formations of Sweden, which are absent in Esthonia, are unmistakably of Beekmantown age. The Normanskill Raymond regards as probably of upper Chazy time.

Twenhofel reports on the higher Ordovician and the Silurian, and as these deposits have many fossils in common with those of America, and more especially those of Anticosti, he has far less difficulty than his colleague in determining the equivalent formations. The lower Lyckholm Bassler regarded as intimately connected faunally with the middle Ordovician, a correlation accepted by none, and now Twenhofel shows that the Lyckholm is not divisible, but that the whole of it is upper Ordovician in age and about equivalent to the middle Richmondian. The following Borkholm is still higher Richmondian and correlates with the Ellis Bay horizon of Anticosti; both are referred to the Ordovician period. Then followed emergence of the region and Esthonia was not again invaded by the sea until long after the Silurian had begun, in about Clinton time.

The Silurian of Esthonia and that of Gotland are very different in their faunal make-up and in the nature of the sediments as well. The difference is apparently wholly due to the fact that the Gotland sea abounded in coral reefs, and as these grew far more quickly than the surrounding sediments accumulated, and show, consequently, a greater variation in strata, this led to the development of many different faunules, of slightly different geologic ages, which are now found in the same stratigraphic horizon. This condition has long perplexed stratigraphers, but Twenhofel now shows from a study of recent coral reefs how the Gotland stratigraphy may be harmonized with that of other Silurian areas. It is interesting reading, and his conclusions are all the more acceptable because he has unravelled a similar condition in the Silurian of Anticosti.

The authors are to be congratulated upon the great amount of first-hand information here presented, and their work clarifies and greatly advances our knowledge of the faunal interrelations of the European and American Ordovician and Silurian systems.

c. s.

2. *Upper Ordovician formations in Ontario and Quebec*; by A. F. FOERSTE. Geol. Survey Canada, Mem. 83, 1916, pp. iii, 279, 8 figs.—This memoir describes in detail the stratigraphic and faunal succession of the Cincinnati series east of Montreal and Ottawa, Canada, west of the Adirondaeks of New York, and in the Lake Huron region. All of the species identified by the author have been arranged in tabular form, so as to show their stratigraphic range, by Miss A. E. Wilson.

c. s.

3. *The Lower Eocene floras of Southeastern North America*; by EDWARD WILBER BERRY. U. S. Geol. Survey, Prof. Paper 91, 1916, 481 pp., 117 pls., 16 text figs.—In this great monograph

are described 10 plants from the Midway formation and over 300 species in 134 genera from the Wilcox formation. The work, however, is far more than a description of species and genera, as 145 pages are devoted to the sections yielding the fossils, the distribution of the floras, their character and ecology, and the correlation of the Wilcox formation. The plants from the Wilcox, which Berry correlates in part with the Fort Union and the Wasatch, are almost wholly angiosperms (94 per cent) and represent a coastal or strand flora under a climate about like that of the Florida Keys. C. S.

4. *On some Permian Brachiopoda of Armenia*; by A. STOYANOW. Mém. Comité Géologique, n. s., Liv. 111, 1915, 95 pp., 6 pls.—The author here describes fully, in Russian and in English, his genus *Tschernyschewia* proposed in 1910. At first sight the form looks like a sinused *Productus*, but as it is attached by the ventral beak, has a long and narrow cardinal area that is bisected by a delthyrium and covered by a very delicate deltidium, with a very high median ventral septum, it is seen to be a genus quite different from all known productids. He also discusses *Richthofenia*, *Scacchinella*, *Tegulifera*, and *Productus*. C. S.

5. *Cambrian Geology and Paleontology, iii, No. 5, Cambrian Trilobites*; by CHARLES D. WALCOTT. Smiths. Misc. Coll., vol. 64, pp. 303-456, pls. 45-67, 1916.—The author here describes 17 genera or subgenera (9 new) and 85 species (54 new) of Cambrian trilobites. Probably the most interesting genus is *Pagetia*, a form not unlike *Agnostus*, with free cheeks and eyes on the dorsal surface of the animals. C. S.

6. *Checklist of the Recent Bivalve Mollusks (Pelecypoda) of the Northwest Coast of America from the Polar Sea to San Diego, California*; by WILLIAM HEALEY DALL. Published by The Southwest Museum, Los Angeles, 44 pp., 1916.—In this interesting checklist Dall lists 474 species and varieties of bivalves living off the northwest coast of North America down to San Diego. Of these, 45 are deep-water forms restricted to waters below 60 fathoms in depth. There are therefore 429 shallow-water forms and of this number 205 are restricted to one of the three provinces (77 to the Arctic, 17 to the Temperate, and 111 to the Tropical), so that about one-half of the shells (219) have a geographic range over two of the provinces. This is the second publication by the new Southwest Museum of Natural History in Los Angeles. C. S.

7. *Interrelations of the Fossil Fuels. Part I*; by JOHN J. STEVENSON. Proc. Amer. Philos. Soc., lv, pp. 21-203, 1916.—In this valuable and comprehensive work the author brings together all that is known regarding the Pleistocene and Recent peats and the coals of the Tertiary. His wide knowledge of the Paleozoic coals and his great industry enable him to summarize the voluminous literature bearing upon the problems in hand in a clear manner. The area of the peats "is apparently greater

than that on which carbon deposits were laid down during any preceding period of similar duration"; nearly a hundred pages of the memoir are devoted to them. C. S.

8. *The Echinoidea of the Buda limestones*; by F. L. WHITNEY. Bull. Amer. Paleontology, No. 26, 1916, 37 pp., 9 pls.—Here are described ten species of echinids from the Comanchian of Texas, four of which are new. C. S.

9. *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 pp. 371-373, April, 1916):

TOPOGRAPHIC ATLAS.—Fifty-two sheets.

FOLIOS.—No. 199. Silver City Folio, New Mexico; by SIDNEY PAIGE. Pp. 19; 3 maps, 13 pls., 17 figs.

No. 201. Minneapolis-St. Paul Folio, Minnesota; by FREDERICK W. SARDESON. Pp. 14; 8 maps, 22 pls., 14 figs.

PROFESSIONAL PAPERS.—No. 89. The Fauna of the Chapman Sandstone of Maine, including descriptions of some related species from the Moose River Sandstone; by HENRY SHALER WILLIAMS, assisted by CARPEL LEVENTHAL BREGER. Pp. 347; 27 pls., 2 figs. See p. 169, August, 1916.

No. 91. The Lower Eocene Floras of Southeastern North America; by EDWARD W. BERRY. Pp. 355; 117 pls., 16 figs.

No. 98. Shorter Contributions to General Geology, 1916. Parts A to N. Pp. 1-261. See p. 438.

MINERAL RESOURCES for 1915.—Numerous advance chapters.

BULLETINS.—No. 610. Mineralogic Notes. Series 3; by WALDEMAR T. SCHALLER. Pp. 164; 5 pls., 99 figs. See p. 85, July, 1916.

No. 618. Geology and Underground Water of Luna County, New Mexico; by N. H. DARTON. Pp. 188; 13 pls., 15 figs.

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No. 630. The Chisana-White River District, Alaska; by STEPHEN R. CAPPS; 19 pls., 9 figs.

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Nos. 640, 641. Contributions to Economic Geology, 1916.—No. 640, Part I, B, C, D, E.—No. 641, Part II, A, B, C, D, E.

No. 645. Bibliography of North American Geology for 1915 with subject index; by JOHN M. NICKLES. Pp. 144.

No. 649. Antimony Deposits of Alaska; by ALFRED H. BROOKS. Pp. 67; 3 pls., 3 figs.

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## III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Diseases of Occupation and Vocational Hygiene*; edited by GEORGE M. KOBER, M.D., LL.D., and WILLIAM C. HANSON, M.D. Pp. xxi+918. Philadelphia, 1916 (P. Blakiston's Son & Co.).—In this large handbook the subdivision of hygiene which deals with relations of occupation to health and longevity is presented in the form of a series of essays prepared by thirty or more writers well known as experts in some field of medicine, public health work, occupational hygiene, physiology, sociology, insurance, etc. The names of these contributors including, in addition to the editors, Prof. Clarence J. Blake of Boston, Prof. L. Devoto of Milan, Dr. Alice Hamilton of Chicago, Prof. Chas. R. Henderson of Chicago, Prof. Frederic S. Lee of New York, Sir Thomas Oliver of England, Professors Southard, Tyzzer and Whipple of Harvard University among others, gives some assurance of the worth of the volume. No detailed reference can be made in this space to their contributions. They include the specific and systemic diseases of occupation, fatigue and the neuroses of occupation, the causation and prevention of occupational diseases and accidents, etc. Somewhat of a novelty is presented in the chapters dealing with the relation of clinics, statistics, governmental study and legislation to occupational diseases. The essays on vocational hygiene, with their descriptions of the dangers existing in special groups of industries which take a prominent place in the commerce of to-day, are full of interesting details evidently compiled from many sources and with much effort. The book is, in fact, a compilation of manifold useful facts and suggestions rather than a "system" of medicine in the usual sense.

L. B. M.

2. *The Problems of Physiological and Pathological Chemistry of Metabolism*; by ORTÓ VON FÜRTH. Translated by ALLEN J. SMITH. Pp. xv+667. Philadelphia, 1916 (J. B. Lippincott Company. Price \$6 00).—Von Fürth's "Probleme der physiologischen und pathologischen Chemie," which first appeared four years ago, immediately gained a deserved popularity because it presented in an enjoyable style an admirable survey of the literature, both historical and modern, covering a large range of timely topics in biochemistry. Evidence was presented, opinions were weighed, conclusions were logically drawn, and the outlook was clearly disclosed with relation to a considerable number of questions which are daily discussed in this field of science. The reader could feel the influence of the authoritative statement of an experienced investigator, yet still preserve an independence of judgment. The young investigator found the new volumes full of stimulating viewpoints. Rarely has the subject been so well presented. It is gratifying to find an excellent translation of the part of von Fürth's volumes dealing with metabolism. Professor Smith has preserved the spirit of the author's diction well, and has done physiological science a service in making von Fürth's essays more readily available to those who prefer to read the English language.

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THE

# AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]



ART. XLIV.—*The Lava Eruption of Stromboli, Summer-Autumn, 1915*; by FRANK A. PERRET.

THE recent phase of exceptional activity at Stromboli—a true eruption in the full sense of being both effusive and explosive—may be considered, in a way, as being a repetition of that of 1891, so ably described by Ricco and Mercalli.\* It differs from it, however, in some important respects, notably in the relative proportions of the different phenomena, the earlier eruption having been characterized by a far greater degree of seismic and explosive activity, while the recent phase was remarkable for its long continued outpouring of lava.

It will scarcely be necessary to point out the peculiar importance of such an event, for it will be recalled that effusive phenomena at this volcano are rare, while the lavas of Vesuvius and Etna do not, in our day, reach the sea. This eruption furnished, therefore, a precious opportunity for the study of the important question of the behavior of incandescent lava in contact with water.

Through a combination of circumstances, however, which can never be sufficiently regretted, the true condition of Stromboli during the months of July, August, September and October was not realized by those volcanologists who are generally most active in field research, and it was not until the first of November that the present writer learned of the magnitude and importance of the eruptive phase. Upon receiving confirmation of the reports through the kindness of Profs. Platania and Ricco, of Catania, he sailed on November 7 for Stromboli via Messina on the ill fated "Firenze."

\* A. Ricco and G. Mercalli, *Ann. Uff. Cent. Met. Ital.*, xi, Part III, p. 187, 1892.

Leaving Naples at 5 P. M. the light of the eruption was plainly visible an hour after midnight. It was so strangely white as to make one doubt, for a time, the possibility of its being caused by the volcano, although no other source of illumination was to be looked for in that locality. In another place\* the writer has referred to this phenomenon, which often has given erroneous impressions concerning the temperature of a lava, and which seems due to the selective absorption and reflection of certain rays by the vapors emanating from the lava. No opportunity has yet been found of experimentally studying the matter to a conclusion.

On approaching and passing the island, it was seen that a stream of lava was flowing from the crater, or just below it, down the western side of the Sciara to the sea. The nearer view gave the normal golden yellow tint of an active lava which flows freely and maintains an incandescent surface, but this condition prevailed for only a third of the descent. In the second section—evidently a deviation from the direct descent and a region of accumulation—this glow was only visible in the interstices of a blackened crust. Emerging anew from this, the lava flowed directly toward, and almost to, the sea in a broad stream of which the brightness was little if at all, inferior to that of the first portion.

From a part of the crater nearest the Sciara a bright glow emanated continuously, while at intervals of from ten to fifteen minutes a fairly strong explosion would project to a height of a hundred meters or more those sheaves of incandescent fragments which are characteristic of this form of activity.

The next evening was spent in the harbor of Lipari, on the local steamer, and Stromboli was reached at daybreak of the 9th. The writer remained until the 30th, when the subsidence of the lava column, the extension of the fumarolic area and the absence of explosion all indicated the approaching end of this exceptional eruption. From the 12th to the 19th the writer had the pleasure of the company of Professor Gaetano Platania.

During this stay three trips were made to the summit, five to the Sciara by boat, one in a circuit of the island, and several to the Punta Labronzo on those days when bad weather prevented the more important excursions. It is proposed to set forth here those observations and studies of phenomena personally made during this time, and to follow this preliminary report—when the analyses of the various products shall have been made—by a more complete paper, which shall include an

\* "Volcanic Research at Kilauea in the Summer of 1911." Frank A. Perret, this Journal (4), xxxvi, p. 480, 1913.

account of the great explosive paroxysms of 1907 and 1912. These, together with the recent eruption, constitute a group of events markedly analogous to the eruptions of other volcanoes, the first two in the formation of a vast crateral abyss and the last in the amplitude and duration of the lava flow.

It will be well first to take a comprehensive view of the initiation and progress of the eruption in the preceding months, as shown in the records of the Stromboli Semaphore Service, kindly furnished by the Chief, Signor D'Aloisio, to whose courtesy and hospitality the writer is deeply indebted.

It should be remarked that these records also contain notes to the effect that in April and in June of 1914\* there were "eruptions of lava"—probably not true continuous flows but ejections from the crater on to the Sciara, which certainly indicate a high lava column with a tendency to overflow.

On the 18th of June, 1915 (and possibly also on the 11th), there was an eruption of lava which ceased the same day. Small shock.

From July 1 to 24, lava in quantity, and from the 25th to 31st, in lesser amount. Increased explosive effects at crater.

During the month of August, continuous emission, always in moderate amount.

September 1 to 14, in considerable quantity; 15 to 23, less; from 25 to 30, abundant.

In great quantity during the entire month of October, and during the first week of November. Also emissions of ash and lapilli.

The rest of the month may now be summarized briefly from the writer's observations:

November 7—Explosions from Bocca A of the crater at intervals of ten to fifteen minutes, with projection of luminous fragments to a considerable height. Ample outflow of lava, forming the most westerly of the streams on the Sciara, and flowing to within a few meters of the sea.

November 9—Same conditions at crater. Lava flow diminished. Great accumulation of lava at about the middle of the descent. Lower extremity immobile.

November 10—Weaker explosions from Bocca A often followed by landslips within the crater, indicating a sinking lava column. Outflow of lava entirely or almost ceased.

November 11—Gradual diminution of all activity.

November 12—The explosions in Bocca A proceed from a constantly lowering lava column, and scarcely reach the crater's edge, but the glow continues. The lava has ceased flowing, but the lava bocca is incandescent.

\* "I fenomeni eruttivi avvenuti allo Stromboli dal 1909 al 1914, ed il loro meccanismo," O. De Fiore, *Zeitschr. f. Vulkanologie*, i, p. 236, 1915.



November 13—Paroxysmal explosion at 9.15 A. M., followed by weaker repetitions. No lava outflow, but the lava bocca emits bluish vapor in strong puffs. At 1.30 P. M. an imposing avalanche of the hardened lava insecurely held on the steep slope of the Sciara (36°).

November 14—Copious outflow of lava, descending the easterly side of the Sciara but not reaching the sea in continuous flow.

November 15—Diminished flow.

November 16.—Outflow continues. One moderate explosion.

November 17—Conditions not sensibly different.

November 18—Copious flow of lava. Fine, full stream descending directly into the sea.

November 19—Lava in large amount—great evolution of steam on entering the sea.

November 20—Same conditions. Quantity of sulphur dioxide carried down by the wind over S. Vincenzo.

November 21—Large amount of lava—bright glow.

November 22—Outflow notably diminished.

November 23—Outflow nearly ceased from 4 to 10 P. M., then continued in great quantity.

November 24—Great quantity of lava.

November 25—Diminished outflow. Copious white vapors at the crater.

November 26—Little or no lava during the night until 5 A. M. At 7.12 strong air concussion followed in less than a minute by a paroxysmal explosion. At 8 A. M. cessation of flow, then a second explosion, small, followed by an abundant outflow of lava, which ceased completely at about 8.30 P. M.

November 27—No lava—the bocca gives blue vapor only. At the crater white vapors.

November 28—No lava.

November 29—At noon a re-fusion at the lava boccas and outflow of lava for a distance of a hundred meters. White vapors without explosion at the crater. Great extension of fumarolic area.

November 30—A sluggish lava flow, tending to cease altogether.

Throughout all this period, when not otherwise stated, and excepting the two great explosions on the 13th and 26th, the gaseous outbursts at the crater continually decreased in intensity and frequency.

We have, thus, an eruption of lava lasting five months, and manifesting powerful explosive phenomena only in the latest phase, in contradistinction to that of 1891 when the emission of lava was spasmodic and was invariably preceded by strong seismic and explosive manifestations.

*The Eruptive Apparatus.*

The formation, and the configuration of the crater of Stromboli conform to the same general type exhibited by other volcanoes, i. e. enlargement and abasement as effects of great explosive paroxysms, interchanging with upgrowth and restriction as results of long-continued and moderate activity. It does not exhibit, however, those colossal fault-block depressions of calderal magnitude which are caused by rapid emptying of the conduit through copious outpourings of lava at low levels. But, inasmuch as the conduit of this volcano divides itself, at the upper extremity, into various ramifications, and as the normal activity is moderate and prolonged, the tendency is to form a number of small crateral mouths—as many as seven, or even more—crowning, as a rule, as many distinct conelets more or less united into groups.

And not even the most powerful and continued explosive paroxysms of which we have knowledge—such as those in 1907 and 1912\*—have been able to excavate any single crater sufficiently profound to unite these several ramifications into one single vent. In fact, although on both these occasions an immense crateral cavity was formed, it was always possible to distinguish four different and distinct centers of explosion, easily recordable by photography, and these have persisted as principal vents during all recent phases of violent activity at this volcano. I have designated them by the letters A, B, C, D.

The actual crater consists of these four main divisions, united in one great group with walls of separation which are common to the vents which are contiguous—four perfect craters, that is to say, which occupy and fill the space of the great crater cavity of 1912. It is probable that these contain further subdivisions, but in the conditions which prevailed during this visit to the island this could not be determined with certainty.

This conformation gives, as usual, a satisfactory measure of the degree of explosive activity which occurred during this phase, and one which here confirms the other observations, viz., that the explosive activity was considerable but not by any means catastrophic, the only truly paroxysmal explosivity having been extremely limited in time.

Bocca A, situated near the center of the upper edge of the Sciara, is generally the most active, especially in those forms of eruption which spring directly from liquid lava. It was the source of the recent flows, and of nearly all the incandescent ejections during the month of November.

Adjacent to it, on the east, lies Bocca B, now much enlarged.

\* G. Platania: *Ann. Uff. Centr. Met. Ital.*, xxx, p. 16 (1908), 1910. F. A. Perret, *Sci. Bull. Brooklyn Inst.*, i, p. 313, 1907. F. A. Perret, *Smithson. Inst. Rep.* (1912), p. 285, 1913.

FIG. 1.



FIG. 1. View of the crater mouths from the south, on the summit crest. At the right, the mouth "D" is obstructed and inactive. Mouths "C" and "A" are seen at the center, and vapor from mouth "B" on the right in the distance.

FIG. 2.



FIG. 2. View of the subdivided crater from the west, and showing the point of lava emission below the crater.

Before this eruption, this had been a very small but active vent situated on the eastern parapet, with a notable tendency to collapse of its walls, giving thus, in its frequent explosions, dense clouds of detritus. At present it is one of the great mouths of the eruptive apparatus, as it has always been one of the most active.

Bocca C—by far the largest of the four—is situated next to the westerly Faraglione, while Bocca D, which is generally the least active and recently was obstructed for the greater part of the time, lies east of C and more or less directly south of the enlarged B.

At the beginning of this eruption the lava overflowed the lower lip of the crater, forming and leaving a consolidated, convex ridge, probably a tunnel; later it issued from lateral vents on the slope of the Sciara. Owing to lack of observations made at the time, we shall probably never be able to reconstruct this phase of the eruption. Near the central line of the Sciara and starting from Bocca A there is a fracture open at the surface for at least two hundred meters, of which the two edges are at different levels, but if the lava ever issued from this the locality has become hidden beneath later flows from the mouth which formed during the month of November. This is situated to the west of the fracture and about 160 meters from the crater and therefore at a level perhaps a little more than a hundred meters below the edge of Bocca A.

This aperture has the usual form of an "oven mouth," and is nothing more than the extremity of a tunnel which conducts the lava from the interior.

From this disposition of the eruptive apparatus there results an effusion of lava which is in the nature of an overflow, notwithstanding the fact that it issues from a lateral opening, inasmuch as it is an outflow of material from the upper portion of the magmatic column—a "sub-aerial" effusive eruption. And this disposition further permits, and produces in its perfection, that separation and segregation of gas and liquid—the first rising and escaping through the central crater, and the second flowing out laterally—which so greatly affects the character of an eruption, as was demonstrated at Teneriffe\* and at Sakurashima† and, as we shall presently see, also here at Stromboli.

#### *The Fluent Lava.*

As a result of the disposition just referred to, the lava issues from its tunnel already freed of those large bubbles of gas at

\* The Volcanic Eruption at Teneriffe in the Autumn of 1909, Frank A. Perret, *Zeitschr. f. Vulkanologie*, i, p. 24, 1914.

† Sakurashima, *Rapporto preliminare per l'istituto vulcanologico sulla grande eruzione del vulcano Sakurashima*, Gennaio, Febbraio, Marzo, Aprile, 1914, *Zeitschr. f. Vulkanologie*, i, p. 137, 1914.



high tension which are the cause of the explosions at the crater, and there results a quiet flow. Although the gas content is still high, it is either still in solution or in the form of innumerable tiny vesicles in which the tension is too small to exert further influence upon the form of the viscous mass, and the lava possesses, in great part, the qualities of the "pahoehoe" type. But the chemical constitution of this material, together with the steepness of the slope upon which it flowed ( $36^\circ$ ), caused the formation upon its surface of a layer of scoriæ which, rolling and sliding over the convex surface of the stream, accumulated in lateral moraines and gave to the flow the appearance of the "aa" type. We may say, therefore, that although both types of lava appear, the pahoehoe quality predominates, which is but natural considering that we have here a lava overflowing from an open conduit.

That the mass of the flow was compact, coherent and continuous was demonstrated by the two "re-fusions," one of which was witnessed by the writer on the 29th. From the well-known point of observation west of the crater it could be seen that the stream of lava, which had ceased flowing several days before, lay black and motionless on the Sciarra slope. At noon a movement was observed among the scoriæ on the surface of the stream nearest to the vent, and soon this movement was propagated some distance forward. The first portion then became incandescence and began to flow downward very slowly, and this same succession of phenomena—movement of scoriæ, incandescence of the mass, and flowing movement—extended progressively along the line of the stream until the whole was in full flow for a hundred meters or more. There was not the least attempt to break through or over in order to seek a new channel, but a revivifying of the original mass under the renewed supply of heat and material from the source. There was no possibility of determining if the center of the flow had retained its original incandescence up to the time of the re-fusion. It is, of course, quite possible that a tunnel had been left, but the writer has on several occasions witnessed true re-fusion of perfectly consolidated lava under the onset of fresh material and does not believe these other conditions to have been essential to the renewing of the flow in the present case.

The temperature of the lava was, in all probability, at its highest during the first period of the eruption when, according to the inhabitants, it was possible to walk about at midnight through the country lanes brightly illuminated by the reflected glare. It would then have been easy to obtain temperature measurements by means of an optical pyrometer if such an instrument had been available. During the month of Novem-

ber the direct employment of a thermoelectric pyrometer was prevented only by the heavy seas which made impossible a sufficiently near approach to the stream flowing into the sea at the Sciara's base. Any approach to the source itself was precluded by its position immediately under the crater.

On the basis of the degree of incandescence, I estimated the temperature at  $1100(\pm)^{\circ}\text{C}$ .—this being mentally compared with the incandescence of lava whose temperature was measured, at Etna and Kilauea.

The solidified lava is a very dense, black basalt, which shows, in an evidently vitreous groundmass, many small phenocrysts of anorthite, few of olivine and none of feldspar. Its petrographical characters and relations will be described later by Washington in connection with other rocks of the Aeolian islands, but it will be as well to put on record here its chemical composition as contrasted with those of other recent Stromboli basalts.

	A	B	C	D
SiO <sub>2</sub> .....	50.00	50.55	50.83	51.05
Al <sub>2</sub> O <sub>3</sub> .....	13.99	16.58	16.66	15.09
Fe <sub>2</sub> O <sub>3</sub> .....	5.13	8.18	1.52	2.07
FeO .....	9.10	.....	6.64	6.88
MgO .....	4.06	6.10	6.08	6.52
CaO .....	10.81	11.45	10.99	11.34
Na <sub>2</sub> O .....	3.02	3.15	2.66	2.53
K <sub>2</sub> O .....	2.87	3.16	2.05	2.02
H <sub>2</sub> O .....	0.24	0.06	0.36	0.15
TiO <sub>2</sub> .....	n.d.	n.d.	0.81	0.83
ZrO <sub>2</sub> .....	n.d.	n.d.	n.d.	none
P <sub>2</sub> O <sub>5</sub> .....	0.71	0.67	1.61	1.44
SO <sub>3</sub> .....	trace	n.d.	n.d.	0.06
Cr <sub>2</sub> O <sub>3</sub> .....	n.d.	n.d.	n.d.	0.05
MnO .....	0.42	n.d.	0.12	0.13
	<hr/>	<hr/>	<hr/>	<hr/>
	100.35	99.90	100.33	100.12

A. Basalt of 1891. L. Ricciardi analyst. Ricco and Merelli, Ann. Uff. Cent. Met. Ital., xi, Pt. III, p. 202, 1892.

B. Basalt of 1894. F. Glaser analyst. A. Bergeat, Die Aeolischen Inseln, p. 44, 1899.

C. Basalt of August, 1914. H. S. Washington, analyst.

D. Basalt of November, 1915. H. S. Washington, analyst.

Although the two earlier analyses, especially that of Ricciardi, are not very satisfactory, it is evident that at Stromboli, as at Vesuvius, Etna and many other volcanoes, the composition of the lavas of the basaltic phase has remained very uniform. As Bergeat points out,\* the chemical composition of

\* A. Bergeat, Die Aeolischen Inseln, p. 45, 1899.

FIG. 3.



FIG. 3. Showing the mass of new lava on the Sciara. This was built up of comparatively narrow streams alternating from side to side and forming the great, convex inverted wedge shown in the center of the view.

FIG. 4.



FIG. 4. The new lava on the Sciara seen in profile; the shore line was formerly concave.

these recent Stromboli lavas differs markedly, notably in lower silica, from that of the older basalts of San Bartolo ( $\text{SiO}_2=52.25$ ) and still more from that of the andesite flows at the earliest Vancori cone ( $\text{SiO}_2=61.78$ ). In this respect, also, Stromboli resembles many other volcanoes.

The writer took pains to coat specimens of the basalt, taken incandescent from the flow, with paraffine as soon as they were sufficiently cool, in order to prevent diffusion of gases from the interior, and it is hoped that this lava, when heated in vacuo, will yield its original gas content for analysis. Direct collection of gas by any other means was not feasible.

The lava streams have formed upon the surface of the Sciarra a very considerable mass, in the form of a fan, with a base line of perhaps six hundred meters. The shape is due to the continual shifting of the course of the flow by the upgrowth of its bed through cooling, with consequent lateral overflow, and to the convexity of the solidified mass which diverted the later material, flowing from above, to one side or the other—in point of fact, the two latest flows are respectively the most easterly and the most westerly of all.

The total quantity of lava emitted during the eruption cannot be computed by the usual method of cubic measurement, as the larger part is beneath the sea surface, and it is impossible to estimate the quantity on the basis of the rate of flow because it was not under observation during four fifths of its period of eruptive activity.

One of the most interesting observations in connection with this eruption undoubtedly is the behavior of the lava stream on coming in contact with the water of the sea and during its continued flow as a sub-aqueous stream, and this not only because of the light which may be shed upon the manner of growth of the many volcanoes which have begun their existence at the bottom of the sea, but also on account of the paramount question of the absorption of water by hot lava—whether, that is to say, with the two in contact and under a certain amount of pressure, there will or will not be any actual acquisition of water by the lava which may result in chemical or physical changes therein.

It goes without saying that rapidly flowing lava—especially if containing large gas bubbles under high tension—will, on entering water, cause considerable commotion and generate great quantities of steam with some appearance of violence. But when massive, highly incandescent lava, free from large gas bubbles, comes slowly into contact with water, also in mass, there is an absence of explosive phenomena or of serious commotion which at first is very surprising. At Sakurashima \*

\* F. A. Perret, *Zeitsch. Vulk.*, i, p. 143, 1914.



there was a submarine lava flow extending from beneath the eastern lava field for a distance of two kilometers along the sea bottom. The lava had a depth of some seventy-five meters, with forty meters of water above it. The pressure at the sides of this mass of lava near the bottom was, therefore, equivalent to the weight of about 115 cubic meters of sea-water (= tons approximately) per square meter of area. The only disturbance visible at the surface was a succession of convection currents in the water, without eruption of gas, and without raising the water temperature above 64° Fahr. at the surface and 72° just over the lava. In this case, however, the entrance of the lava into contact with water was mostly sub-surface and therefore removed from direct observation, so the Stromboli event was welcomed as a rare opportunity for the study of this phenomenon.

The best observations were made on Nov. 18 and 25, when the sea and weather permitted—although with difficulty—an approach to the base of the Sciara by boat, while the lava was flowing into the sea in a massive, compact stream. This was about twenty meters broad at sea-level, with moraines of another twenty meters on either side, formed of the scoriæ which slid and rolled in avalanches down the side slopes of the convex stream, amid clouds of brown attrition dust.

The full length of the flow was visible, from the mouth of emission to the place of disappearance below the sea, and presented a striking spectacle, by day as well as by night. The narrow upper portion, flowing rapidly down the slope in a sinuous curve and slowly broadening, was divided on its surface by a "medial moraine" of scoriæ forming a black streak between two ribbons of light—a phenomenon not uncommon in flows of this kind, as for example, Etna in 1910. From the upper portion of the stream arose the familiar transparent bluish vapor, which was replaced in the middle section by the brown dust due to the attrition of scoriæ, while from the lower extremity arose the dazzlingly white clouds of the vaporized water at the point of entrance into the sea.

The hot lava, with a front of twenty meters, entered the water at an average rate of about three centimeters per minute, but the area of contact between water and incandescient lava, at any given moment, was rendered very variable by reason of the strong sea swell which alternately invaded the hot surface of the flow above mean water-level and then left exposed to view the cooled surface below. The result was a succession of strong steam puffs synchronous with the period of the swell.

It is interesting to note that, even with a perfectly calm sea there is rarely a continuous and uniform evolution of vapor.

At Sakurashima, on March 12, 1914, the lava, at one place, was entering a sea as smooth as glass, yet the evolution of steam was spasmodic and resulted in a series of puffs, of which one of the photographs taken by the writer might be mistaken for a copy of another made at Stromboli in 1915. In the case

FIG. 5.



FIG. 5. The descent of a lava stream on the Sciara into the sea. On the first third of the descent the vapors are of a transparent blue, very actinic and photographing as if white. The middle portion is a cloud of brown dust from attrition of scorix and below is pure white steam from water vaporization.

of the smooth sea some disturbance, such as the flaking off of superficial layers of scorix, exposes fresh, hot surfaces to the water which is momentarily repelled by the sudden evolution

of vapor and returns in a wave, thus instituting a recurrent action which continues for a certain time.

The sudden contact of water and incandescent material, over a considerable area, results in a violent evolution of steam with a rushing, blowing roar, and the projection outward of fine scoriae and dust which gives a dark color to the lower portion of the cloud of steam. The vapor is often evolved in the form of high pressure spiracles proceeding from the interstices of the scoriae, of which the temperature is such that the vapor is invisible for some centimeters above the source, thus rendering difficult the precise photographing of the jets.

But all this commotion—spectacular and impressive though it may be—is confined to the water *surface* at the point of entrance of the lava, and there remains the outstanding, all-important fact that the stream of compact liquid lava continues on its course beneath the waters of the sea. There is no surface indication of its existence as it disappears into the depths with a smooth, unagitated surface, and we are confronted by the fact of a mass of highly heated liquid moving through water without conflict—a sub-aqueous lava comporting itself as quietly as when sub-aerial.

That this is possible is due to the formation—by rapid cooling through contact with a cold, conducting liquid of great heat capacity—of a porous lava sheath of low heat conductivity which intervenes to hinder the free passage of heat into the water. This may be assumed to be quasi-flexible throughout most of its thickness (that portion which includes the temperature gradient between  $500^{\circ}$  and  $900^{\circ}$ ), and is probably very tough. The “*icicles*” which fringe the entrance to the spatter-grottoes at the Kilanea lava lake are often several meters in length, but so tough and flexible as to remain suspended though buffeted in and out by belches of gas from the caves.

A sheath of water vapor (spheroidal state) will also suggest itself as a heat insulator interposed between the hot lava and the water, but this well-known phenomenon, under the conditions here prevailing, is of such short duration that its influence to protect the flowing lava stream must be accounted secondary.

The protective lava sheath will have a total temperature gradient from the temperature of the outside water (say  $30^{\circ}$ ) to a thousand or more within. Rapid cooling is essential to the formation of such a skin, for only in this way is a surface of such tough viscous quality and little crystallization obtainable in most lavas. Through the interposition of such a non-conducting sheath an incandescent flowing lava will protect itself from reaction with water, while a hot crystalline rock has no protection beyond the momentary check afforded by the spheroidal state of the water. At Etna the writer has seen a lava which

FIG. 6.



FIG. 6. Lava entering the sea. Photographed during a receding swell, to show the formation of the protective sheath, in contact with which no water is vaporized.

FIG. 7.



FIG. 7. Lava entering the sea. Showing development of high pressure steam spiracles.



flowed for hours over snow without melting its way through it, and the masses of liquid lava thrown from the craters upon the snow fields remained virtually upon the surface and later formed "alpine mushrooms" by remaining poised on snow pedestals as the rest of the field disappeared under the sun's rays—a merely hot rock will rapidly melt its way to the bottom of the snow. At Sakurashima, the water was most heated by the lava where this entered the sea in a tumble of hot blocks—in the case of a liquid stream there was little heating, as has already been shown.

We may say, therefore, that a flowing lava may exist in contact with water without the disintegration of either, thanks to the formation of a protective sheath, and this fact helps us to understand the quiet growth of submarine volcanoes. In such cases the only surface commotion need be that due to true gas emission at the central vent.

In point of fact, a sub-aqueous lava stream comports itself more decorously than a similar sub-aerial one. This is due to an important fact which should here be mentioned. It is not to be supposed, of course, that the protective sheath absolutely and always prevents the entrance of water into contact with hot material. Cracks must form at its outer surface and a little water enter and be vaporized in the act of sheathing the raw places. But that which is thus evolved is simply the vapor of water and this, in the presence of water in mass, condenses to water again—there is nothing to reach the surface and cause ebullition. At Stromboli, when incandescent masses, detaching from the lava stream, rolled off the beach into the sea, those of which a portion remained projecting above the surface would steam copiously for a considerable time, while others, precisely similar but completely submerged, gave no surface indication of their existence.

#### *The Explosive Phenomena.*

In contradistinction to that of 1891 the recent eruption was not characterized by important precursory explosive phenomena. There was, apparently, an emission of ash preceding the outflow of lava, but no sample of this could be obtained, and the emission was unimportant in point of quantity. But, toward the end of the eruption, on the 18th and 26th of November, two very violent explosions opened the conduits of the crater which had evidently become obstructed by collapse of the walls as a result of the falling lava column. The first of these explosions, occurring a few hours after the first complete cessation of the lava flow, seemed a direct result of this new condition—"post hoc, ergo propter hoc." The second

explosion took place under diametrically opposite conditions, some hours after a copious outflow, following a temporary cessation, but it is probable nevertheless that obstruction by collapse was, in both cases, the determining cause.

The explosion of Nov. 13 at 9.15 A. M. was sudden, powerful, but remarkably superficial in its nature, and without seis-

FIG. 8.



FIG. 8. First phase of the great explosion on Nov. 13, seen from S. Vincenzo.

mic effects, sending rapidly upward a dense, ball-headed cauliflower cloud of detritus of which a shower of large but lightweight scoriæ fell at S. Vincenzo in from five to six minutes after the explosion. In ascending the mountain directly afterward, the detritus was found in masses of constantly increasing

density as the crater was approached. On the slopes of the cone were splashes of fresh lava which had fallen in an incandescent state and set fire to dry grass and straw, a woman working in the vineyards being slightly burned in this way.

FIG. 9.



FIG. 9. Final phase of great explosion on Nov. 13, showing effect of following puffs in enlarging base of the "pino."

There was also ejected a large quantity of gray, vesicular lava in small fragments with edges rounded as by attrition, and large blocks half buried by their fall, still too hot to be touched. Many of these were coated with fresh lava which had been drawn by the movement into a filiform condition. Finally,

there were large conglomerate boulders, consisting mainly of old altered lava masses cemented together by fresh lava. Both of these explosions, but especially the second, threw out a large quantity of free augite crystals, many in the form of the well known cruciform twins.

This first explosion, which was heard at Lipari, was followed, at 9.30, by a weaker one. The main explosion was also followed, as is generally the case, by a succession of puffs which

FIG. 10.



FIG. 10. Large conglomerate boulder (about one cubic meter) ejected by the explosion of Nov. 26th.

are comparatively so unimportant as to be noticed only as contributing to the maintenance of the great ash "pino" and the enlargement of its base.

The second great explosion, on Nov. 26, was much more profound, and was preceded by a strong concussion which violently shook the windows of the town from half a minute to a minute before the sound of the explosion itself reached it. We have here a phenomenon, also observed at other volcanoes, which requires further study before a satisfactory explanation can be reached, the difficulty here being the greater because of the uncertainty as to the elapsed time between concussion and explosion. No windows were broken, but the flat roofs were made to leak.



The products of this second explosion were more compact than those of the first—fresh lava masses of a beautiful steel-gray luster, and conglomerate boulders of great general density and up to a cubic meter in size.

In connection with the crater emanations a series of phenomena of great importance to volcanology were so well revealed by this eruption that the writer feels that he should not close this paper without reference to them.

From a crater in moderate activity, the usual gaseous emanation in fair weather takes the form of a light cream-colored vapor, which rarely fills the whole area of the crater cavity, but rises as a column of smaller diameter. At other times, however, a dense mass of pure white vapor fills the entire orifice, apparently pouring out of the crater in enormous volume and giving the impression of great activity. But it is often noticed that these two widely differing appearances may occur during the same state of actual eruptive intensity, and even that one condition may be replaced by the other in a few minutes and without any increase or decrease of volcanic activity.

Further observation reveals the fact that the condition depends upon the weather, the first condition prevailing on a fair day and dry state of the air, while a humid wind produces the second. The usual explanation—simple, and applicable to mere fumarolic emanation—is that the water vapor in the volcanic exhalations is absorbed in a dry atmosphere but condenses in contact with moist and already saturated air. But, to apply this explanation in the case of an active volcano would be to assume that these great volumes of water vapor are being continuously exhaled from the volcano even when the visible “panache” is a slender column rising in the center of a great basin, as is so often the case.

At Stromboli, on Nov. 27, the weather in the morning was clear, but threatening change. From Punta Labronzo the crater could be seen emitting light columns of creamy vapor from the open mouths while the most easterly mouth was obstructed, and emitted nothing. At noon a chill, moisture-laden wind suddenly supervened, and immediately there poured from the craters—including the obstructed mouth—a dense column of pure white vapor, without the least increase in explosive activity having occurred.

The present writer has long suspected the atmosphere of being the source of this water vapor, but while it is easy to conceive of a condensation from humid air by a cold mountain peak—as in the case of Alpine “cloud banners”—it was more difficult to account for it over a hot crater. It is here, nevertheless, that we have to seek the explanation of the phenomenon, which is merely due to the nucleation by the

volcano of saturated air from without. The great cloud of water vapor is not an emanation of the volcano, but a condensation from the atmosphere upon nuclei furnished by the stream of dust particles emanating from the volcano, aided, particularly in its initial stages, by direct ionization (electrons) in case the volcanic gases are escaping from liquid lava or through incandescent conduits. The well-known experiment, at solfataras, of holding a lighted torch near a fumarole to produce a condensation of the emanating water vapor, may be cited as an illustration of the phenomenon with, however, the conditions exactly reversed—at the more active vent the water is supplied by the atmosphere and the volcano is the torch.

This atmospheric condensation will not always take place. Too high a temperature—as over a crater full of incandescent lava—will often prevent it, and even at a solfarata if the walls of a small fumarole are sufficiently heated artificially it will be found impossible to condense the issuing vapor by nucleation with a torch; but these cases are due solely to excessive heating of the saturated air which then returns to an unsaturated condition. The importance of an understanding of this phenomenon lies mainly in avoiding erroneous impressions of a volcano's state of activity based on the apparent emission of great volumes of steam from a crater which may really be almost quiescent at the time. Reports of this kind are constantly being made, and the dynamic record is often correspondingly faulty.

Precipitation of salts from gas emanations was not marked, during this eruption, excepting in the fumarolic area, towards the end. This is perhaps but natural, considering that gaseous emanation was not the salient feature of this almost wholly effusive activity. There was evidence during the eruption of response to the influence of favorable luni-solar combinations.

In conclusion it may be pointed out that this last eruption offers further proof of the view already expressed elsewhere\* that this volcano has, since 1907, entered upon a new period of increased activity which has been characterized by powerful explosive and effusive eruptions having a greater resemblance to the processes of other volcanoes than to what has been generally considered to be the normal Strombolian form of action. There can be no doubt that Stromboli, to-day, is a mine of wealth for the direct observation of volcanic phenomena, and every effort should be made to provide for a more continuous study of it.

Geophysical Laboratory,  
Carnegie Institution of Washington,  
Washington, D. C., Sept. 29, 1916.

\* Perret, F. A., *Bull. Brooklyn Inst.*, i (1), p. 313, 1907; *Ann. Uff. Cent. Met. Ital.*, xxx (1), p. 27, 1910; *Smithson. Reports* (1912), p. 285, 1913.

ART. XLV.—*Determination of Fluorine in Soluble Fluorides*; by J. G. DINWIDDIE.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxxxiv.]

IN determining fluorine gravimetrically there are several methods in use. The method of Rose\* consists in precipitating calcium carbonate together with calcium fluoride so that the precipitate of calcium fluoride may, with some degree of satisfaction, be filtered and washed. After being ignited, the calcium carbonate is dissolved out by means of 1.5 N acetic acid and the residue of calcium fluoride is washed, ignited and weighed. This procedure is open to two objections: that the calcium fluoride is very appreciably soluble in the dilute acetic acid, and that two filtrations are required. Starck and Thorin† precipitate calcium fluoride along with a known weight of calcium oxalate and determine the fluorine by difference. These authors claim that the precipitate so formed is granular and easy to wash but Adolph‡ found it very hard to handle. Starck§ makes use of the mixed chloride and fluoride of lead. This method is said to give good results provided that care is taken to use very little wash water.

In the attempt to precipitate fluorine so that it could be separated from fluosilicic acid by filtration, an excess of powdered calcium sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was used. This gave a precipitate of calcium fluoride and sulphate which was easier to filter and wash and had almost no tendency to run through the pores of the filter. It was thought that it might be possible to adapt this to the determination of fluorine in soluble fluorides. Calcium fluoride when treated with sulphuric acid is converted to sulphate, the fluorine being expelled as hydrofluoric acid. Now if a mixture of fluoride and sulphate of calcium be similarly treated with sulphuric acid, the only change will be the conversion of the fluoride to sulphate. A gram molecule of calcium fluoride, 78, when changed to sulphate will weigh 136, so that an increase of 58 parts by weight will mean that the precipitate contained 78 parts of calcium fluoride.

In perfecting this method there were several difficulties which arose in connection with the filtering, ignition, etc., of the precipitates. These will be enumerated, and then will be described the expedients which were used to avoid these difficulties.

\* Rose, *Liebig's Annalen*, lxxii, 343, 1849.† Starck and Thorin, *Zeit. Anal. Chem.*, li, 1912.‡ Adolph, *J. Am. Ch. Soc.*, xxxvii, 2500, 1915.§ Starck, *Zeitschr. anorg. Chem.*, lxx, 173, 1911.

1. Since the fluoride has to be treated with acid, it cannot be filtered on asbestos because the hydrofluoric acid set free will attack the mineral of the filter.

2. If an ordinary filter is used, particles of the precipitate adhere to it and, when burnt along with the paper, the calcium sulphate is partly turned to sulphide and leads to incorrect results.

3. If the mixed precipitate is heated to redness in order to obtain a constant weight, the mass fuses together and it is almost impossible to completely decompose the solid mass with sulphuric acid so as to convert all of the fluoride to sulphate.

4. When the excess of sulphuric acid is being driven off so that the residue of calcium sulphate may be weighed, great care has to be exercised to prevent spattering if the heat is supplied by placing a bunsen burner beneath the crucible.

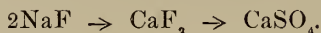
The detailed directions for the determination of fluorine by use of powdered calcium sulphate as mentioned above will now be given, and it will be made clear how each of the above difficulties was surmounted.

The solution of the fluoride, which should occupy as small a volume as practicable, say about thirty or forty cubic centimeters, and should be neutral, is heated to boiling and powdered calcium sulphate is added. After standing from thirty minutes to one hour, with frequent stirring, the precipitate of fluoride and sulphate of calcium is washed by decantation several times and then is put onto the filter for final washing. The filter consists of a perforated platinum crucible in the bottom of which is a small disc of ashless filter paper, cut so as to fit exactly in the bottom without being bent up around the sides. By keeping gentle suction upon the crucible, the disc is held in place and the filtrate comes through without the least turbidity. As soon as the precipitate has been sufficiently washed, it is transferred with the aid of a fine jet of water from a wash bottle to an ordinary platinum crucible; the disc of paper is washed free of the precipitate and is ignited on the lid of the crucible, while the precipitate in the crucible is evaporated on the steam bath to dryness. If now this residue is heated to redness to obtain a constant weight, it melts and becomes very difficult to decompose with sulphuric acid. By experimenting it was found that at a temperature around  $300^{\circ}\text{C}$ . the calcium sulphate loses all of its crystal water and a constant weight is obtained. The proper temperature is obtained by heating the platinum crucible within an ordinary iron crucible of diameter about three inches at the top, used as a radiator. In order to equalize the heat a thin piece of asbestos was placed in the bottom and upon this was placed a small triangle for the platinum crucible to rest upon.



By heating the bottom of the iron crucible with a bunsen burner to a low red, the contents of the platinum crucible reach a constant weight within one hour or less.

When a constant weight has thus been obtained, the residue is mixed with a little water and several cubic centimeters of pure sulphuric acid. This mixture is now evaporated on the steam bath as far as it will go at this temperature and then, by heating further, the sulphuric acid is driven off, the last traces requiring the application of a red heat for a few moments. As was stated above, there is great danger of spattering when the excess of acid is being driven off. In order to avert this danger and to permit the acid to be driven off very quickly the following method was adopted: The lid is placed on the crucible, which is resting on a triangle. A Meker burner is fastened above and slightly to one side of the crucible by means of an adjustable clamp. The flame of the burner is allowed to impinge from above at an angle of about forty-five degrees, on the farther side of the lid of the crucible. In this way, the heat can easily be regulated so that the sulphuric acid volatilizes rapidly and, since the heat radiates from above, there is almost no tendency to spatter. The residue obtained by igniting at 300° consists of a mixture of calcium fluoride and sulphate while the residue remaining after volatilization of the sulphuric acid consists entirely of calcium sulphate. The increase in weight of the contents of the crucible is due to the replacement of two atoms of fluorine by the sulphuric acid radical. The changes which have taken place may be represented by



Thus 84 of sodium fluoride gives 78.0 of calcium fluoride and 136.07 of calcium sulphate. Therefore 58.07 of increase corresponds to 84 of sodium fluoride and 78 of calcium fluoride, and to estimate the calcium fluoride present in the precipitate, multiply the increase in weight by  $78/58.07 = 1.3431$  and for the sodium fluoride multiply by  $84/58.07 = 1.4465$ .

In order to test out the method which has been described in detail, a solution of pure sodium fluoride was used. Commercial sodium fluoride, even that marked C. P., contains silica and so, for a standard solution, pure hydrofluoric acid was neutralized to phenolphthalein with pure sodium hydroxide obtained by allowing moist air to act on metallic sodium in absence of carbon dioxide. This solution was diluted so that it contained about three grams of sodium fluoride per 100 cubic centimeters. To ascertain the exact concentration of this solution, first the method of Rose, of precipitating the fluoride along with the carbonate of calcium, was tried. This precipi-

tate was so hard to handle, in that it ran through into the filtrate and clogged up the pores of the paper as well, that the attempt was abandoned. Since the solution of which the standard was desired contained no other compound besides sodium fluoride, its concentration was finally determined by evaporating measured portions to dryness in a platinum crucible, igniting to about 300° C. and weighing. The following results were obtained on several portions. 10<sup>cc</sup> portions of the sodium fluoride solution gave 0.2724, 0.2721, 0.2723, 0.2725, 0.2721 grams of sodium fluoride. One determination with 20<sup>cc</sup> gave 0.5450 grams. The average of all gave for the standard of the solution that 10<sup>cc</sup> contained 0.2724 grams of sodium fluoride.

The table following shows the results obtained by carrying out the determinations as outlined above :

TABLE VI.

	Sol. NaF used	NaF	Increase F <sub>2</sub> → SO <sub>4</sub>	NaF equiv.	Diff.	% error
<i>a</i>	10 <sup>cc</sup>	0.2724	0.1894	.2740	+ .0016	+ 0.62
<i>b</i>	10 <sup>cc</sup>	0.2724	0.1888	.2731	+ .0007	+ 0.25
<i>c</i>	10 <sup>cc</sup>	0.2724	0.1885	.2727	+ .0003	+ 0.11
<i>d</i>	10 <sup>cc</sup>	0.2724	0.1882	.27223	− .00017	− 0.062
<i>e</i>	10 <sup>cc</sup>	0.2724	0.1883	.27237	− .00003	− 0.015
<i>f</i>	10 <sup>cc</sup>	0.2724	0.1876	.2714	− .0010	− 0.37
<i>g</i>	20 <sup>cc</sup>	0.5448	0.3752	.5427	− .0021	− 0.385
<i>h</i>	10 <sup>cc</sup>	0.2724	0.1881	.2721	− .0003	− 0.082
<i>i</i>	10 <sup>cc</sup>	0.2724	0.1886	.2728	+ .0004	+ 0.11

On account of the solubility of calcium fluoride, there will be a tendency for the results to run low and, unless the filtrate and washings are kept to a low volume, large negative errors are liable to occur. In several determinations the filtrate was about 200<sup>cc</sup> and the results here were about 1.4 per cent low. On account of this danger, a solution saturated with pure calcium fluoride and calcium sulphate was used for wash water in order to eliminate the solubility error and results very close to the calculated value were obtained even when the filtrate was allowed to get quite large. These results are shown in *h* and *i* of Table VI.

The weighed precipitate of calcium fluoride and sulphate might be converted, according to Loczke,\* into chloride and sulphate, by evaporating with hydrochloric acid, and the calcium sulphate be weighed, the fluoride being determined by difference. However this would require another filtration and would be less accurate.

\* Loczke, Zeitschr. anal. Chem., xlix, 329, 1910.

Since, during the precipitation of the fluoride of calcium by the sulphate, an equivalent amount of sulphate ion is set free, it is obvious that this method is adapted without any modifications to the separation and determination of fluorides in the presence of sulphates. It may also be used for the separation of fluorine from other radicals which do not form insoluble compounds with calcium.

The method of Bunsen for determining fluoride in the presence of phosphoric acid would be applicable here provided that it were accurate. This consists in weighing a mixed precipitate of orthophosphate and fluoride of calcium and then converting it to phosphate and sulphate by ignition with sulphuric acid. He claims that the final residue after ignition consists entirely of calcium orthophosphate and calcium sulphate, but Treadwell and Koch,\* in experimenting to decide upon the best method for this separation in wines and beers, heated a weighed amount of calcium orthophosphate with sulphuric acid, as directed by Bunsen, until a constant weight was obtained. Instead of obtaining the original weight they obtained a much greater weight. Upon testing the residue, they found that the precipitate contained a large amount of calcium sulphate and that metaphosphoric acid had been formed and condensed partly on the lid of the crucible.

\* Treadwell and Koch, *Zeitschr. anal. Chem.*, xliii, 469.

ART. XLVI.—*The Albertella Fauna Located in the Middle Cambrian of British Columbia and Alberta* ;\* by LANCASTER D. BURLING.

As announced at the Washington meeting of the Geological Society of America† the reference of the *Albertella* fauna to the Middle Cambrian† has been confirmed by the discovery on

FIG. 1.



FIG. 1. Outcrop of the *Albertella* shale member of the Cathedral formation on Mt. Bosworth, B. C. The thickness of the bed is 7 feet, the figure being so far back of the beds shown in foreground as to make them appear thicker.

Mount Bosworth of the parent ledge of the drift block which has been so often described. The inability of either Mr. Walcott or myself, jointly or severally, to find this bed during the

\* Published by permission of Deputy Minister of Mines.

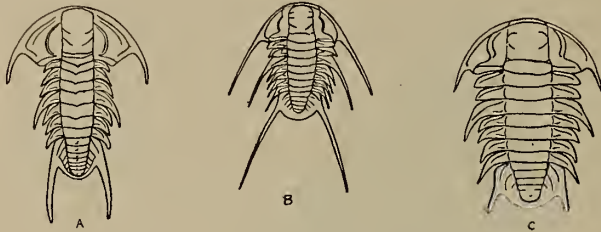
† See 1 and 2 of the literature references at the end of the article.



years in which search has been prosecuted is due to the fact that its reference to the Lower Cambrian led us largely to confine our efforts to the series of thin beds underlying the Cathedral formation.

The fauna actually occurs in a 7-foot band of shale which interrupts the sedimentation of the massive limestones of this Middle Cambrian formation 375 feet above its base. The outcrop of this shale, to which the name of *Albertella* shale mem-

FIG. 2.

FIG. 2. Described species of American *Albertellas*.

- A. *Albertella bosworthi* Walcott (British Columbia).  
 B. *Albertella helena* Walcott (Montana). (After Walcott.)  
 C. *Albertella helena* Walcott (British Columbia).

ber of the Cathedral formation is hereby applied, has a horizontal extent of several hundred feet on the east and northeast face of Mount Bosworth at an elevation of about 8000 feet (see fig. 1). Mount Bosworth lies on the continental divide just north of the main line of the Canadian Pacific Railway between Alberta and British Columbia. The relations of the *Albertella* shale to the over- and underlying beds is given in the following section of the lower portion of the Mount Bosworth and Castle Mountain sections:

	Formations	Mount Bosworth	Castle Mountain, 20 miles southeast
Middle Cambrian	Eldon.	feet	feet
	Stephen .....	400	315
	Cathedral (upper) ..	775	565
	<i>Albertella</i> shale ...	7	10
	Cathedral (lower) ..	375	200
	Mount Whyte.....	250	200
Lower Cambrian (St. Piran)			

Attention should be called to the apparent agreement in the thinning of the formations to the eastward; but changes in sedimentation in the Canadian Pacific Railway section are so frequent and important that measures of thickness are usually local only in their application.

In 1914<sup>3</sup> I did not presume to question Walcott's reference of the *Albertella* fauna to the Mount Whyte formation, indeed the writer's assignment of that fauna to the Middle Cambrian necessitated a change in the systemic reference of the Mt. Whyte formation. I am now as thoroughly convinced that all but the lowest beds of the Mt. Whyte formation are Middle Cambrian in age, but the discovery that the *Albertella* fauna occurs in a shale member embedded 375 feet up in the overlying massive arenaceous limestones of the Cathedral formation robs me of one of the main arguments which I used in 1914 for the Middle Cambrian age of the Mt. Whyte.

The reported discoveries of the *Albertella* fauna to date are as follows, recording them in the order of their discovery:

1. Gordon Creek, 6 miles from the south fork of Flathead River, Ovando quadrangle (U. S. G. S.), Powell County, Montana, in a shale 75 feet above a quartzitic sandstone (1905).<sup>4</sup>

2. Mount Bosworth, British Columbia, in drift near railroad right of way between Hector and Stephen (1907).<sup>5</sup>

3. Mount Stephen, British Columbia, 200 feet above the quartzitic sandstones of the St. Piran formation (1907).<sup>6</sup>

4. Lake Agnes section, near Lake Louise, Alberta, in a shale correlated with the horizon on Mount Stephen, No. 3 (1907).<sup>7</sup>

5. Liau-tung, Manchuria, on the shore of Tschang-hsing-tau Island (1909).<sup>8</sup> The correlation of this species with *Albertella* is somewhat doubtful, but it occurs above well marked Middle Cambrian horizons.

6. Mt. Robson region, British Columbia, 550 feet above the base of the Chetang limestones (1912).<sup>9</sup>

7. Elko, British Columbia, in the Burton formation (1913).<sup>10</sup>

8. North Kootenay Pass, British Columbia, in shale (1915).<sup>11</sup>

9. Mount Bosworth, British Columbia, the horizon of the drift blocks mentioned in "2" found interbedded in the massive limestones of the Cathedral formation 375 feet above its base (1915).<sup>12</sup>

10. Castle Mountain, Alberta, at the same horizon as the one on Mount Bosworth (1915).<sup>13</sup>

11. Mount Robson region, British Columbia, in a limestone whose exact stratigraphic relations have not yet been worked out. The horizon is comparable, however, with that on Mount Bosworth (1915).<sup>14</sup>

The genus *Albertella* has been figured by Walcott in the following publications: Smithsonian Misc. Coll., vol. liii, 1908, plates 1 and 2; and Research in China, vol. iii, 1913, plate 12,

figs. 1 and 2. Figures of the three species so far described are inserted here because *Albertella* deserves prominence as one of the best horizon markers of the early Middle Cambrian.

Geological Survey of Canada, Ottawa.

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4. Walcott, Mon. U. S. Geol. Surv., vol. li, pt. 1, p. 168, 1912; locality 4v.
5. " Smithsonian Misc. Coll., vol. liii, p. 214, 1908.
6. " Canadian Alpine Journal, vol. i, p. 241, 1908. (p. 10 of reprint.)
7. *Idem*, p. 214.
8. Walcott, Research in China, vol. iii, pp. 27 and 106, 1913.
9. " Smithsonian Misc. Coll., vol. lvii, p. 338, 1913.
10. Schofield and Burling, Geol. Survey Canada, Mus. Bull. No. 2, pp. 82, 93, and 125, 1914.
11. Adams, Bull. Geol. Soc. America, vol. xxvii, 1916, pp. 62 and 63; and Commission of Conservation, Discovery of Phosphate of Lime in the Rocky Mountains, by Adams and Dick, 1915, p. 13.
12. Burling, Summary Rept. Geol. Survey Canada for 1915, pp. 99 and 100, 1916.
13. *Idem*.
14. *Idem*.

ART. XLVII.—*Some New Forms of Natrolite*; by  
ALEXANDER H. PHILLIPS.

SOME interesting specimens of natrolite were collected by Mr. Edward Sampson in the Ice Valley region of British Columbia. They were found along the contact of a nephelite syenite and limestone. The crystals were very large and individually developed, but forming reticular masses with angular cavities. Individual crystals were 6<sup>cm</sup> in length and 4<sup>cm</sup> in diameter.

A second generation of small, water-clear crystals occurs implanted upon the large individuals and terminating freely in the angular cavities. The large crystals are milky and translucent from inclusions. This second generation of small crystals are very rich in crystal forms and with very bright and perfect faces. On one crystal, although only a millimeter in diameter and terminated at one end, 38 faces were measured, representing 13 crystal forms. The large crystals are simple in habit; in the prism zone they are combinations of the unit





were all that could be desired. The measurements for this face were  $\phi = 63^{\circ} 58'$  and  $\rho = 90^{\circ}$ . The average value of these angles, yielded by the ten brightest signals, is:

	$\phi$	$\rho$	Maximum	Minimum
Measured . . . .	$63^{\circ} 56'$	$90^{\circ}$	$64^{\circ} 11'$	$63^{\circ} 46'$
Calculated . . . .	$63^{\circ} 52'$	$90^{\circ}$		

The prism  $r(120)$  was represented by two narrow faces on one crystal which yielded fair reflections:

Measured . . . .	$\left\{ \begin{array}{l} 18^{\circ} 00' \\ 18^{\circ} 36' \end{array} \right.$	$\left. \begin{array}{l} 90^{\circ} \\ 90^{\circ} \end{array} \right\}$
Calculated . . . . .		

The pyramid  $o(151)$  was measured 16 times and was represented on 4 crystals. The signals varied with the size of the face; taking the average of eight measurements where the signals were satisfactory, the angles are,

	$\phi$	$\rho$		$\phi$	$\rho$
Measured . . . .	$11^{\circ} 33'$	$60^{\circ} 54'$	Maximum . . . .	$11^{\circ} 42'$	$61^{\circ} 05'$
Calculated . . . .	$11^{\circ} 31'$	$60^{\circ} 49'$	Minimum . . . .	$11^{\circ} 27'$	$60^{\circ} 46'$

The pyramid  $t(531)$  was represented by three faces on one crystal, two of which were well developed, yielding satisfactory reflections, while the third was very small with an indistinct signal.

Measured . . . . .	$\left\{ \begin{array}{l} 59^{\circ} 25' \\ 59^{\circ} 23' \end{array} \right.$	$\left. \begin{array}{l} 64^{\circ} 31' \\ 64^{\circ} 31' \end{array} \right\}$
Calculated . . . . .		

There were several other forms represented, by very small faces, yielding signals too dull or indistinct to give satisfactory measurements. The best of these, which occurred several times, indicated a pyramid in the zone of the new prism  $e(210)$ , with indices (211).

Princeton, N. J., Oct. 9, 1916.

ART. XLVIII.—*On Pre-Cambrian Nomenclature*; by  
CHARLES SCHUCHERT.

DURING the past ten years there have appeared a number of most excellent studies on the structure and correlation of the pre-Cambrian rocks of the Canadian Shield and the Lake Superior region. To get these results in such form that undergraduate students in geology could easily understand the broader sequence of events, the writer asked his colleague, Professor Barrell, to set them forth in the shape of a geologic time-table.\* We held that this classification "must be regarded as provisional only, another step toward a larger and more accurate knowledge of the long eons which preceded the fossiliferous record" (p. 17). Since then other classifications have appeared, and the one by Professor Lawson† stimulates the writer to the following remarks.

The writer admits that he has no knowledge at first hand regarding the pre-Cambrian rocks but he is nevertheless deeply interested in the wisdom unearthed by those capable of working in this exceedingly difficult field. Some of this knowledge he is called upon each year to present to students in his course in Historical Geology. In this paper the writer will limit himself entirely to the terminology, and more especially to the primary terms, the eras. As for the nomenclature of these ancient times, the paleontologist is as well trained to look into it as is the geologist, and it is therefore beside the mark for Lawson to state that "the paleontologists should refrain from insisting on their nomenclature in a field in which they do no work" (19). The rules relating to nomenclature apply to all geologists, and if any one has constructive ideas that will help to build up a better geologic time-table, it is his duty to present them to his colleagues. As for "insisting on their nomenclature," we are all bound to observe the rules of nomenclature and to accept that which is well done.

In regard to rules of nomenclature, Weeks in his *North American Geologic Formation Names*‡ states: "In determining the names to be applied to formations the laws of priority and prescription (general usage) should be observed. The name first given to a definite formation or series of strata should hold, unless this name is superseded in literature by

\* Schuchert and Barrell, A revised geologic time-table for North America. This Journal, (4) xxxviii, 1-27, 1914.

† A. C. Lawson, The correlation of the pre-Cambrian rocks of the region of the Great Lakes. Univ. Calif. Pub., Bull. Dept. Geology, x, No. 1, 1-19, 1916.

‡ F. B. Weeks, Bull. 191, U. S. Geol. Surv., 1902, 11.

another which has come into general use. In the latter case the first name should be dropped for this formation; and, where there can be no question as to the general usage of the subsequent name, the first name might be used again for a different formation without causing serious trouble." "The duplication of formation names has become a serious matter, as will be seen from an examination of this list. . . . New names should replace those which can not hold their present varied definitions."

Weeks has a separate list of the geographic names that have been applied to masses of igneous rocks occurring in North America. Two identical names, one for a stratigraphic unit and another for an igneous mass, may therefore remain in use.

The rule of priority as to formation, series, and period terms is now generally adhered to, but in regard to era names the rule is not so rigidly followed, because they are more expressive of ideal conditions than are the smaller divisions of time. It is the same in biology in relation to family, order, and class terms, and it is from this source that paleontologists and geologists get their ideas of fixity in nomenclature.

The principles of correlation adopted by Lawson (and to which the writer also adheres) are, for pre-Cambrian formations:

"(1) The principle of lithologic similarity and the community of conditions of deposition inferred from this similarity. (2) The principle of the similarity of sequence. (3) The principle of coincidence of unconformities in the sequence. (4) The principle of irruptive contacts" (4). On the basis of these principles the hypothesis of two periods of granitic invasion "states that in post-Keewatin time there were two and only two periods in which great granitic batholiths were developed in the earth's crust in the region of the present Great Lakes" (5). Furthermore, "in every one of the fifteen districts, considered individually, geological time is blocked out into three grand divisions by the two granite invasions: the pre-granitic, the inter-granitic and the post-granitic" (12).

In regard to the major unconformities Lawson correctly holds that "Wherever the earth's crust is known to have been extensively invaded by granite, an important concomitant condition has been the uplift of the region affected and the inauguration of a prolonged period of degradation, culminating in the removal of the cover from extensive areas of the granite. . . . The time necessary for the invasion of a region by granite is unknown, but it may well have been a long drawn-out process. The stripping of the cover of the granite, however, and particularly the reduction of a high region to low relief, requires a long time in the geological sense; and the

Lawson Classification 1916		Schuchert Classification 1915*		
		Waucobian (Cambrian) Paleozoic		
Paleozoic & Era	Algonkian (Period, System)	Great Epi-Proterozoic Interval		
	Keweenawan (Epoch, Series)	Late Proterozoic Era (Primitive life) Algonkian (Major division)	Keweenawan (Period)	
Animikian (Epoch, Series)	Animikian (Period)			
Eparchean Interval. Major Unconformity			Huronian (Period)	
Algomian Revolution		Ep-Algomian Interval		
Archean Era	Huronian (Period, System)	Algomian Revolution		
	Temiskamian (Epoch, Series)	Early Proterozoic Era (Primitive life) Neo-Laurentian (Major division)	Sudburian (Period)	
	Unconformity			
Bruce (Epoch, Series)				
Epilaurentian Interval. Major Unconformity		Ep-Archeozoic Interval		
Laurentian Revolution		Laurentian Revolution		
Ontarian (Period, System)	Grenville (Epoch, Series)	Archeozoic Era (Primal life) Paleo-Laurentian (Major division)	Keewatin (Period) Coutchiching (Period)	} Grenville
	Keewatin (Epoch, Series)			
	Coutchiching (Epoch, Series)			

\* Essentially the same as Schuchert and Barrell 1914.



interval of no deposition, between the sediments resting on the worn surface of the granite and the sediments into which the granite is intrusive, constitutes an unconformity of a major order. We may for practical purposes take the appearance of a worn surface of granite upon which as a basement sedimentary strata rest as *prima facie* evidence of a major unconformity" (12).

On the basis of these principles and their application by Lawson and many other geologists in fifteen districts in the Great Lakes, Ontario, and Adirondack regions, Lawson presents a "Correlation of the pre-Cambrian on the basis of two and only two granitic invasions." The first column of this table is reprinted here and is set side by side with the one in the Pirsson-Schuchert *Text-book of Geology*. It will be seen that there are several nomenclatorial differences, and one marked discord regarding the time of the second granitic invasion, the Algomian Revolution. The correct determination of the latter point is not within the writer's scope, and is left to those knowing the field relations.

The above two tables show that we agree that there were two times of granitic invasions—Laurentian and Algomian—and that there are two major unconformities. The writer believes (not knows) that the Keweenawan and more especially the Animikian are pre-Cambrian in age, that is, are older than the Waucobian or Olenellus fauna, the accepted base of the Paleozoic era. Holding to this belief, it follows that there should be another major unconformity above the Keweenawan and below the Waucobian of the Cambrian. Therefore the writer divides pre-Cambrian time into three eras, while Lawson holds that there is but one—Archean—and refers the Animikian and Keweenawan doubtfully to the Paleozoic era. What the writer calls eras and periods, Lawson terms periods and epochs. This seemingly trivial matter is, however, not one of nomenclature but is of fundamental importance in the classification of geologic time. In other words, are we to hold with Lawson (1) that all pre-Cambrian time is structurally representative of but one era; (2) that eras may have within themselves "revolutions," "major unconformities," and very long intervals of erosion; and (3) since pre-Cambrian time "is blocked out into three grand divisions by the two granitic invasions," that these two "revolutions," as Lawson also terms them, are but of the value of the breaks that separate the accepted periods of post-Keweenawan time? Long before the writer presented a text-book on Historical Geology most geologists were holding that revolutions and major unconformities were indicative of era delimitation. Further, that pre-Cambrian time was as long as and even much longer than all Pale-

ozoic, Mesozoic, and Cenozoic time. In this connection it may be well to call attention to some conclusions by Van Hise,\* who states that pre-Cambrian time may represent, according to some biologists, nine-tenths of geologic history since life began on earth. "In some cases the volume of rock and great intervening erosions represent a lapse of time which may be not inaptly compared with all subsequent time. If geological history were to be divided into three approximately equal divisions, these divisions would not improbably be the time of the Archean, the time of the clastic series between the Archean and the Cambrian, and post-Cambrian."

As it is generally admitted that pre-Cambrian time is very long, the conclusion must naturally follow that the revolutions and the major unconformities noted by geologists are of the value that distinguish the eras one from another. The Laurentian and Algonian granitic invasions have the value of revolutions—the elevation of mountains and their removal through erosion—and the major unconformities in the geologic succession must be the places that distinguish eras. These unconformities are altogether too pronounced to be representative of the breaks that distinguish periods.

The next point of importance is, what shall be indicated in the term or terms to be used for the era or eras back of the Paleozoic? The strata of post-Cambrian time are usually replete with fossils, and their primary value in geologic chronology is accepted by all geologists. For this reason the Greek ending *-zoic*, meaning life, has long been acceptable for the Paleozoic, Mesozoic, and Cenozoic eras. Again, it is admitted by nearly everyone that life existed long before the Cambrian and there are leaders, as for instance Chamberlin, who hold that it was present even before the Coutechiching at the base of the Archeozoic. Therefore why should not all era terms have the ending *-zoic*, as Archeozoic and Proterozoic? The writer regrets to learn from so good a teacher as Lawson that he questions "the advisability of teaching visions to beginners in geology." It is true that pre-Cambrian life is not yet well enough known to be the basis of chronology, nor will it seemingly ever be, but what harm can there be in the visions of primitive life that are brought to mind by the terms Archeozoic and Proterozoic? Is it not far better to bring up these visions founded on such knowledge as we have, than to suggest eras barren of life by the use of the non-committal terms Archean and Eparchean? Until more reasonable evidence is forthcoming, the writer prefers to adopt terms for all eras that end in *-zoic*.

Let us now examine the various terms that have been pro-

\* C. R. Van Hise, Bull. 86, U. S. Geol. Surv., 1892, 491.

posed for the rocks of pre-Cambrian time. It appears that Professor Phillips was the first to use a term for all pre-Cambrian rocks in his *Manual of Geology* (London 1832), grouping them under *Hypozoic*. The writer does not have access to this book, but in the second edition of it, published in 1855, on page 655 the term is defined as follows: "Hypozoic. A term proposed . . . for the lowest primary strata, such as gneiss, mica, schist, etc., found below all those which contain organic remains," i. e., below the Cambrian and Silurian. The word is taken from the Greek words for *below* and *life*. In this book Phillips further says it equals Murchison's term *Azoic*. The latter, however, dates from 1845\* and therefore should not dispossess Hypozoic; it is defined as follows: "To the crystalline masses [of Norway and Sweden] which preceded that palæozoic succession to which our researches were mostly directed, we apply the term 'Azoic,' not meaning thereby dogmatically to affirm, that nothing organic could have been in existence during those earliest deposits of sedimentary matter, but simply as expressing the fact, that in as far as human researches have reached, no vestiges of living things have been found in them. . . . Professor Phillips has applied the word Hypozoic to the same rocks which we term Azoic."

"One of the Scandinavian features which first strikes the ordinary observer with surprise, is the enormous amount of crystalline rock that occupies the surface of the country. In the term Azoic rocks, we include all the crystalline masses belonging to the ancient group of gneiss, together with ancient granitic and plutonic rocks by which they have been invaded."

The older term Hypozoic was not widely used and finally was altogether displaced by Azoic. The first geologists to use this term in America, and for all pre-Cambrian rocks, were Foster and Whitney.† Sir William Dawson used it also for all the pre-Cambrian rocks, the "oldest metamorphic rocks of Canada," in the first edition of his *Acadian Geology*;‡ in the second edition of this book we read:§ The rocks below the Paleozoic "until lately, were regarded as azoic, or destitute of remains of life; but the discovery of *Eozoon canadense* [this is certainly not a protozoan as held by Dawson, but appears to be an algal calcareous secretion] now entitles them to the name Eozoic [= dawn life], or those that indicate the morning of that great creative day in which the lower forms of animal life were introduced upon our planet." Dana also used Azoic in the first edition of his *Manual*,|| as follows: "The Azoic

\* R. I. Murchison, *Geology of Russia in Europe*, 10\*.

† Foster and Whitney, *Geology of the Lake Superior Land District*, Pt. II, Washington, 1851, 3 and Chapter II.

‡ *Acadian Geology*, Edinburgh, 1855, 22 and Chapter 15.

§ 1868, 658.

|| *Manual of Geology*, 1863, 134.

age is the age in the earth's history preceding the appearance of animal life," which he then held ceased with the Potsdam or the Cambrian. Earlier H. D. Rogers\* had used both Azoic and Hypozoic in a modified sense, thus:

"*Azoic* (Gr. *a*, without, *zoe*, life).—Applied to a group of rocks underlying the Palæozoic, and destitute of all traces of once vital organisms."

"*Hypozoic* (Gr. *hypo*, under, and *zoe*, life).—A term for the gneissic and other rocks which lie beneath the fossiliferous strata. The term is conveniently restricted to the more ancient metamorphic rocks which underlie the Azoic or semi-metamorphic strata, which are also destitute of fossils, but which in many countries immediately support the Palæozoic, or those containing organic remains." On page 742 it is used in the sense of the oldest rocks, beneath the Azoic.

Sir William Logan† refers the Huronian series and the Laurentian series to the Azoic and remarks as follows: "To the Azoic rocks no local names have yet been applied in any part of America except in Canada, and as these rocks are here more extensively exposed than anywhere else on the continent, . . . the names of the Laurentian and the Huronian systems or series . . . are allowed to remain unchanged."

According to the history above recited we should retain the term Hypozoic if there is but one geologic era back of the Cambrian, and the significance of the word is in harmony with the other accepted era terms in that it implies that there is life—of course as yet almost wholly unknown—in the rocks below the Paleozoic. In this event Azoic becomes a synonym, and further, the word is a misnomer in that it labels the pre-Cambrian rocks as being without life. However, as we now know that there are at least two eras back of the Cambrian, the question arises, can we redefine Hypozoic and Azoic so as to be expressive of modern views? To all holding that life existed during Ontarian and Huronian time as defined by Lawson, it is at once apparent that Azoic should be rejected, and as Hypozoic was based upon a theoretic conception and not upon a defined rock area, it also seems to have no present value. As the writer holds that *Eozoon canadense* is evidence of algal life, and as Walcott has demonstrated the presence of much life in the younger pre-Cambrian strata, it seems best to reject the names Azoic and Hypozoic. This becomes all the more advisable if there are three eras back of the Cambrian.

The term *Archeozoic* was proposed by Chamberlin and Salisbury in 1906.‡

The evidence now being unearthed by geologists in the

\* *Geology of Pennsylvania*, ii, Pt. II, 1859, 1025, 1026.

† *Geology of Canada*, 1863, 20–21.

‡ *Geology*, ii, 1906, 137–139.



pre-Cambrian rocks tends to show, in the writer's opinion, that there are at least three eras back of the Paleozoic. Therefore we have to consider what they are to be called. The oldest one so far revealed is the Archean, which the writer prefers to know as the Archeozoic. This takes in the oldest known rocks of the Canadian Shield, which are invaded by the Laurentian granites as these are now delimited. Lawson names this time the Ontarian period, or the Ontarian system of rocks. He well knows that his term is preoccupied by the Ontario division of the New York State Geologists, but concludes that the term was "still born". The term, however, has been alive ever since 1842, has always had the value of a period, and is occasionally used even now, as Lawson may see if he will look up the references cited below.\*

According to the rules of nomenclature, Lawson's Ontarian must be abandoned; from the writer's standpoint there is no need for it in any event, because the rocks included within it by Lawson represent an era of time and therefore the selection is to be made from Archean or Archeozoic. If, however, a term is needed as a division of Archeozoic time, then Miller and Knight's substitute, Loganian, should be accepted. This term need not be abandoned because of the Logan sill mentioned by Lawson, nor on account of the Logan sandstone proposed in 1869 for a Mississippian formation in Ohio; the latter is a formation name, while Loganian is a different word, has a much larger time value and is, furthermore, based on altogether different rocks.

Until recently the writer thought that Proterozoic was in good standing because of its use in Chamberlin and Salisbury's *Geology*. It appears, however, that Agnotozoic has priority, as the following clear definition will show. R. D. Irving in 1887 wrote:† "Some term is necessary to cover all of that great gap which lies between the base of the Cambrian and the summit of the Archean gneiss and schistose basement. This name cannot be one of the group rank, since it

\* *Ontario division*. Vanuxem, Geol. N. Y., Rep. Third Dist., 1842, 13, 15. Includes Shawangunk, Medina, Oneida, Clinton, Niagara, but not the highest Silurian.

— Mather, *Ibid.*, Rep. First Dist., 1843, 2, 353-365.

— Hall, *Ibid.*, Rep. Fourth Dist., 1843, 18.

— Emmons, *Agriculture N. Y.*, I, 1846, 141. Includes all Silurian formations.

*Ontarian or Ontaric*. Clarke and Schuchert, *Science*, Dec. 15, 1899, 875, 876.

— Weeks, *Bull.* 191, U. S. Geol. Surv., 1902, 306.

— Grabau, *Science*, Feb. 26, 1909, 356.

— Schuchert, *Bull. Geol. Soc. America*, xx, 532, 1910.

— Hartnagel, *Handbook* 19, N. Y. State Mus., 1912, 44, tables 1, 2.

— Clarke and Ruedemann, *Mem.* 14, N. Y. State Mus., 1912, 87.

† This *Journal*, (3) xxxiv, 372-373, 205, 1887.

must cover two or more groups itself; it must be of the same rank with Paleozoic, Mesozoic and Cenozoic."

"The new term should have some reference to the life-conditions of these early times." It "should then express the existence of this early life, and our present ignorance with regard to its nature." Many new terms and one old one were considered by Irving. Among these was Proterozoic, a term suggested by Mr. Emmons; while the name is "simple and made from a Greek word of not too uncommon use, [it] seemed to fail in covering the ground sufficiently. I have therefore been disposed to return to a term early proposed by Professor T. C. Chamberlin. . . . I would advocate therefore the use of the term Agnotozoic (unknown life), to cover all of the geological interval lying between the base of the Cambrian and the summit of the Archean crystallines."

"It is suggested therefore that the term Archean be used to cover only the pre-Huronian basement crystallines; that the Cambrian group remain as the basal member of the Paleozoic System, and that the new system name Agnotozoic . . . be used to cover, at least provisionally, such clastic groups as intervene between the Cambrian base and the Archean schists."

In another place\* Irving writes: "It seems, therefore, desirable that a new term should be introduced of equal classificatory rank with Paleozoic, indicating that these great Pre-Cambrian and Post-Archean series are zoic in character, and that they cannot, as yet at least, be admitted to the Paleozoic series proper. . . . I advocated the adoption of the term Agnotozoic, indicating at once the presence of life and its unknown character."

As stated beyond, Irving credits the first use of the term Agnotozoic to Chamberlin, but the latter writes,† "Although I have used the term in correspondence, conversation, discussion, and other informal ways for the past two years, more or less, I have nowhere formally proposed it in a scientific publication." Through first publication therefore the name belongs to Irving.

In this connection it is best also to give the conclusion of Van Hise‡, who says: "It is imperative that some term shall be available to cover the great mass of rocks between the Cambrian and Archean. Irving was the first to realize and urge the necessity for such a term and proposed for it Agnotozoic. This term implies the existence of life in this system, and the evidence upon this point is conclusive."

"The clastic rock masses below the *Olenellus* fauna are so enormous that the proposal to introduce a general term like

\* Seventh Ann. Rep. U. S. Geol. Surv., 1888, 453-454.

† This Journal, (3) xxxv, 254, 1888.

‡ Bull. 86, U. S. Geol. Surv., 1892, 491, 493.

Agnotozoic as the equivalent of Paleozoic, Mesozoic, Cenozoic, to cover this great group is a conservative one. Irving foresaw that the term would be objected to because sooner or later the life will become to a greater or less degree known, and he suggested as an alternative for Agnotozoic, Eparchean in contradistinction to Archean, which was reserved by him to cover the fundamental complex. As the character of the life of this group is already beginning to be known, it seems to me that the term Proterozoic, considered for the place by Irving, but rejected, is preferable to either Agnotozoic or Eparchean."

We, therefore, see that the name Proterozoic has not been defined and furthermore that it is synonymous with Agnotozoic, a term in good standing. If the pre-Cambrian rocks are separable into three eras, and it so appears to the writer, then it would seem that Agnotozoic should be applied to that interval between the Laurentian and Algonian granites. If, however, there are only two eras, it should refer to the second one, that following the Archeozoic. In any event, it should be applied to the greatest series of pre-Cambrian clastic rocks younger than the Archeozoic.

In regard to the term Algonkian, it appears to have no standing at all, since it is a substitute for and a synonym of Agnotozoic, as stated by Dana, and Chamberlin and Salisbury.\* The term Algonkian is usually ascribed to Walcott,† and while he did use it first in print, in 1889, he did not define it. It appears that Director Powell was the first to define Algonkian, as follows:‡ "This series of rocks [in the Lake Superior region] lies beneath the Cambrian and above the Archean, and represents a period of the earth's history during which lowly forms of life doubtless existed, but left few definite traces of their existence in the form of fossils. . . . The name 'Agnotozoic' was . . . designed as one of the greater terms of geologic classification, coördinate with Paleozoic, Mesozoic, and Cenozoic. In the geologic atlas of the United States such larger classification will not be employed, but the largest time unit recognized will be the period. At a recent conference of geologists . . . it was decided to make but one period of the Agnotozoic, and the name 'Algonkian' was chosen to designate that period. It is not proposed to cancel the name Agnotozoic, but to leave its use to students having occasion to employ terms of higher classification."

If there are three eras in pre-Cambrian time, and if the lowest is to be known as either Archean or Archeozoic, the

\* J. D. Dana, *Manual of Geology*, 4th ed., 1896, 445; T. C. Chamberlin and R. D. Salisbury, *Geology*, ii, 1906, 162.

† C. D. Walcott, *this Journal* (3), xxxvii, 383-384, 1889.

‡ J. W. Powell, *Tenth Ann. Rep., U. S. Geol. Surv.*, 1890, 20, 66; also see Van Hise, *Bull. 86, U. S. Geol. Surv.*, 1892, 493.

middle one as Agnotozoic, the youngest remains without a name. The writer will not embarrass the workers in this field of geologic endeavor by proposing a new name for it, but will remark that Proterozoic could be made use of for the youngest era. It will be remembered that Agnotozoic and Proterozoic are equal terms, but that the former has priority through definition, and that both were applied to all the rocks between the Archean and the Cambrian. Since it appears that this long time is divided by a revolution and at least one major unconformity, Lawson's "intergranitic" division could well be agreed upon as the Agnotozoic era and the "post-granitic" division as the Proterozoic era; or the terms could be reversed if they should be found to agree better with the definition of Irving and with the actual field relations.

From the quotations given it was seen that Eparehean was applied by Irving to the same time as Agnotozoic and that we may therefore write of *Archean and Eparehean time*. The latter term conflicts somewhat with Lawson's Eparehean Interval, but the latter has a wholly different meaning. Lawson is correct in insisting that we should, in our geological time-tables, take account of the "intervals," the erosion intervals when the geologic record is being removed, and emphasize at least the major ones by giving them distinct names. His method is to add as a prefix the Greek word *epi* (=upon or after) to the name of the time previous to the erosion interval, as Epareheozoic, Epalgomian, and Epiproterozoic. So long as we keep clearly in mind the fact that Irving's term is monomial—Eparehean—and that Lawson's is binomial—Eparehean Interval—there need be no misunderstandings. In any event, we must begin to name the breaks in the geologic succession.

In conclusion the writer offers the following amended terminology for pre-Cambrian time:

- Paleozoic Era. Basal series: Waucobian of Cambrian Period.
- { Epi-Proterozoic Interval.
- { Proterozoic Era.
- { Ep-Agnotozoic Interval and Algomian Revolution.
- { Agnotozoic Era.
- { Ep-Archeozoic Interval and Laurentian Revolution.
- { Archeozoic Era.
- The unrecoverable beginning of earth history.
- Cosmic history.



ART. XLIX.—*Plotting Crystal Zones on Paper*;  
by JOHN M. BLAKE. (Article 3.)

MANY years ago the writer became interested in the study of crystals, and took up the subject of the relative lengths of the crystal axes as one step that might lead toward a better understanding of crystal laws. Leading up to the present paper he wrote two others, one on zone measurement, which will be found in this Journal in 1866, and a second in May, 1915, this second paper relating to the growing of suspended crystals for the purpose of showing the proportional development of the planes on different members of an isomorphous group. To supplement this was mentioned the brief growing of polished crystal spheres of a salt with the object of bringing out the maximum number of planes belonging to the species, some of which planes may have been undeveloped by the first treatment.

The mystery connected with the irrational axial lengths appears not to have been solved up to this day, and that this mystery still exists must be laid in great part to the difficulty in making exact measurements. These measurements as a rule may vary ten minutes or more in angle, and under these conditions, it seemed useless to depend upon the ordinary methods of utilizing such measurements for the purpose of solving our problem.

The evident need of greater accuracy led the writer to adopt several methods for improving and facilitating work on crystals. In part, these methods were original. It was hoped that by attacking the problem in different ways, some progress might be made in the solution of the axial question. One of these methods is here described. The experimental trials with these methods have thus far been limited mostly to the orthorhombic and the oblique systems of crystals.

It appears to be generally accepted that the length of the axes of a crystal belonging to these systems cannot be expressed in whole numbers, or by a vulgar fraction. These axial lengths may be square roots multiplied by some rational quantity. The parameters or the lengths cut off on the axes by the planes of the crystal are generally considered to have the relation of simple rational numbers when compared with one another.

Variations in angle are mostly due to what are called vicinal planes. These planes and the related curved surfaces have been regarded as secondary and as superposed on the ideally perfect crystal. This, however, may be regarded as a tentative supposition. These vicinal planes and the related curved surfaces are doubtless subject to certain laws by themselves,

but their presence prevents exact measurement of the perfect crystal, while the want of exactness in determining the perfect crystal likewise interferes with the study of the laws of the vicinal planes.

A common practice has been to measure two or three of the angles between prominent crystal faces, and to calculate the angles between the remaining faces from these measurements. These angles have sometimes been measured from certain planes which, in a given species, are found to be habitually subject to variation, and in such a case all the calculated angles would be subject to error.

In carrying out this present method, the zones are plotted from the goniometer measurements, and by this means the system of equal spacing can be at once developed. We will thus have our work mapped out and the position of the axes indicated. The goniometer measurements should furnish a record of the character of the planes in regard to their reflections, and this record will guide us in our selection of the most suitable of the developed spaces from which to estimate the axial ratios. This plan will be found very simple and will require no resort to equations or formulas, while the results in very many instances may be made to exceed in accuracy those obtained by the present commonly used methods.

Epidote has been selected for the purpose of illustrating the present paper. DeCloiseau has collected data from many sources, and he gives elaborate tables of angles in his *Mineralogy* (1862). He mentions various groups of associated planes on specimens from widely scattered localities. It would seem that the search had been thorough for all possible planes. There remains the possibility that some planes of uncertain standing may have been included, and other errors are possible. The process of clarification and elimination usually adopted in making up crystal descriptions may at times destroy details which would be valuable in making future revisions.

*Plotting an Individual Zone.*—This can be done with ease from the complete serial goniometer readings, but more difficulty is encountered when we have to work from a published description, as in the case of epidote. In this published description, scattering measurements are given, and also the solid angles and not the angles between the normals; and besides, some of the planes are difficult to locate for the reason that we miss the sequence which complete zone measurements should furnish. Under the conditions as we proceed, we are constantly reminded that our method is leading us outside the regular traveled paths.

The work of DeCloiseau is valuable for its thoroughness. It does not, however, have all the elements we could desire for

our present purpose. Such omissions occur in many similar descriptions. These wanted elements can only be supplied by a further study of the original crystals.

We begin our zone plot by first drawing a circle, and we dot the position of the normals of the planes on this circle by means of a protractor. We now draw radii through these normal points. Then we take a scale of equal parts and rotate it in the plane of the paper, and at the same time move it out and in from the center until we have the equal spaces on the scale coinciding with the extended radii. The straight edge of the scale will now represent a tangent line, and the distance of this line from the center will be the radius, and one of the equal spaces so developed divided by the radius, will give a tangent ratio commonly known as the axial ratio. This ratio will be that between the two axes that are included in the selected zone.

Guided by our zone plot, we may reach further accuracy up to the limit we have secured by our goniometer measurements, by taking the values from a table of natural tangents. Planes which do not fall into the system of equal spacing as shown on the plot, will be open to the suspicion of being false entries, and so, also, complex fractional indices should be subject to inquiry. The latter may be due to the position of the selected axes, or to the adopted axial lengths. At the same time, fractional indices are not impossible. The half spaces that are shown on fig. 2 appear to belong to the general make up of the crystal. The positions of some of the fractional planes have been dotted, but the letters designating them have been omitted in fig. 2.

Fig. 1 gives the zone of epidote that contains the inclined axis. The horizontal line within the circle represents the plotted tangent line on which the equal spacing is developed by the intersection of the radii with the equally spaced scale. The inner circle gives the symbols from DeCloiseaux, and the outer circle, the symbols from Dana's Mineralogy. The radii are drawn on fig. 1 to show the equal spacing characteristic. These radii are also marked on the marginal ring in fig. 2.

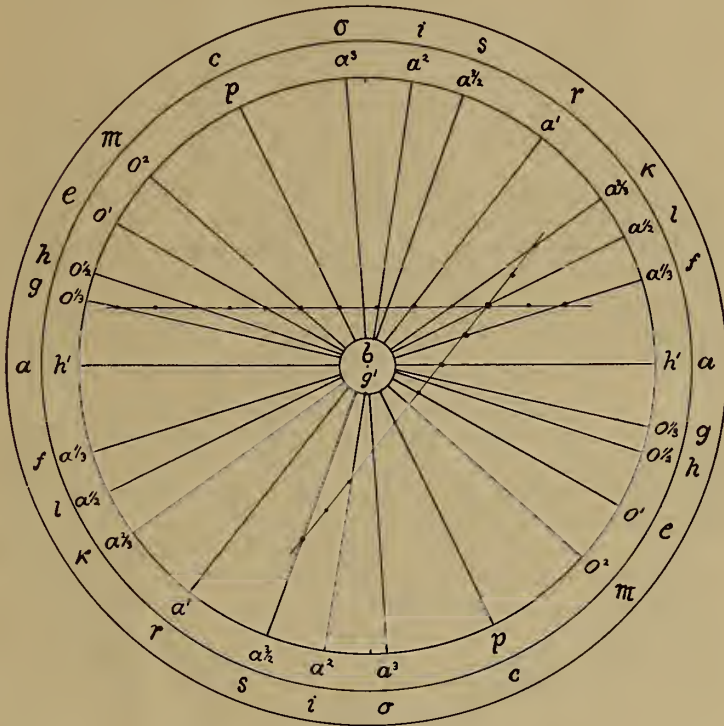
These two diagrams differ in this way. Fig. 1 shows the plane of the plotting paper with the radii drawn upon it. The plane in fig. 2 is parallel to this plane and is the plane *b* of Dana, and the plane *g'* of DeCloiseaux. On this plane *b*, is a projection of all the planes of the crystal whose normals pierce this plane at the points lettered on the diagram. The normals of the zone which is being plotted are parallel to this plane *b* and do not pierce it, and their position is marked on the margin near the circle in fig. 2.

DeCloiseaux's stereographic projection is much confused by

many circles. This is also a fault with certain more recent stereographic drawings. The gnomonic projection is given in fig. 2, and the general relation of the zone being plotted to the other planes on the crystal can be better traced out upon this projection. The direction of the two tangent lines shown in fig. 1 is indicated on fig. 2.

In the zone represented in fig. 1, the clarifying process has,

FIG. 1.



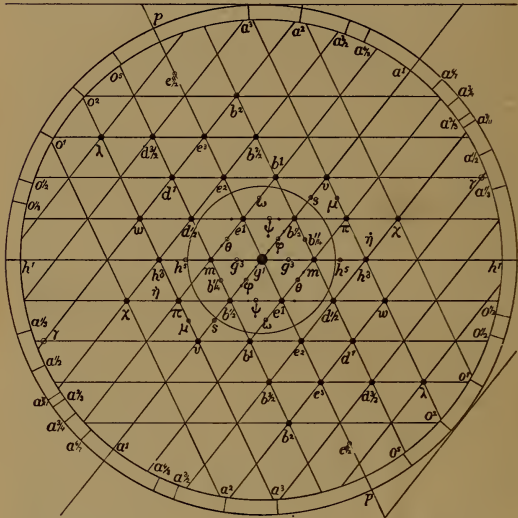
of course, been already applied, and we can only follow, and have to accept that which remains of the preliminary work, as we find it. If we could refer to an original measurement of this zone, we would have our choice in selecting the developed tangent spaces we regarded most suitable for estimating the axial ratio. In this selection we would discriminate against imperfect reflecting surfaces, and also spaces too far removed from the zero point, because far out from this point the tangent changes rapidly with small change of angle. We would take the average of the most suitable available spaces. In this



way we could have a control by using the tangent projection system which we would lose when relying on a few single measured angles.

Since the crystals of epidote came from different sources, and had different isomorphous compositions, as is indicated by the analyses, it would not seem impossible that there might

FIG. 2.



be different proportional developments of the prismatic planes in this zone in the different specimens, and that disconnected measurements of angles might not always be successful in bringing the prism in the correct position to make a correct reading of the planes to accord with the originally adopted position. This is suggested as a possible result of there being two well developed tangent equal-space positions, though the spacings slightly differ, and one set does not include all that are in the other set. In fact, this last mentioned point led to the suspicion that there was some duplication.

The diagram in which the tangent line is drawn horizontally (fig. 1) is the one which has been made the basis of the generally adopted system of symbols. The other tangent equal-space position as shown by the oblique tangent line in fig. 1 might, it would seem, with equal propriety have been selected as a basis of the symbols.

This condition of things being unusual, if it could be shown that it has been the cause of such a mistake leading to duplication, it would furnish an argument for making complete zone measurements as a preventive measure.

In attempting to account for these various features we will quote Miers' *Mineralogy* (1902). He says: "The law of rational indices is true if any three edges are taken as axes." We would expect, as a rule, that this would result in very complicated rational indices.

The two selected tangent positions in epidote carry out Miers' theory to an unexpected degree. If we take the two tangent sets and compare the developed spaces in each set by using a table of natural tangents, we find that the DeCloiseaux calculated angles carry out the equal spacing for each set with great exactness. That is, the same zone series of angles when started from different points, with certain exceptions as shown in fig. 1, develop the equal spacing shown on our scale of equal parts.

It should be understood that by construction as given in fig. 1, the two sets of spaces are there drawn as of equal length, being controlled by the scale spaces, but if we make the radius unity in each case as it should be for comparison, we find the axial ratios differ somewhat in the two sets because the spacings as revised become different.

When we have measured and plotted all the planes on the crystal in the way represented for epidote in fig. 2, our chances of selecting and averaging suitable spaces from the whole crystal system would become much more extended than would be the case when we deal with individual zones. We would then have command of the crystal planes as a whole, and a system of averaging the results of all the measurements could then be carried out.

Since the best selection, and the averaging of the results on the crystal as a whole will depend on individual judgment, the preservation of the data on which the completed work is based would appear to be a wise precaution for use in any future revision.

There is a method of obtaining the gnomonic or tangent plane projection which should be a subject for another article. This plotting of separate zones leads up to this tangent plane projection from the several zone plots.

When the exact laws on which crystal architecture is based are definitely determined, we may see a way to condense crystal descriptions and still retain the essentials. Some crystal descriptions retain the skeleton but lack the substance.

We have shown how, by means of a single circle goniometer and a few simple tools, we can get interesting results in studying crystals. There are means of facilitating this crystal work still further, and by their use we may follow this partly explored field with good prospects of securing valuable results. The act of partially measuring a large number of species, and storing away sometimes very bare details, does not advance the science in a way we could wish.

Only a comparatively few out of a very large number of subjects have been tested by these methods up to this time, but every species appears to present some interesting features of its own.

New Haven, Conn., Aug. 1916.

ART. L.—*A Graduated Sphere for the Solution of Problems in Crystal Optics*; by CHARLES H. WARREN.

AMONG the many useful adjuncts to work in crystal optics is the graduated, porcelain hemisphere devised by Nikitin.\* Inasmuch as it has been impossible, since the outbreak of the European war, to procure this piece of apparatus, it occurred to the writer to attempt the construction of a piece of apparatus to take its place. The result was so successful that it has seemed worth while to publish a brief description of this new sphere, with the idea, that others engaged in work in crystal optics, and desiring such a piece of apparatus, might find the description useful in constructing a similar one.

While the general design of the sphere was the writer's, the greatest credit is due to Mr. Carl Selig, mechanician for the Department of Physics at the Massachusetts Institute of Technology, for his skill and ingenuity in working out the details of the construction.

The material first used for the sphere was an eight-inch bowling-alley ball. This was found, however, to depart slightly from a true sphere, so that a hollow brass sphere was substituted. This was cast with a shell of about  $\frac{3}{8}$ " thickness, and the surface was then machined down on a lathe to a perfectly spherical shape.

The sphere was next given three coats of white enamel paint, and then polished with pumice and water. Vertical and horizontal meridians, ten degrees apart, were then ruled on the enamel surface, this being done on a lathe, using black drawing ink.

The graduated sphere was then mounted in a hollow metal cup about five inches in diameter, which was carefully lined with felt (see *a*, fig. 1). The cup was accurately centered with reference to the holding frame with its attached scales, and so mounted on a post as to allow the cup and sphere to be rotated rigidly in the horizontal plane. Three short, brass pins (see fig.) serve as handles to make the rotation easier.

The standard carrying the sphere is surmounted by three polished steel scales mounted on a brass backing  $\frac{1}{8}$ " thick. One is a horizontal scale (*b*, fig.) and two are vertical scales, ninety degrees apart. The three scales are graduated in degrees, every five-degree mark being accentuated, and every ten-degree graduation being numbered. One of the vertical scales (*c*, fig.) is mounted so that it can be rotated about a horizontal diameter through a range of  $125^\circ$ . To make such

\*Zeitschr. f. Kryst., xlvii, 381, 1910.



a movement possible, the back of the brass plate to which the scale is fastened, was bevelled down to a very thin edge, the bevel beginning about an inch and one-half back from the ends of the scale. The bevelled ends are fastened to a small brass block (see *d*, fig.) to which is attached a pin that rotates in another metal block which in turn is firmly attached to the horizontal scale (see *e*, fig.). The end of the vertical scale is set at  $0-180^\circ$  on the horizontal scale. A clip, fitting into a

FIG. 1.



FIG. 1. Photograph of an eight-inch graduated sphere for use in work on crystal optics. It is so mounted that it can be rotated rigidly about its vertical axis, or moved in any desired direction upon the cup in which it rests (*a*). It is provided with three graduated, metal scales, two vertical and one horizontal. One of the vertical scales, (*c*), can be rotated about the horizontal diameter through an angle of  $125^\circ$  by means of a mounting device shown by the letters *d* and *e*.

shallow notch in the second vertical scale (not shown in the figure) can be used to hold the first scale at the vertical center-point of the sphere, if desired. In practice, however, the writer has not found it necessary to use this clip.

As the sphere can be rotated rigidly about the vertical axis, or turned in any desired direction, and as one of the vertical scales can be moved through a large angle ( $125^\circ$ ), it will be evident that there is an entirely adequate freedom of movement to make possible the solution, with this sphere, of any of the usual problems met with in crystal optics where spherical projections are used. Great circles, polar to any point, can be located and drawn in with a pencil, and angular values may be determined with great rapidity and ease. For drawing small

circles, a pencil may be held firmly against one of the vertical scales while the sphere is rotated about its axis by means of the cup in which it rests, or a small metal clip could be easily made which would serve to hold the pencil instead of using the fingers.

The accuracy which can be attained with this sphere depends, of course, on the accuracy of its construction. A skillful mechanician should, however, be able, with a little pains, to construct it so accurately that the results obtained with it will be of the same order of accuracy as those which can be obtained by the use of stereographic plats, provided, of course, that the same amount of care is taken in drawing, and in reading the angles. It has seemed to the writer that this form of a graduated sphere has an advantage over that of Nikitin in being somewhat more flexible and easier to use. It has been found to be invaluable for purposes of rapid demonstration in the laboratory.

The cost of the sphere built for the writer was about forty dollars (labor and materials). The standard, however, was taken from another piece of apparatus, so that the probable cost of the sphere and mountings would be in the neighborhood of fifty dollars.

Department of Geology, Massachusetts  
Institute of Technology,  
Cambridge, Mass., Aug. 1916.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. *The Separation of Lithium from Potassium and Sodium.*—SAMUEL PALKIN has modified the old method of Rammelsberg, which consisted in treating the dry chlorides with a mixture of anhydrous alcohol and ether in order to dissolve the lithium chloride. This method is known to be unsatisfactory, both on account of the tendency of lithium chloride to be partially converted into the insoluble carbonate when dried in the air, and also on account of the occlusion of some of the lithium chloride by the insoluble chlorides of sodium and potassium. The present method avoids these difficulties by precipitating the greater part of the sodium and potassium chlorides in the first place by adding alcohol slowly and then ether to a slightly acid, very concentrated aqueous solution of the chlorides, then after filtration on a Gooch crucible, evaporating the filtrate to dryness, taking up the residue with absolute alcohol containing a drop of hydrochloric acid, adding ether until the small amounts of sodium and potassium chlorides are completely precipitated, and collecting the precipitate with the original one. One volume of alcohol to about 5 volumes of ether is the mixture recommended for the precipitations and for washing. From the results of test analyses it appears that the method gives excellent results. However, it does not seem probable that the method will supersede in general analytical practice the more convenient and very satisfactory method of Gooch, unless, perhaps, there may be some who prefer the fumes of ether to those of amyl alcohol.—*Jour. Amer. Chem. Soc.*, xxxviii, 2326. H. L. W.

2. *The Action of Light upon Iodine and Iodide of Starch.*—It is stated by M. H. BORDIER that not only does the well-known blue iodide of starch form colloidal solutions, but that the solution of iodine itself in water is also colloidal, showing ultra-microscopic particles. He has found that sunlight has an action upon very dilute solutions of these two substances. For instance, when 10 drops of 10 per cent tincture of iodine are added to 1000<sup>cc</sup> of water with agitation after the fall of each drop, a pale yellow solution containing about 18<sup>mg</sup> of iodine is obtained. If a little starch paste is then added a blue color is obtained and this disappears after several hours of exposure to sunlight. Moreover if the iodine solution is exposed to sunlight first and the starch paste is added afterwards, no blue color is produced. The author's explanation is that the iodine simply goes into the ionic condition under the influence of the light, but this does not appear to be a very satisfactory explanation. The reaction was applied to a test of the colored glasses used for bottles to protect substances from the action of light, and it was found that the yellow glass most extensively employed for this purpose gives no

protection at all from the action of sunlight upon the iodide of starch. Further experiments showed that the action of X-rays upon this substance gave the same effect as sunlight.—*Comptes Rendus*, clxiii, 205, 293.

H. I. W.

3. *The Crystallization of Calcium Tartrate*.—Few salts have been more frequently prepared than calcium tartrate, on account of its employment for the recognition of the acid, and it is surprising to find that little is known of its behavior when crystallizing from aqueous solution. It has been observed by F. D. CHATTAWAY, of Oxford University, that when equal volumes of 0.2 *N* solutions of calcium chloride and potassium sodium tartrate are mixed at ordinary temperature the liquid remains clear for a short time, then small tufts of needle-shaped crystals make their appearance and rapidly grow until in a few minutes the whole is filled with such tufts, which finally interlace, producing a felted mass of crystals to such an extent that the vessel may be inverted without loss of mother-liquor. This salt is the hexahydrate,  $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O}$ . This form is unstable, and after a short time at ordinary temperature small orthorhombic crystals of the tetrahydrate,  $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , make their appearance and grow rapidly, settling to the bottom of the liquid, while the needle-shaped crystals dissolve and disappear. The change takes place more rapidly when the mass is stirred or shaken vigorously, and it is still more rapid upon heating. This phenomenon should furnish a striking lecture experiment.—*Jour. Amer. Chem. Soc.*, xxxviii, 2519.

H. L. W.

4. *The Basic Copper Sulphates*.—S. W. YOUNG and A. E. STEARN, observing that the results of the analyses of the mineral brochantite, a basic copper sulphate, vary widely, and that a very large number of artificial products have been described which vary between the limits  $10\text{CuO} \cdot \text{SO}_3$  and  $2\text{CuO} \cdot \text{SO}_3$ , with varying amounts of water, have made an investigation upon the subject. By treating finely divided copper oxide in closed bottles in a thermostat they obtained some products which appeared to be crystalline, but could not be shown to be homogeneous by microscopic examination. No definite chemical formula was indicated except perhaps in the cases where two molecules of copper oxide were used with one of copper sulphate, and where practically all of the copper sulphate was removed from the solution, a composition corresponding nearly to the formula  $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$  was found. The authors believe that no more basic salt than this can be formed under the conditions of their experiments, which were made at 25°, 37.5° and 50° with the same results at all the temperatures. In the cases where less than 2 molecules of copper oxide were used for one of copper sulphate there was only a moderate but gradual change in composition, reaching about  $2.3 \text{CuO} \cdot \text{SO}_3 \cdot 2.4 \text{H}_2\text{O}$  where  $\frac{1}{2}$  molecule of copper oxide was used. Although the authors do not suggest it, it appears probable that these are mixtures of two basic sulphates and it is to be hoped that they will continue their



investigation using still greater proportions and more concentrated solutions of copper sulphate at similar temperatures. It is to be regretted that the authors did not fully analyze the basic sulphates that they prepared by simply heating aqueous solutions of copper sulphate of widely varying concentration. Their results, 66.34, 67.00 and 68.21 per cent of  $\text{CuO}$ , although they regard the composition as "highly influenced by the concentration of the solutions," show fairly good agreement for a compound that cannot be recrystallized, and the average corresponds closely to the formula  $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ , which they have suggested for another product.—*Jour. Amer. Chem. Soc.*, xxxviii, 1947.

H. L. W.

5. *The Determination of Chlorides in Presence of Thiocyanates.*—It was shown several years ago by Rosanoff and Hill that thiocyanates can be destroyed by suitable treatment with nitric acid, leaving chlorides unattacked in a condition suitable for determination by Volhard's volumetric method. F. W. BRUCKMILLER has now shown that this treatment will permit the determination of chlorine by the use of silver nitrate and chromate indicator, particularly in water analysis. His process is as follows: The solution containing chlorides and thiocyanates is heated to boiling and concentrated nitric acid added drop by drop, the amount depending upon the thiocyanate present. If present in large quantities the nitric acid is added until the solution turns light brown. For small quantities 2 to 3<sup>cc</sup> are sufficient. The solution is boiled for 15 minutes and filtered if sulphur has separated, and after cooling is neutralized with normal  $\text{HNaCO}_3$  solution using methyl orange as indicator. A little more than enough for neutralization is added, then after adding the chromate indicator silver nitrate solution is added to the usual end point. It was shown by experiment that there was no loss of chlorine by boiling solutions containing .015<sup>g</sup> of sodium chloride after adding from 1 to 5<sup>cc</sup> of nitric acid in volumes varying from 100 down to 25<sup>cc</sup>. It was shown further that hydrocyanic acid was so far removed in the operation as not to interfere with the process, and that the titration in the presence of the methyl orange was accurate.—*Jour. Amer. Chem. Soc.*, xxxviii, 1953.

H. L. W.

6. *A New Method of Determining Refractive Indices.*—Since the usual methods for making accurate determinations of refractive indices require special preparation (prismatic form) of the specimen to be tested and since it sometimes becomes necessary to investigate figured objects (lenses) or fragments of irregular shape which may not be cut, the new method of general applicability recently worked out and tested by R. W. CHESHIRE merits attention. It is based on the "Schlierenmethode" of Töpler.

The following objects are arranged along a straight line. First a source of monochromatic light. Then an opaque screen with a vertical straight edge. An achromatic lens (focal length 125<sup>cm</sup>,

aperture 8<sup>cm</sup>) forms a real image of this screen in front of the observing telescope in such a manner as to cover one-half of the full aperture (3.5<sup>cm</sup>) of the objective. The distance between the lens and telescope is about 5 meters, and the magnifying power of the latter is  $\times 24$ . Not far from the emergence surface of the first lens a specially designed cell is mounted on the prism of a Pulfrich refractometer. The cell contains the specimen of glass to be studied and a certain solution (*vide infra*). A second opaque screen with a vertical straight edge is mounted in front of the observing telescope so that its plane coincides with the plane of the image of the first screen. The planes of both screens are at right angles to the common optic axis of the centered system of lenses. The second screen is provided with a rack and pinion combination which enables the observer to impart a slow horizontal motion to the edge and so cause it to gradually eclipse the telescope objective.

The immersion fluid finally selected was an aqueous solution of mercury potassium iodide, commonly called Thoulet's solution. The index of refraction for D light of this liquid can be decreased continuously from 1.72 to 1.33 by increasing the proportion of water. The solution possesses two advantageous properties: (a) the excess of water can be driven off by heating, consequently the double salt can be used repeatedly, and (b) it does not attack the Canada balsam employed in cementing together the walls of the cell. On the other hand, the mercury compound exercises marked absorption at the more refrangible end of the visible spectrum. The curve given in the paper shows that the percentage transmissions for the four lines, C, D, F, and G', are approximately 70, 63, 16, and 2, respectively. Although the temperature coefficient of refraction of Thoulet's solution is very high ( $-0.0006$  per degree C.) the author states that no difficulty is experienced on this account.

The experimental procedure consists essentially in moving the screen next the observing telescope slowly across the beam of light and noting whether the field of view darkens uniformly. When the solid specimen in the cell has a refractive index different from that of the surrounding liquid the portion of the field of view corresponding to the image of the object under investigation will not darken simultaneously with the rest of the field. By varying the concentration of the liquid a match or balance may be quickly obtained and then the index of the liquid (and hence of the specimen) is determined at once with the refractometer. The accuracy of which this method seems to be susceptible is about two units in the fifth decimal place. For example, the index for D light for a certain glass prism, having a refracting angle of  $10^\circ$ , was found to be 1.51492 by the new method and 1.51490 by direct use of the refractometer.—*Phil. Mag.*, xxxii, p. 409, Oct., 1916.

H. S. U.

7. *Fluorescent Vapors and their Magneto-optic Properties.*—The theoretical aspect of the beautiful experiments by R. W.

Wood on resonance spectra has been successfully attacked by L. SILBERSTEIN. Since the paper requires a fairly large amount of elementary mathematics for the adequate exposition of the subject, the following non-analytic outline is, in the very nature of the case, only suggestive and highly fragmentary.

A resonator obeying the equation  $\ddot{x} + k\dot{x} + N^2x = 0$  is called a *Hookean* resonator by the author for the obvious reason that the restitutive force is assumed to conform to Hooke's law (force  $= N^2x/m$ ). When such an oscillator is acted upon by an external force of frequency  $n$  it will execute vibrations of the same frequency  $n$  but will not perform oscillations of any other frequency. Consequently this simple type of resonator cannot be responsible for all the lines of one series in Wood's resonance spectrum. If, on the other hand, the term  $N^2x$  be replaced by a non-linear function of  $x$ , an impressed force of frequency  $N$  will stimulate oscillations of frequency  $N$  together with an infinite number of other frequencies. It follows at once that the excitation and emission of fluorescent line spectra may be described mathematically by writing either  $\ddot{x} + k\dot{x} + N^2x = c_0e^{iNt} + c_1e^{in_1t} + c_2e^{in_2t} + \dots$ , or  $\ddot{x} + k\dot{x} + N^2x + f(x) = c_0e^{iNt}$ . The first equation is tantamount to postulating that the atoms of the radiating vapor behave as if each contained a Hookean resonator under the simultaneous action of forces of all the frequencies  $n_0 = N, n_1, n_2, n_3, \dots$  etc. The second equation is an expression of the hypothesis that each atom contains an appropriate non-Hookean resonator acted upon by  $c_0e^{iNt}/m$  only.  $f(x)$  is some non-linear function of the displacement. The equivalence of the two methods of treatment is manifest, for the non-Hookean resonator will be the "appropriate" one when, and only when, the supplementary term  $-f(x)$  ultimately reduces to  $c_1e^{in_1t} + c_2e^{in_2t} + \dots$ . The first equation is best adapted to the study of the properties of *each line of the spectrum separately*, whereas the second form is required only when we desire to make a guess concerning the law of succession of the lines of the spectrum. So much for the underlying principles of the mathematical investigation.

By making use of the second equation and assuming the form  $ax^p$  for  $f(x)$  Silberstein deduces the solution  $n_j = N - j(1-p)N$ ,  $j = 0, 1, 2, 3, \dots$ , whence  $\delta n = (1-p)N$ . This means that the lines of the resonance spectrum succeed one another at *constant frequency-intervals*. When Wood's wave-lengths for iodine fluorescence are transformed into numbers proportional to their frequencies, it is found that the intervals are constant within the given limits of experimental error. Hence the theory accords with the facts. The values of  $p$  for three different series are 0.9889, 0.9882, and 0.9881 corresponding respectively to  $\delta n = 202.53, 203.61, \text{ and } 205.38$ .

Throughout the rest of the paper the first equation is alone employed. The author deduces the following results which are especially important for the reasons that none is in contradiction with known facts, new phenomena are predicted, and unexplored

fields of investigation are suggested. When the fluorescent vapor is placed in a uniform magnetic field and is excited by plane polarized light there can be no ordinary Zeeman effect. The fluorescent light will be elliptically polarized in the magnetic field and plane polarized in the absence of this field. The eccentricity and the orientation of the major-axis of the ellipses will vary from line to line of the resonance spectrum. In particular, the fundamental line will remain plane polarized while the plane of polarization will be rotated around the magnetic field through a formulated angle. The theory shows very clearly that the intensity of the fundamental fluorescent light will decrease and tend toward zero as the strength of the magnetic field is augmented. This phenomenon has been observed and studied by Wood and Riband. In these experiments the angle of rotation is predicted to be  $71^{\circ}565$  for a field of 30,000 gauss. The possibility of rotation was not suspected at the time of the experimental research and hence numerical data for testing this deduction from the general theory are wanting. For further details reference must be made to the original article.—*Phil. Mag.*, xxxii, p. 265, Sept., 1916.

H. S. U.

8. *Problems in Physics for Technical Schools, Colleges, and Universities*; by WILLIAM D. HENDERSON. Pp. viii, 205, with 167 figures. New York, 1916 (McGraw-Hill Book Co.).—These exercises are intended to supplement the usual one year's course in general physics and they have been thoroughly tested by the author who causes his students to devote one class-hour a week wholly to the solution of practical problems bearing upon the fundamental principles treated in the lecture room and laboratory. The problems are numerous (1025), they cover the entire field of elementary physics, and most of them are original. Each set of questions is preceded by a brief statement of the definitions and fundamental principles involved and a comparatively large number of illustrative examples are worked out in the text. The data involved are modern and conform to the recommendations and practice of the United States Bureau of Standards. The index is preceded by an appendix containing thirty tables of formulæ and physical constants. Answers to the unsolved problems are not given.

It is difficult for a reviewer, who has not tested the book in the class room, to form a just opinion of the merits of the text. The following impressions, however, acquired by the present writer after having looked over the pages very thoughtfully, may merit recording. With few exceptions the remarks introductory to each group of problems seem very lucid, concise, and accurate. The general plan of the text also seems excellent. With regard to minor details, on the other hand, there is room for revision. For example, the distinction between the scientific meaning of the terms "fluid" and "liquid" is not made clear. In the tables no attention has been paid to percentage accuracy. Thus we find (on page 193): "Pressure of one atmosphere = 76 cm. mercury = 30 in. mercury = . . . = 1,012,634 dynes per  $\text{cm}^2$  = . . ."



Table IX, on coefficients of linear expansion, contains no explicit indication of the temperature degree involved. The term *bougie décimale* is consistently written "Bourgie decimale." Finally, the number of typographical errors is quite appreciable.

H. S. U.

9. *General Physics. Third Edition*; by HENRY CREW. Pp. xiv, 617; 441 figures. New York, 1916 (The Macmillan Co.).—A careful comparison of the latest edition of this work with the first (see vol. xxvi, page 241) shows that the text has been very carefully revised. The principal changes are: (i) a more concrete and historical presentation of dynamics with greater prominence to statics; (ii) a simpler and more unified treatment of magnetism and electricity, secured by use of the electron theory; (iii) a new chapter on electromagnetism, in which the entire discussion is based upon the two great discoveries of Oersted and Faraday. The usefulness of the book is enhanced by numerous minor additions such as sections on liquid air, diamagnetism, atmospheric electricity, photometry, Gaede's rotary pump, the Gnome gasoline engine, etc. We also note that many new references to text-books have been incorporated at the ends of the chapters and that the problems are now numbered consecutively from 1 to 456. As usual, the author's style is clear and interesting, and the text as a whole is polished and elegant.

H. S. U.

## II. GEOLOGY AND MINERALOGY.

1. *The Coal Measures Amphibia of North America*; by ROY LEE MOODIE. Carnegie Institution of Washington, Publication No. 238, 1916, x + 222 pp., 26 pls., 43 text figs.—This excellent monograph does great credit to its author and to the Carnegie Institution. It brings together all that is known of Paleozoic amphibians, and describes in detail 88 species in 49 genera found in the Coal Measures of North America. Linton, Ohio, has yielded 50 species; Mazon Creek, Illinois, 10; and the Joggins coal field of Nova Scotia, 18. The author informs us that these stegocephalians of the Coal Measures are highly differentiated and specialized animals of aquatic, terrestrial, and arboreal habitats. Specialization is seen in loss of limbs, ribs, and ventral armature, and in the acquirement of claws, running legs, and a long, expanded propelling tail. In size they range from an inch to several feet. "No known characters of these animals tend to ally them directly with any known group of fishes . . . indicating a long antecedent history for the amphibian group." Their origin is probably even pre-Devonian. On the other hand, even the modern tailless forms seem to be related to *Pelion lyelli*, which may have been a jumping animal. Most of the forms belong to the order Miosauria, "lizard-like animals with a well-developed ventral scutellation"; they are

all small forms and the stock died out early in the Permian. Far more rare are the branchiosaurians, also small animals, which are essentially naked, and are water inhabitants; they are "without doubt, ancestral to the modern Candata." The relatively large Temnospondylia are very rare in America, and of the Stereospondylia, common in the Triassic, there appear to be none present.

c. s.

2. *Papers from the Geological Department, Glasgow University*, Volume II, 1915.—There are here fifteen papers reprinted from various scientific journals appearing during 1915. The following three papers by Professor Gregory are of general interest and should be read by American geologists: (1) Suess's Classification of Eurasian Mountains, (2) Deserts, and (3) The Relative Distribution of Fjords and Volcanoes.

c. s.

3. *West Virginia Geological Survey*, I. C. WHITE, State Geologist. *Raleigh County and the Western Portions of Mercer and Summers Counties*; by CHARLES E. KREBS, aided by D. D. TREETS, JR. Pp. xx, 778; 31 pls., 10 figs., and a separate case of geologic and topographic maps of the entire area in two sheets.—This is another of the important detailed County reports issued by the West Virginia Survey. Raleigh County is very rich in coal and is believed to contain the greatest thickness of coal beds in one mountain (1750 ft. in height, near Dorothy) in the Appalachian field. The area described embraces the great New River and Pocahontas smokeless coal districts, while western Raleigh holds immense deposits of Kanawha Splint and gas coals.

Part IV of the volume contains a paper (pp. 663 to 734 and plate xxxi) by WM. ARMSTRONG PRICE on the paleontology of Raleigh, Wyoming, McDowell and adjacent counties. The price of the Report with case of maps, including soil report and map, is \$2.50. Extra copies of geologic maps, 75 cents each, and of topographic maps, 50 cents each.

Included with this Report is a folded plate, 40x6 inches, showing the names, number and intervals separating the Coal Beds of West Virginia, and extending from the top of the Dunkard Series to the base of the Pottsville Series, on the scale of 1 inch to 200 feet. This has been compiled and revised to June 2, 1916, by Ray V. Hennen, Assistant Geologist. Price, 25 cents.

4. *Papers on Coal and the Coal Industry*.—Illinois Geological Survey. Engineering Experiment Station University of Illinois. U. S. Bureau of Mines. Bulletin 3. *Chemical Study of Illinois Coals*; by S. W. PARR. Pp. 86; 1 pl., 10 figs., 28 tables. Bulletin 15. *Coal Resources of District VI*; by GILBERT H. CADY: Field work by R. D. WHITE, FRED. H. KAY, and others. Pp. 94; 7 pls., 25 figs., 13 tables.

Virginia Geological Survey. THOMAS L. WATSON, Director. Bulletin No. XII. *The Coal Resources of the Clintwood and Bucu Quadrangles, Virginia*; by HENRY HINDS. Pp. vii, 206; 11 pls., 21 figs.

Canada, Department of Mines, Mines Branch; EUGENE

HAANEL, Director. An investigation of the Coals of Canada, with reference to their Economic Qualities. Extra Volume. Weathering of Coal; by J. B. PORTER, assisted by S. L. BRUNTON, and others. Pp. xii, 194, 6 pls., 65 figs. Ottawa, 1915.

The Coal Industry of Colorado; by RALPH W. SHUMWAY. Colorado School of Mines Quarterly, vol. ii, No. 2, pp. 26-32.

"The Cost of Coal" is the title of an important paper of especial interest at the present time by George Otis Smith and C. E. Leshar of the U. S. Geological Survey, read before the American Mining Congress at Chicago on November 14.

5. *Notes on Radiolarian Cherts in Oregon: a Correction*; by WARREN D. SMITH (communicated).—In the recent notes on "Radiolarian Cherts," published on pp. 299, 300 of the October number, *Cretaceous* in the first paragraph should read *Jura Trias* (?). Dr. Diller submitted his specimens to Dr. Hinde in the British Museum, who recognized imperfect casts of radiolaria, and, as I understand, it was he who assigned these rocks to that age. I believe that I found some more determinable specimens, and my information merely confirms and amplifies that published by Dr. Diller.

6. *New Mineral names*; by W. E. FORD (communicated—continued from pp. 566-570, June, 1916).—

**Creedite.** E. S. Larsen and R. C. Wells, Nat. Ac. Sc., ii, 360, 1916.—In grains and poorly developed prismatic crystals. Probably monoclinic. Nearly colorless.  $H. = 3.5$ .  $G. = 2.73$ . Perfect cleavage parallel to the elongation of the crystals and bisecting the obtuse angle of the prism. Cleavage fragments show parallel extinction with the emergence of an optical axis nearly normal to the cleavage plane. Sections cut in the prismatic zone at right angles to the cleavage show extinction angles of  $41^\circ$  and the emergence of the bisectrix  $Y$ , with irregular twinning. Refractive indices,  $\alpha = 1.461$ ,  $\beta = 1.478$ ,  $\gamma = 1.485$ ;  $2V_{Na}(\text{meas.}) = 64^\circ 22'$ . Comp.— $\text{CaSO}_4 \cdot 2\text{CaF}_2 \cdot 2\text{Al}(\text{F.OH})_3 \cdot 2\text{H}_2\text{O}$ . Fusible with intumescence to a white enamel, giving the calcium flame. Slowly but completely soluble in acids. Found at a fluorite-barite vein near Wagon Wheel Gap, Colorado. Intimately associated with a dull white kaolinite and barite. Named from the Creed Quadrangle in which it is found.

**Hibbenite.** A. H. Phillips, this Journal, xlii, 276, 1916.—Orthorhombic. Tabular parallel to  $a(100)$ .  $a:b:c = 0.589:1:0.488$ . Forms present,  $a(100)$ ,  $b(010)$ ,  $s(120)$ ,  $p(111)$ ,  $d(101)$ . Cleavage parallel to the three pinacoids.  $G. = 3.21$ .  $H. = 3.75$ . Birefringence weak. Optically —. Comp.— $2\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ . Easily fusible. Decrepitates in the closed tube, yielding water. Found with spencerite at Hudson Bay Mine at Salmo, B. C. Named after Pres. Hibben of Princeton.

**Leifite.** O. B. Böggild, (Medd. om Grönland, li, 429, 1915). A silicate from Greenland with the composition  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{22} \cdot 2\text{NaF}$ . A complete description of this mineral has not as yet been available.

**Margarosanite.** W. E. Ford and W. M. Bradley, this Journal, xlii, 159, 1916.—Probably triclinic. In rhombic-shaped cleavage plates, with angles of  $102^\circ$  and  $78^\circ$ . Extinction angles on cleavage plates of  $44^\circ$ , and  $54^\circ$  with the outlines of plates (secondary cleavage directions). Colorless and transparent with a pearly luster.  $H. = 2.5-3$ .  $G. = 3.99$ . Comp.— $Pb(Ca, Mn)_2(SiO_3)_3$ . Fuses easily and quietly in the reducing flame to an opaque glass. Found at Franklin, N. J. Named from Greek words meaning, *pearly* and *tabular*.

**Spencerite.** A. H. Phillips, this Journal, xlii, 275, 1916.—In radiating and reticulated crystals. Color white with pearly luster on a good cleavage.  $G. = 3.12$ .  $H. = 2.7$ . Comp.— $Zn_3(PO_4)_2 \cdot Zn(OH)_2 \cdot 3H_2O$ . Decrepitates in the closed tube, yielding water. Found at the Hudson Bay Mine, Salmo, B. C.

**Sulphatic Cancrinite.** E. S. Larsen and George Steiger, this Journal, xlii, 332, 1916.—A cancrinite with nearly one-half the  $CO_2$  replaced by  $SO_4$ . Differs from cancrinite by having lower refractive indices and birefringence.  $\omega = 1.509$ ,  $\epsilon = 1.500$ . Found in an altered rock (uncompahgrite) on Beaver Creek, a branch of Cebolla Creek, Gunnison Co., Col.

### III MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Centennial Celebration of the United States Coast and Geodetic Survey*; E. LESTER JONES, Superintendent. April 5 and 6, 1916. Washington, D. C. Pp. 196; 45 figs.—The one hundredth anniversary of the United States Coast Survey was celebrated in Washington on April 5th and 6th. The event was a memorable one and it is well that the occasion should be permanently commemorated in the present volume. It is remarkable that, so early in the history of this country, those in charge of the Government should have had the foresight to lay the foundations for an organization so essential to the welfare of the nation, so useful in its different lines of work, and so broad and thorough in scope.

There were three public sessions on the days noted, presided over by the Superintendent, also a banquet at which some two hundred and fifty gentlemen were present. The addresses are given in this volume in full, and in addition to those from the President and the Secretary of Commerce, others also of general interest were delivered, notably by members of allied scientific institutions connected with the Government, which have profited by the work of the Survey. An interesting series of portraits of the gentlemen who have served as superintendents, from the time of Dr. Ferdinand Rudolf Hassler in 1816, is likewise included.

The work which has been and is being accomplished was presented to the eye by the extensive exhibit in the National Museum. This displayed "the various types of instruments used



in the operations of the Survey, ranging from historic examples of apparatus designed and used by Hassler and Bache to the latest forms employed at the present day. Notable features were astronomical, geodetic, tidal, topographic, and hydrographic apparatus which owe their origin to the Survey and were constructed in its workshops. The manifold experiences of the field parties of the Bureau under the various conditions encountered in the field of operations, extending from the Arctic Ocean to the southern limits of the Philippine Archipelago, were illustrated by prints from photographs made in the field. The progress of the developments that has marked the improvements in surveying results between 1816 and 1916 was graphically shown by comparison of field sheets and by published charts from various periods."

2. *National Academy of Sciences.*—The autumn meeting of the Academy was held on November 13, 14, and 15, in the new buildings of the Massachusetts Institute of Technology in Cambridge. The meeting was presided over by the President, Dr. William H. Welch, and was largely attended. Besides the many papers presented (in part by title only) there were some sixty interesting exhibits open on Monday afternoon and evening, each personally explained by the exhibitor. The members of the Academy were entertained on Monday evening by President and Mrs. MacLaurin of the Massachusetts Institute of Technology and President and Mrs. Lowell of Harvard University. The general Academy dinner was held on Tuesday evening, and on Wednesday evening the American Academy of Arts and Sciences held a special meeting, when the Rumford medal was presented to Charles G. Abbot, for his researches on Solar Radiation.

The titles of papers presented are as follows:

RAYMOND PEARL: Some effects of the continued administration of alcohol to the domestic fowl, with special reference to the progeny.

EDWARD S. MORSE: Protoconch of *Solemya*.

ALFRED G. MAYER: Further studies of nerve conduction.

E. G. CONKLIN: The share of egg and sperm in heredity.

JACQUES LOEB: Diffusion and secretion.

L. B. MENDEL and S. E. JORDAN: Some interrelations between diet, growth, and the chemical composition of the body.

ALESSANDRO FABBRI: Micro-cinematographs of marine and freshwater organisms.

HENRY L. ABBOT: Hydrology of the Isthmus of Panama.

JOHN M. CLARKE: The strand and the undertow.

W. LINDGREN: Notes on the deposition of quartz, chalcedony, and opal.

W. M. DAVIS: Sublacustrine glacial erosion in Montana.

EDWIN H. HALL: Electric conduction in metals.

EDWARD B. ROSA: The silver voltameter as an international standard.

R. W. WOOD: One-dimensional gases and the reflection of molecules. Series in resonance spectra.

ELIHU THOMSON: Inferences concerning auroras.

A. A. MICHELSON: Report of progress in experiments for measuring the rigidity of the earth. The laws of elastico-viscous flow.

C. G. ABBOT: On the preservation of knowledge.

- FRANZ BOAS: Further evidence regarding the instability of human types.  
 ROSS G. HARRISON: Transplantation of limbs.  
 CHAS. B. DAVENPORT: Heredity of stature.  
 F. R. MOULTON: On analytic functions of infinitely many variables.  
 HENRY S. WHITE, F. N. COLE and LOUISE D. CUMMINGS: Enumeration of all triad systems on fifteen elements.  
 WILLIAM E. STORY: Some variable 3-term scales of relation.  
 CHARLES P. OLIVIER: The meteor system of Pons-Winnecke's comet. 139 parabolic orbits of meteor streams.  
 A. G. WEBSTER: Practical tests of a new phonotrope.  
 EDW. L. NICHOLS: New data on the phosphorescence of certain sulphides.  
 G. P. BAXTER and H. W. STARKWEATHER: A revision of the atomic weight of tin.  
 T. W. RICHARDS and H. S. DAVIS: Improvements in calorimetric combustion.  
 T. W. RICHARDS and C. WADSWORTH, 3d: Further study of the atomic weight of lead of radioactive origin.  
 GILBERT N. LEWIS: Chemical Affinity.  
 WM. TRELEASE: The American oaks.  
 H. S. JENNINGS: The numerical results of diverse systems of breeding, with relation to two pairs of factors, linked or independent.  
 W. R. MILES: Some psycho-physiological processes as affected by alcohol.  
 WALTER B. CANNON: Oscillatory variations in the contraction of rhythmically stimulated muscles.  
 WM. H. DALL: On some anomalies in the distribution of Pacific coast mollusca.  
 G. H. PARKER: The responses of hydroids to gravity.  
 W. M. WHEELER: The phylogenetic development of subapterous and apterous castes in the Formicidæ.  
 W. J. CROZIER: On cell penetration by acids: the chloracetic acids. On the immunity coloration of some nudibranches.  
 HOVEL JORDAN: The rheotropism of the marine fish known as "hamlet" or "grouper" (*Epenephalus striatus*).  
 A. C. WALTON: The occurrence of *Ascaris triquetra*, Schrank, in dogs.

The sessions of Monday evening and Tuesday afternoon were devoted to a meeting of the National Research Council with the National Academy. The following addresses were made:

- W. H. WELCH: The formation of the National Research Council at the request of the President of the United States.  
 S. W. STRATTON: Target practice in the Navy and some of the research problems involved; illustrated with moving pictures.  
 GEORGE E. HALE, Chairman of the National Research Council. The work of the National Research Council; Recent observations of organized science in England and France.  
 LIEUT. COL. GEORGE O. SQUIER: Scientific research for national defense, as illustrated by the problems of aviation.  
 ARTHUR A. NOYES: The nitrogen problem in war and in agriculture.

### 3. *The American Association for the Advancement of Science.*

—The American Association for the Advancement of Science, and more than thirty national scientific societies affiliated with it, will meet in New York City during the last week of December, 1916, under the auspices of Columbia University, New York University, the College of the City of New York, the American Museum of Natural History and the other scientific and educational institutions of the city. Dr. Charles R. Van Hise, president of the University of Wisconsin, will preside; the address of the retiring president will be given by Dr. W. W. Campbell,

director of the Lick Observatory. The executive committee of the general local committee consists of Henry F. Osborn, chairman, J. J. Stevenson, M. I. Pupin, Charles Baskerville, N. L. Britton, Simon Flexner, E. B. Wilson and J. McKeen Cattell, secretary. Dr. R. S. Woodward, president of the Carnegie Institution of Washington, is treasurer of the Association, and Dr. L. O. Howard, of the Smithsonian Institution, is the permanent secretary. This is the sixty-ninth meeting of the American Association, which was established in 1848; it is, further, the first of the greater convocation week meetings, to be held hereafter once in four years, successively in New York, Chicago and Washington. When the association last met in New York ten years ago, there were about 5,000 members, the attendance was over 2,000 and there were nearly 1,000 papers on the programs; the membership of the association at present numbers over 10,000; the coming meeting may, therefore, be expected to be large and interesting.

4. *Publications of the Carnegie Institution of Washington.*—Recent publications of the Carnegie Institution are noted in the following list (continued from p. 305, March, and p. 378, April, 1916):

No. 34. American Fossil Cycads. Volume II. Taxonomy; by G. R. WIELAND. 4to. Pp. vii, 277; 58 pls., 96 figs. A notice of this important work will appear in a later number.

No. 74. The Vulgate Version of the Arthurian Romances; edited from manuscripts in the British Museum by H. OSKAR SOMMER. Index of names and places to volumes I–VII. 4to. Pp. 85.

No. 151. A Sylow Factor Table of the First Twelve Thousand Numbers giving the possible number of Sylow sub-groups of a group of given order between the limits of 0 and 12000; by HENRY W. STAGER. Pp. xii, 120.

No. 202. A Concordance to the Works of Horace; compiled and edited by LANE COOPER. Pp. ix, 593.

No. 215 B. History of Manufactures in the United States 1607–1860; by VICTOR S. CLARK. With an Introductory Note by HENRY W. FARNAM. Pp. xii, 675, 7 pls.

No. 220. Guide to the Materials for American History in Swiss and Austrian Archives; by ALBERT B. FAUST. Pp. x, 299.

No. 237. Six-linked Inheritance in *Drosophila*; by T. H. MORGAN and C. B. BRIDGES. Pp. 87, 2 pls., tables and figures.

No. 238. The Coal Measures Amphibia of North America, by ROY L. MOODIE. Pp. x, 222, 26 pls., 43 text-figs. See p. 502.

No. 240. The Jukes in 1915; by ARTHUR H. ESTABROOK. 4to. Pp. vii, 85.

No. 241. Studies of Inheritance in Guinea-Pigs and Rats; by W. E. CASTLE and SEWALL WRIGHT. Pp. iv, 192; 7 pls.

No. 242. Plant Succession: An Analysis of the Development of Vegetation; by FREDERIC E. CLEMENTS. Pp. xiii, 512.

No. 243. Gonadectomy in relation to the secondary sexual characters of some domestic Birds; by H. D. GOODALE. Pp. 52; 7 pls.

The Carnegie Institution has also undertaken the republication of the leading Classics of International Law, under the editorship of Dr. James Brown Scott. Sufficient reason for this undertaking is found in the difficulty of obtaining texts in convenient form for scientific study; of the earlier works, for example, few are to be found in the libraries of this country. Further than this, some of the most important works have never been translated into English, being only accessible in the Latin texts.

The following works have been recently issued:

*Le Droit des Gens ou Principes de la Loi Naturelle. Appliqués à la conduite et aux affaires des Nations et des Souverains*; par M. DE VATEL. With an Introduction by ALBERT DE LAPRADELLE.

Volume I. Reproduction of Books I and II of Edition of 1758. Pp. lv, XXVI, 541; with a portrait of Vattel.

Volume II. Reproduction of Books III and IV of Edition of 1758. Pp. 375.

Volume III. Translation of the Edition of 1758; by CHARLES G. FENWICK. With an Introduction by ALBERT DE LAPRADELLE. Pp. lix, 398.

*De Jure Naturae et Gentium Dissertationes*; by SAMUEL RACHEL. Volume I. A reproduction of the text of 1676, with Introduction by LUDWIG VON BAR, and list of errata. Pp. 335.

Volume II. A Translation of the text; by JOHN PAWLEY BATE; with index of authors cited. Pp. 233.

#### OBITUARY.

PROFESSOR CLEVELAND ABBE, the distinguished meteorologist, died at his home in Chevy Chase, near Washington, on October 28, in his seventy-eighth year. His early work was largely in astronomy and it was when Director of the Observatory at Cincinnati in 1870 that he was invited by Chief Signal Officer Gen. A. J. Myer to come to Washington and undertake the work of weather prediction in this country. The system of weather forecasting then established through his efforts not only grew to have a broad, scientific basis in this country but was adopted from here by many other civilized countries. He was also an active student of problems relating to meteorological subjects, and his contributions to this department of science were many and important.

DR. PERCIVAL LOWELL, Director of the Lowell Observatory at Flagstaff, Arizona, died on November 12 in his sixty-first year. Born in Boston, of a distinguished family, he brought to his life's work as an astronomer rare intellectual gifts, keenness of observation, a vivid imagination and great industry. His investigations of Mars, as also of some of the other planets, led to conclusions which excited great interest and won him recognition by many astronomical and learned societies, but sober science has generally held that some of these conclusions were based more upon imagination than upon actual fact.

PROFESSOR PIERRE DUHEM, the eminent French writer on mathematical physics, died at Cabrespine on September 14.



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