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## AMERICAN JOURNAL OF SCIENCE

#### [FOURTH SERIES.]

#### ART. I.—*Retarded Diffusion and Rhythmic Precipitation*; by J. STANSFIELD, Geological Dept., McGill University, Montreal.

#### Historical.

Owing to the fact that the greater part of the literature of this subject is in the German language, it has been considered advisable to give the following somewhat detailed account of it.

The rhythmic precipitates formed by diffusion of reagents in gelatine or other media, now generally known as Liesegang rings, were first described in a publication which is not generally available \* (1). The precipitates appear to have been shown to W. Ostwald by Liesegang, as a result of which Ostwald published a short note regarding them (2). The ring-formed precipitates were formed by diffusion of silver nitrate from a drop placed upon a gelatine containing potassium chromate. Ostwald considered that the diffusion outward of the silver nitrate and the inward diffusion of the chromate resulted in the formation of silver chromate, which was present, at first, as a super-saturated solution in the meta-stable state. Consequent upon the setting up of the labile state a precipitate formed removing the silver chromate in excess of saturation and the diffusion continued with similar results. As the removal of silver chromate continued the solutions became continuously more dilute, so that the precipitates were formed at continuously greater distances apart.

In 1903 Morse and Pierce (3) regarded the precipitation as certainly due to a super-saturation effect. They produced by diffusion ring precipitates of mercurous chromate, lead chromate, and Berlin blue, which had been obtained previously by Liesegang, and also ring precipitates of lead sulphate, silver

\* See literature references at the end of this paper.

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carbonate, silver pyro-phosphate, silver thiocyanate, silver bromide, cobalt hydroxide, barium chromate, mercurous bromide, and carbon di-oxide, the last-named as rings of bubbles.

They performed experiments of a quantitative character. using capillary tubes containing a weak potassium chromate solution in gelatine, which were dipped into silver nitrate solutions of different strengths. The precipitates appeared suddenly as bands across the capillary tubes, and were observed and measured by means of a cathetometer, the times being observed at the formation of the precipitates. Assuming that the chromate solution is completely dissociated, they proved mathematically that the  $\frac{\text{distance}}{(\text{time})}$  for all the layers in all tubes √/time with the same initial concentrations is constant. They gave twenty-three tables of observed figures, which show this constancy, within the limits of experimental error. At a lower temperature, with the same initial concentrations, the distances appear to be greater, i. e. the diffusion is more rapid at higher temperatures.

In a saturated solution, for equilibrium  $\operatorname{Ag}_{2}' \times \operatorname{CrO}_{4}'' = k$ . In an unsaturated solution, for equilibrium  $\operatorname{Ag}_{2}' \times \operatorname{CrO}_{4}'' = k$ . AgCrO<sub>4</sub>. Is there a boundary which cannot be overstepped in a super-saturated solution without precipitation following? e. g. :—

$$\operatorname{Ag}_{2}' \times \operatorname{CrO}_{4}'' = H.$$

Morse and Pierce found that for a given concentration of one ion a certain definite concentration of the other causes precipitation. They calculated that when precipitation takes place the concentrations of the solutions are  $\frac{N}{75}$  for the chromate and  $\frac{N}{200}$  for the silver. Both solutions must be fully dissociated at these dilutions. They calculated, further, that H is a definite super-saturation limit, which is  $1.4 \times 10^{-6}$  gram molecules per liter, at 16° C. They found that the diffusion is quicker in gelatine than in water, the diffusion constant calculated for silver nitrate being 1.24 cms. per day, that observed being 1.54 (They also suggested that the precipitate is colloidal, but this appears not to be the case.)

Small finer white lines are mentioned as forming between the main precipitates, which become red and then are obliterated when the main precipitate forms over them. These are said to be due to impurities, and are not formed in pure gelatine. They found that gelatine is not essential to the formation of the banded precipitates, but that capillary tubes containing aqueous solutions give similar results, and that the precipitates break up, say after about four in series have been formed. When the experiment is performed in gelatine they are held in place and do not break up.

In 1904 Hausmann (4) carried out experiments with capillary tubes containing gelatine solutions of silver nitrate dipping into solutions of sodium chloride, etc., and found that the heights to which the precipitates extend in any given time depend on the concentration of the silver nitrate and of the sodium chloride, etc., also. Liesegang had claimed that equivalent weights of sodium chloride, strontium chloride, potassium bromide, and potassium iodide diffuse to equal heights in equal times. Hausmann found that the distances varied with the reagents, with their concentrations, and with the concentrations of the gelatine. In some of the reactions banded precipitates were formed.

Mention is made of little brown bands between the main ones and also to secondary rings in the upper part of the tube, which are broader than those in the lower part and increase in breadth upwards. With increase of gelatine concentration the bands were found to be brought closer together. (Curves given pp. 117, 118, loc. cit.)

The precipitation of metallic sulphides is discussed. Certain compounds are formed in the colloidal state, e. g., silver iodide, mercuric oxide, ferric hydroxide, copper hydroxide, and copper ferro-cyanide. The following substances were formed in nonbanded crystalline precipitates:—barium sulphate, strontium sulphate, calcium sulphate, barium oxalate, silver oxalate, thallium chloride, bromide and iodide. In certain reactions compounds separate out which are not stable at atmospheric temperatures under normal conditions, e. g. the yellow form of mercuric iodide, which is stable above 126° C., and certain thallium salts.

Attention is called to the results obtained by Larsen on cooling a salt solution whose concentration decreases at higher temperatures. Regular layers are formed with increasing distances between them, and having decreasing concentrations, upward (5).

With regard to the banded precipitates Hausmann suggests that the compounds are present in the colloidal state before precipitation which only ensues upon super-saturation.

By diffusing different chlorides against a constant strength of silver nitrate he showed that the distances diffused were independent of the metal combined with the chlorine, depending only on the silver and chlor-ions, their speeds of diffusion and concentrations. As the concentration of the chloride decreases it is able to penetrate less and less into the (slightly less than  $\frac{N}{400}$ ) silver nitrate. Weaker solutions of copper and iron chlorides penetrate farther, perhaps because hydroxyl ions are present. Cadmium chloride diffuses more slowly in a stronger solution, possibly due to association.

By diffusing different salts of silver into gelatines containing the same reacting salts, in the same concentrations, the reactions were found to proceed at the same speed regardless of the combined ion, showing that the silver ion is the important one for the reaction.

Solutions of potassium chloride, bromide and iodide were diffused against silver nitrate, the distances being measured, with the following results:

Ratio of distances diffused  $\frac{\text{AgBr}}{\text{AgCl}}$  1.034 Vel. of diffusion  $\frac{\text{Br}}{\text{Cl}}$  1.0366  $\frac{\text{AgBr}}{\text{AgI}}$  1.017  $\frac{\text{Br}}{\text{I}}$  1.0185  $\frac{\text{AgI}}{\text{AgCl}}$  1.0167  $\frac{\text{I}}{\text{Cl}}$  1.0146

Other cases gave equally satisfactory results, while some gave discordant results.

Hausmann thus proved that the reaction depends only on the ions involved in the precipitate, and not on those combined with them, and that the speed of the reaction depends on the ion which diffuses into the jelly and not on the one which is present in the jelly. He also confirmed the result of Morse and Pierce (see page 1) that  $\frac{\text{distance}}{\sqrt{\text{time}}}$  is constant. He pointed out that this constitutes the first non-electric method of determining diffusion velocities.

In 1905 Bechhold (6) called attention to the importance of rhythmic precipitation in the development of layers of silica, horn, and calcium carbonate in sponges, the development of layered calcareous shells in the perforated Foraminifera, in gasteropod and lamellibranch shells, the development of layers in the bones of some vertebrates, and its importance in intussusception in plants.

Bechhold agrees with Ostwald concerning the super-saturation idea. He used ammonium chromate or bichromate in making ring precipitates and found that owing to the fact that silver chromate is slightly soluble in ammonium salts that the bands are more widely spaced. He mentioned the strong contractive forces which are set up in gelatine when silver nitrate is added to it, and suggested that these forces may have something to do with the formation of the rings. But this appears not to be the case because under crossed nicols there is not a maximum brightness between the bands.

He found that on diffusing ammonium chromate into a silver solution in gelatine no precipitate forms. In the diffusion of silver nitrate by increasing the ammonium nitrate thicker rings were obtained.

In 1907 Liesegang (7) showed that a later set of rings may be formed cutting across an earlier set, apparently without being disturbed or influenced by the rings already present. Close examination shows that the earlier formed rings are extended in comb-like forms to a very small distance by the second deposition. But the "sowing" action of the first formed precipitates is almost negligible.

In 1912 Hatschek (8) produced by diffusion in gelatine, agaragar or in silicic acid precipitates of calcium sulphate, and carbonate, barium carbonate, sulphate and chromate, lead chloride, iodide, bromide, chromate, ferro-cyanide, ferri-cyanide, strontium carbonate, sulphate, phosphate, oxalate and silicofluoride, copper phosphate, cadmium sulphide, manganese ferro-cyanide, silver bichromate, and silicofluorides of sodium and potassium. Some of these were always formed in layers and some always as macroscopic crystals. According to Hatschek the results are always the same, no matter which ion diffuses into the jelly containing the other ion.

With a view to testing the super-saturation theory of Ostwald he impregnated a jelly with lead iodide and potassium iodide, diffusing a solution of lead into it. The rings of lead iodide were formed just as though the medium were not sown with lead iodide. He holds that super-saturation cannot be used as a general explanation of the formation of precipitates in layers. The work of Liesegang quoted above would appear to invalidate this conclusion.

In 1914 Liesegang (9) claimed that the presence of a small amount of acid and of gelatose is necessary for the formation of the rings in gelatine, none being formed in pure gelatine. If the amount of acid is increased the rings do not appear, so that a definite amount is essential. By increasing the amount of acid present the silver chromate, which is soluble in acid, is enabled to diffuse to a greater distance before precipitation takes place. The result is the bands are more widely spaced, and are thicker. Finally, by greater increase of the acid the silver chromate forms as a continuous mass. Spiral bands were produced, and an examination of some of the older published figures reveals the fact that they are spiral and not actually rings as they were thought to be. Liesegang mentions the presence of spirals on the retina in some birds.

When the drops of silver nitrate from which the diffusion proceeds are not circular, cracks appear, cutting the bands, and are free from precipitate. This shows how short spaces may

4.0

separate the ends of bands without the formation of precipitate by "sowing." The formation of the rings is due to the production of super-saturation at innumerable individual points. Thus the spiral form does not afford any difficulty to the super-saturation hypothesis.

Bradford (10) has recently investigated the effect of the byproducts of the reactions resulting in the formation of the ring precipitates, and by varying the concentration of the by-product was unable to affect their formation in any way. Hatschek had shown that the particles formed in the ring precipitates are larger than those obtainable in aqueons solutions. Bradford suggests that this phenomenon is due to adsorption by the precipitate of substance dissolved in the gel, which merely serves to retain the precipitate in place.

Bradford finds that the distances between the layers formed are roughly inversely proportional to the molar strength of the reagent in the gel, and not to that of the diffusing reagent.

In a more recent paper (11) the same author has developed the idea of adsorption in connection with the formation of banded precipitates. It might be suggested that the term pseudo-stratification would be preferable to stratification as used by him.

## Retarded Diffusion and Rhythmic Precipitation.

By reason of its application to geology the subject of rhythmic precipitation has assumed an importance to geologists which cannot be neglected. In connection with an investigation of Eozoon the writer had occasion to consider the question of the causes governing the formation of rhythmic precipitates. A series of experiments has been made in order to afford a basis for a comparison with banded structures in rocks. The experiments were carried out using diffusion from a drop placed upon a gelatine layer on a glass plate, as described by Liesegang. The gelatine was prepared according to his directions by preparatory washing in several portions of distilled water, to remove some but not all of the impurities, then dissolving in distilled water, a convenient concentration for use at a room temperature of 12° C. being 1 gr. of gelatine in 35 c.c. The solution was used after standing one or two days, water. reheating the jellied mass to bring it to the liquid state again, care being taken both in the solution and re-solution of the gelatine to avoid over-heating. Care was taken to keep the relative gelatine concentrations the same in any set of experiments. This was done by adding 1 c.c. of a solution ten times as strong as the one to be investigated to 9 c.c. of the gelatine solu-Thus a gelatine solution of known strength was obtained, tion. containing any desired concentration of the reagent to be examined. This was poured out on to several glass plates and allowed to set, after which drops of the second reagent, of different strengths, were placed upon them. These solutions gradually diffused through the gelatine and precipitates were formed, sometimes continuously, sometimes in separated bands. (See figs. 1, 2, and 3.)

It is found that with different concentrations of the diffusing reagent (the one in the drop) against a constant concentration of the reagent in the gelatine the diffusion goes at different rates, the stronger solutions diffusing more quickly and to greater distances than the weaker. Again, by keeping the diffusing reagent constant and varying the concentration of the opposing reagent the diffusion is retarded by increasing the opposing concentration, and also the total distance of diffusion is decreased. When the molecular concentrations of the solutions approach closely there is a definite limit to the distance to which the stronger solution is able to diffuse. In many of the experiments the gelatine dried before the limit was reached, if any exists, with the solutions of more unequal concentrations, but with the solutions mentioned above the limit was clear, and was reached, in many cases, within a few hours.

The following tables for different experiments, showing the distances to which diffusion has taken place with different strengths of the reacting solutions, illustrates the point. The figures enclosed in a double line are for experiments using one batch of gelatine and are comparable with each other, but not strictly comparable with those within another double line, by reason of possible differences in the preparation of the gelatine.

The experiments which yielded clearly separated bands of precipitate are indicated by a small ring within the squares belonging to them. It is seen that the production of the bands in gelatine takes place best when a strong silver solution diffuses against a weak chromate solution. In those cases which did not show clearly separated bands, the precipitate appeared to be continuous, but examination with the hand lens or sometimes with the microscope showed that the bands were present, but that they were more closely spaced, so as to appear continuous. Some cases are clearly banded, to the naked eye, but with the stronger solutions this fine banding of the apparently uniform silver chromate can only be seen under the microscope.

When clearly separated bands are formed, our experiments have sometimes shown these passing into fragmentary banded layers toward the outside. In some cases this may be quite extensive, corresponding to ten or more bands. In other cases,

8N	$6\mathrm{N}$	4N	2N	N	N/2	N/4	N/6	N/10		
·235	145	.09	·08	_					N/2	
•45	•3	•25	·14						N/4	
·66	·59	·425	·28	•2					N/6	
•775	•705	·65	·435	·255					N/10	
1.11	·865	(.875)	·725	•55	•2	·1	-	-	N/20	
1.275	1.12	1.03	·85	•77	·365	·16	•1	-	N/40	
1.4 0	1.28 0	1.2 0	1·1 o	·775 。	•5	·18	·11	_	N/60	$K_2$ CrO
1.46 6	1.31 0	1.26 0	1.11 ،	1.1 0	·62	·375	·26	•24	N/80	
(1.35)0	1.32 0	(1.21)0	1.21 0		•65 0	•54	·31	·25	N/100	
1.54	1.47 0	1.4 0	1.28 0	1.27 0	·84 o	·6 o	•535	•41	N/200	
· .	-									
·115	•1	·085	·075						N/2	
·285	·25	·24	·115						N/4	
·375	·365	·325	·21	•1					N/6	
•47	•425	•4	•3	·19					N/10	
·625	•5	(.525)	•45	·335	·18	·1			N/20	
·725	·625	•6	·5	•425	·295	·16	·1	_	N/40	
•79 0	·71 o	·71 。	·635 。	·51 o	·345	·175	11	_	N/60	$K_2 CrO$
·83 o	·75 o	·73 0	·675 。	(.76)0	(*445)	·305	·225	·21	N/80	
(.79)0	·76 o	(.71)0	·715 o		·435 0	·385	·225	·19	N/100	
·85 o	·84 o	·8 o	.75 0	•74 0	·54 o	·425 。	•35	·28	N/200	

 $\mathrm{AgNO}_3$ 

this is followed, on the outside, by an area in which the precipitate occurs as a continuous non-banded area containing the precipitate as small granules.

In other cases the fragmentation is not so prominent and the non-banded area of "disseminated" precipitate is followed outward by "secondary" bands of precipitate, which differ from the "primary" ones within, in that they are evenly spaced and not farther apart, with greater distance from the center, and in being made up of large, irregularly shaped grains of silver chromate, sometimes separate from each other, whereas the "primary" bands are continuous and consist of exceedingly minute granules of silver chromate. (See fig. 1.) There is always a clear "halo" outside the circle of diffusion which appears to be free from precipitate, but under the microscope is seen to contain minute grains of silver chromate. In some cases "subsidiary" bands have been noticed in this "halo." They correspond to the very fine lines noticed by the earlier workers and ascribed, by them, to the presence of impurities in the gelatine.

A set of experiments was made with silver nitrate in the gelatine and potassium chromate as the "dominant" reagent in the central drop, having the higher molecular concentration. The results in this case were remarkably interesting. The following table gives the scheme of concentrations used. Numbers 26 to 30 showed only isolated spots or granules formed here and there in the gelatine as the chromate diffused outward. Numbers 21 to 25 showed the beginning of a very indefinite arrangement of the spots in bands. Numbers 16 to 20 showed an inner set of apparently continuous bands consisting of large granules of silver chromate followed by a space with the precipitate as isolated granules, and outside this again the arrangement in bands as in 21 to 25, but more clearly shown. (See fig. The inner bands are less well shown the stronger the chro-4.) mate solution. The outer bands often show discontinuity and

Table (p. 8) showing distances diffused in a radial direction, measured in centimeters. The head of the column shows the strength of the silver nitrate solution diffusing and the strength of the potassium chromate solution in the gelatine is indicated at the extreme right. Upper left part of table—distances diffused after 6 hrs. 15 mins. Upper right, after 6 hrs. Lower left, after 1 hr. 50 mins. Lower right, after 2 hrs. The results which show discrepancies are indicated by parentheses. These

The results which show discrepancies are indicated by parentheses. These are due to inaccuracies in measurement. Those which recur in the same positions in both parts of the table are due to incorrect measurement of the size of the original drop, the others to inaccuracies in those individual measurements. The figures on the right side of the table are comparable with each other, and those on the left side with each other, but as they were obtained from experiments using two separately prepared batches of gelatine, the figures on the left are not comparable with those on the right, except in a general way. relative displacement of the bands, which are doubtless due to inequalities of diffusion. Both the inner and outer bands are more widely spaced toward the outside.

Numbers 12 to 15 show similar bands to those in 16 to 20. Numbers 1 to 11 show three similar areas, but in 1 to 7 there appears to be a continuous precipitate round the drop. This

		3N	N	N/2	N/10	N/20
	N/10	1	2	3		
	N/20	4	5	6	7	
	N/40	8	9	10	11	
AgNO <sub>3</sub>	N/80	12	13	14	15	
	N/100	16	17	18	19	20
	N/200	21	22	23	24	25
	N/400	26	27	28	29	30

 $K_2CrO_4$ 

The strength of the potassium chromate in the drop in any experiment is given by the heading of the column in which the number falls, the strength of the silver nitrate in the gelatine being given at the extreme left, thus in the case of number 13 normal potassium chromate diffused into a gelatine containing an eightieth normal solution of silver nitrate.

is seen to have bands on the surface as with the stronger silver solutions cited above.

The experiments with the weakest silver solutions  $\left(\frac{N}{100}\right)$  show that bands are not produced nuless a certain concentration is present. From this it may be argued that the areas between the two sets of bands, in numbers 1 to 20, had an insufficient concentration of silver ions to allow of the formation of bands, as a result of the removal of silver ions by precipitation, the precipitation being followed by decrease of concentration outside the bands as a result of diffusion of silver ions inward to take the

place of those precipitated. The result is somewhat analogous to the thinning of a sheet of rubber by stretching. With the diffusion of the chromat-ions farther outward, however, a sufficient concentration of silver ions to allow of the formation of bands will again be met with and the "secondary" bands will result.

A similar explanation would apply to the unbanded layer in results cited above with diffusion of silver against a weaker solution of chromate. (See figs. 1 and 2.) It is possible, how-



FIG. 1.  $x_3^3$ . The result of diffusion of 6N silver nitrate into a gelatine containing N/200 potassium chromate. The drop is surrounded by an area of apparently continuous precipitate, which actually shows fine bands on its surface. This passes outwards into the zone in which the bands are clearly separated, and become more widely spaced. Outside this zone is a nonbanded zone of granular precipitate, beyond this a zone of granular precipitate arranged in evenly spaced bands. This is followed by a clear "halo." It is probable that the potassium chromate may not have been thoroughly mixed with the gelatine so as to give uniform conditions. At one point the non-banded zone is crossed by a narrow strip of bands. This is doubtless due to the presence of a streak of gelatine richer in potassium chromate than the rest. The unequal extensions in a radial direction of the inner banded zone may be explained in a similar manner.

Fig. 1.

ever, that this explanation is too simple, and that the hydrions present may have to be taken into account.

Another question should be discussed at this point. In all the bands and in the non-banded layer in the experiments with diffusion outward of chromate, and in the outer bands and the granular non-banded area in the case of outward diffusion of

FIG. 2.



FIG. 2. x 5. A portion of the same (fig. 1) enlarged to show the character of the precipitate in the "granular" zones.

silver, the precipitate consists of large isolated granules sometimes taking on irregular shapes, in the more pronounced and well-marked bands, probably as a result of accretion of several granules. (See figs. 1 and 2.) But in the "primary" bands of the outward silver diffusion the precipitate is made up of exceedingly numerous and very small granules. In watching the development of one of these bands under the microscope it was seen that the very numerous small granules were developed apparently independently of each other. The band grew quite slowly, being extended laterally. As it developed the central part extended itself in advance of the two sides, and



FIG. 3. x 5. The result of the diffusion of 8N silver nitrate into a gelatine containing N/60 potassium chromate. It shows the close bands (apparently a continuous mass of precipitate) passing outward into separated bands, which are broken toward the outside, and surrounded by a zone of "granular" precipitate and then by a clear "halo." The bands are broken by several clear channels. The bands on opposite sides of these are not directly opposite to each other, and they bend inwards toward the drop from which the diffusion took place. These may be explained by uneven distributions of concentrations of chromate or silver ions, or of both.

these followed, sometimes more slowly, sometimes more rapidly on the central part. Again, a little distance away from the

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small cloud of granules, but along the line of the band, another cloud may appear, more thickly crowded with granules in the central line of the band. This would develop as before, in both directions, finally uniting with the other advancing part. The precipitate on each side of the central part gradually thickened. Thus, while the result is a series of bands of pre-



FIG. 4.

FIG. 4.  $x \ 2 \ 1/4$ . The result of the diffusion of N/10 potassium chromate into a gelatine containing N/100 silver nitrate. (No. 19.) There is an inner set of close bands round the drop, which appear to be continuous precipitate, in the photograph : outside this zone is one in which the precipitate occurs as isolated granules, and this is followed by bands in which the precipitate consists of separate large granules. Examination with a lens will show this. The outer bands are broken by clear channels, the bands being offset with regard to each other on opposite sides of the channels, in some cases. Both the inner and outer sets of bands become more widely spaced outwards.

cipitate, of apparently striking regularity, yet each separate small portion is developed independently of the rest at such point as the super-saturation boundary is over-stepped. We are able to understand more clearly, now, how the development of spiral forms may ensue, and how breaks may occur in the bands, with accompanying displacement of the bands (see fig. 4), and also the presence of cracks passing through the bands, which are free from precipitate, and along both sides of

which there may be a bending of the bands. (See fig. 3.) These are doubtless due to irregularities of the diffusion, and perhaps, in part, to irregular distribution of certain impurities or disturbing factors. The quite leisurely deposition of the very fine silver chromate granules suggests that each one is formed almost independently and kept independent, at least for some time, by the gelatine. The experiments of Hatschek and Liesegang investigating the possible sowing action of precipitate already in the gelatine have shown how little this action needs to be taken into account in the formation of the Liesegang rings. The question as to whether this isolation of precipitated granules is entirely due to the action of the gelatine



next arises. An experiment was made with diffusion of silver into a chromate-bearing gelatine to which a small amount of citric acid had been added. No banded precipitate was formed but a continuous precipitate in the colloidal state. That is to say, by increasing the concentration of hydrions the number of points at which precipitation takes place had been increased and the size of the particles resulting from precipitation had been decreased. (The definition of a colloid suspension being that the particles range in size somewhere between the limits of  $\cdot 1\mu$  and  $1\mu\mu$  in diameter.)

In the case where the chromate solution is diffusing outwards this action of the hydrions appears to be prevented or very much curtailed, possibly owing to the potassions present. Also in the "secondary" bands of the silver diffusion this action appears to have been prevented. This is also probably due to the "dominance" of potassions relatively to the hydrions in that part of the gelatine. Liesegang (9) has shown how gradual increase of hydrions present in a silver diffusion against chromate, in gelatine, results in the formation of broader bands, i. e., not only increases the number of centers of formation of the precipitate, but also increases the area over which these may form.

In a case where diffusion of silver from a drop and of chromate from a line drawn around the drop took place through a space free from both reagents, the first precipitate did not form at the point where the solutions first met. The silver diffusion



is quite visible as there is a clearly marked line in the gelatine at the outward front of the advancing solution. The first formed precipitate was situated about one millimeter within this line, i. e. nearer the center of the silver drop. This would suggest that the halo which surrounds the silver diffusion is an area in which the concentration is below the super-saturation boundary.

### Rate of Diffusion a Controlling Factor.

From the foregoing it is seen that the explanation offered by Ostwald (see page 1) has been confirmed by later work. By the diffusion outwards of the silver and inwards of the chromate a depletion of the reservoirs of those ions takes place, i. e., the ionic concentration is gradually reduced, with the result that the silver ions are enabled to diffuse to a greater distance before the precipitation concentration is attained.

Thus ionic concentration is an important governing factor in determining the distances between the bands of precipitate.

Rate of diffusion is also an important factor, which has not been given adequate consideration in the past. Considering the case of silver chromate deposition, the rate of diffusion of the silver solution is greater than that of the chromate solution. So that, after the formation of one band the silver ions pass through it and outward beyond it, or continue onward from





 I.
  $8N \text{ AgNO}_3 / \frac{N}{60} \text{ K}_2 \text{CrO}_4$ .

 II.
  $4N \text{ AgNO}_3 / \text{ do}$  

 III.
 2N do / do 

 III.
 2N do / do 

 IV.
 N do / do

 V.
 N do /  $\frac{N}{20} \text{ K}_2 \text{CrO}_4$ .

their position in front of it, before meeting the chromat-ions which have not yet crossed the free space. At such point as the concentration is high enough to give labile conditions precipitation ensues. The distance of this point from the last formed band must therefore depend upon the relative rates of diffusion of the two solutions. Thus, if other disturbing con-

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ditions, such as gelatine concentration and amount of acid or other solute present, remain constant the distance between the rings depends upon the ionic concentrations and also upon the relative rates of diffusion. It thus appears that if in any reaction the increase in distance between the bands due to the effect of the difference of rates of diffusion could be counter-balanced by an equal effect in the opposite direction due to concentrations, the spaces between the bands would remain constant.



FIG. 8. Diffusion of normal lead nitrate against potassium chromate of different strengths.

Agate structure has been ascribed to the formation of Liesegang rings by diffusion of solutions through gelatinous silica. The discovery of gelatinous silica in a cavity in the Simplon tunnel is of interest in this connection. On examining certain agates the writer was struck by the fact that many of them show bands *which are equally spaced* and not at successively increasing distances, as in the ordinary Liesegang rings.

The writer does not consider that agates in general can be held to be produced by the Liesegang reaction; out of a large number examined but very few seem to be explicable only along these lines, by far the greater number allowing of other explanations. Each specimen of agate needs to be examined by itself, the history of each one being, of necessity, a separate entity, and only comparable with others by an accidental reproduction of a similar series of events.

Considering the formation of bands of silver chromate in outward diffusion of silver, if the concentrations for precipitation are  $A_0$  for the silver ions and  $C_0$  for the chromat-ions and  $X_0$  for the silver chromate, then for equilibrium

$$\mathbf{A}_{0} \cdot \mathbf{C}_{0} = \mathbf{k} \cdot \mathbf{X}_{0} \tag{1}$$

k will vary with temperature.

Consider a space into which diffusion is taking place, just in front of a band of precipitate which is newly formed. The



FIG. 9. Simple diffusion (no reaction).

silver ions are "dominant" and the chromat-ions in excess of saturation of silver chromate have been removed from a certain space on each side of the band. The silver ions being "dominant" the value  $A_o$  is large compared with  $C_o$ , so that the silver ions may be regarded as starting their diffusion from the precipitate band (or perhaps some plane outside it), while the chromat-ions begin their diffusion from some plane at a distance D outside the band. (See fig. 5.) It should be noted that in keeping with the generally accepted conception regarding aqueous solutions the reagents involved will diffuse partly as molecules and partly as ions. When silver ions are referred to it is understood that each of these is associated with an oppositely charged nitrat-ion the two charges neutralizing each other. For the purposes of discussion of the reaction with the potassium chromate it is convenient to speak of the silver ions and chromat-ions, but the fact should not be lost sight of that these ions do not diffuse as isolated entities, but each charged ion must be associated with a charge of equal amount and opposite sign borne by some other ion or ions.

Suppose that the concentrations of the silver and chromate ions at the planes from which they begin to diffuse are a and c respectively, that the rates of diffusion are  $V_a$  and  $V_c$ , and that



FIG. 10.

FIG. 10. Simple diffusion.

a precipitate is formed at some plane P at a distance d from the original silver diffusing front.

Then the concentrations of silver and chromate ions at P are  $\frac{V_{a}a}{d}$  and  $\frac{V_{c}c}{D-d}$  respectively. But the product of these two is the precipitation value, so that  $\frac{V_{a}V_{c}ac}{d(D-d)}$  has a value which is susceptible of measurement, because  $A_{0}.C_{0} = k.X_{0}.$  (1)

Assuming that the distance D remains about the same for two or three consecutive bands, the condition for the formation of a precipitate is from (1)

$$\frac{\mathbf{V}_{a} \cdot \mathbf{V}_{c} \cdot \mathbf{a} \cdot \mathbf{c}}{\mathbf{d}(\mathbf{D} - \mathbf{d})} = \mathbf{k} \cdot \mathbf{X}$$
(2)

or, since  $V_a$  and  $V_c$  are constants for given concentrations and for a given temperature, the relation between the initial con-
centrations a, and c, and the distances between successive bands is of the form

$$d(D - d) = K.ac$$
 where K is a constant. (3)

It seems legitimate to assume that D varies very slowly over the region occupied by a few consecutive bands. In these circumstances the variation of d with the product ac is exhibited graphically in fig. 6, the curve being a parabola having a maximum ordinate at d = D/2, when  $ac = \frac{1/4D}{K}$ .

It will be seen from this curve that as the concentration product a.c decreases, the distance between successive bands will diminish or increase according as  $d < \text{or} \quad 1/2\text{D}$ . If the concentration product happens to take the value  $\frac{1/4\text{D}}{\text{K}}$  the bands

will be equally spaced; otherwise they will be spaced at diminishing or increasing distances according as the rate of variation of a.c with d is positive or negative.

For most cases of outward diffusion of a strong solution against a weak solution d > 1/2D so that the usual result is that the bands are formed at successively increasing distances apart. An illustration of this is seen in the inner part of fig. 1. The outer part of the same figure illustrates equal spacing of the bands, which is only rarely obtained. An example of the third case, where the bands become successively closer, is discussed below. (See page 24.)

In some of the experiments described above measurements of distances of diffusion were made over an extended period, the results being plotted in the form of curves, with times as abscissae and distances as ordinates. These curves bring out clearly the way in which diffusion is prevented by approach of the molecular concentrations of the two reacting solutions toward the same point. They also show that in those cases where the diffusion proceeds rapidly at first there is a remarkably sudden drop in the rate of diffusion, and that this drop coincides with an almost uniform distance of diffusion. Some of these curves are reproduced in figs. 7 and 12. A comparison with figure 12 appears to indicate that the flat portions of the upper curves in figure 7 are due to a change in the viscosity of the gelatine.

A comparison of the curves for silver and lead solutions against the same concentrations of chromate solution shows that the lead diffuses the more slowly. This is in agreement with the higher rate of diffusion of the silver solution in pure gelatine.

From this a consideration of the possibility that the speed of





FIG. 11. Simple diffusion of silver nitrate of different strengths.



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the lead nitrate solution in gelatine may be less than that of the potassium chromate solution led to a measurement of the rates of diffusion of several solutions, in pure gelatine. Wellwashed gelatine was placed on glass plates, allowed to set, and drops of different reagents of different strengths were placed upon them. The reagents diffused outwards. In some cases, e.g. silver nitrate, lead nitrate, ferric chloride, and sodium hydroxide, the diffusing solution had a clearly visible outline in the gelatine, which is susceptible of measurement. The measurements were made as before, by means of a millimeter scale, estimating to tenths of a millimeter, taking care to eliminate parallax. The diameter of the drop was taken and the diameter of the circle of diffusion (in the case of the precipitates above, to the outer limits of the precipitates). Subtracting the diameter of the drop from the total diameters of diffusion, and dividing by two the radius of diffusion is obtained. It is the rate of elongation of this radius which has been measured and plotted, and which is called the radius of diffusion here. The chromate solutions did not give a diffusing front which was clearly visible and susceptible of easy measurement. The yellow color due to the chromat-ions became gradually fainter away from the drop, coming to an indistinct and diffuse margin. Therefore, in the curves given in fig. 9 those for the chromate solutions are dotted, since they are not as reliable as the other curves.

The curves (see figs. 9, 10, 11) show that a strong solution of any reagent diffuses at a greater rate than a weaker solution of the same. They show that silver nitrate diffuses more rapidly than potassium chromate solutions of the same molecular concentrations. (The crossing of the silver and chromate curves cannot be regarded as established, for the reason stated above. Also the apparent straight lines of the chromate curves cannot be considered final determinations. The sudden stoppage appears to be correct, though this may be due to invisibility of the chromat-ion below a certain dilution.) It is certain that the lead nitrate solutions diffuse more slowly than the potassium chromate solutions of equal molecular strengths.

It was considered that this pair of reagents, the lead in outward, the chromate in inward diffusion, offered a good chance of testing the theory that with such a couple bands of precipitate might be formed which would become closer together outwards, instead of farther apart. Several different strengths of these reagents were tried against each other, the precipitates formed being apparently continuous to the naked eye. In the case of normal lead nitrate against N/200 potassium chromate an apparently continuous precipitate was formed. The hand lens showed no banding, but under the microscope the desired result was observed. Toward the outer part of the precipitate a very fine banding was seen and the bands were closer together outwards. An attempt to reproduce this was not successful, owing to different hygroscopic character of the atmosphere, but a recent paper by Bradford (10) describes an experiment in which the diffusion of N/5 lead nitrate against N/10 potassium chromate, in a agar gel. gave rise to bands of precipitate which became more closely spaced in the later deposited layers. The first eight bands were  $1.15^{\text{mm}}$  apart, the ninth one being  $.9^{\text{mm}}$ from the eighth. No chromate was left between the bands.

The same strengths of lead nitrate and potassium chromate used by Bradford were tried in gelatine. Three gelatine layers were placed in a test-tube, the lower one being a N/10 solution of potassium chromate, the middle layer being clear gelatine, and the upper one a N/5 solution of lead nitrate. Another test-tube was prepared with the same solutions reversed, the lower one being lead nitrate and the upper one potassium chromate. In both cases the chromate solution diffused the more rapidly so that the first formed precipitate was nearer to the starting point of the lead solution than to that of the chromate solution, while in both cases the later formed precipitate was on the side remote from the lead solution. With the chromate solution above the precipitate was a continuous mass, but when the lead solution was above the precipitate was formed in bands, which became closer and closer together, passing into a continuous mass. These experiments were repeated with the same results. This illustrates a controlling effect of gravity, which does not come into play when the diffusion takes place horizontally, as in the glass plate experiments.

### Miscellaneous Diffusions.

In comparing the rates of diffusion of ferric chloride and sodium hydroxide the observation was made that ferric chloride possesses in a marked degree the property of inducing coagulation in gelatine, a property possessed by silver and lead nitrate solutions in a much smaller degree. This coagulant property of ferric chloride is well known. In comparing the rates of diffusion of the two reagents it was found, contrary to expectation, that the sodium hydroxide diffuses much more slowly than ferric chloride. (See fig. 10.) But the diffusion of the sodium hydroxide is not a simple case of diffusion. A reaction takes place with the gelatine, and this is at once apparent in the unexpected nature of the curve.

Diffusion of normal ferric chloride against N/100 and N/200 sodium hydroxide—(stronger solutions prevent the setting of the gelatine)—gave a colloidal precipitate of ferric hydroxide.

This is surrounded by a broad clear zone marked by a clearly visible circumferential line. The nature of this zone is unknown, at present.

A set of nine diffusions was carried out with 5N, 2N and N potassium iodide against N/20, N/40 and N/80 lead nitrate, and another set of nine with 2N, N, and N/2 lead nitrate against N/20, N/40 and N/80 potassium iodide. Probably owing to the state of the gelatine (not thoroughly free from acid) the precipitates were colloidal and not visibly banded except in the cases of 2N and N potassium iodide against N/20lead nitrate, which showed fine rings to microscopical examination. They all showed that the diffusion proceeds more rapidly with greater difference of concentrations of the two reagents and all showed a broad indefinite band around the drop in which the precipitate was thinner, and a broad band on the outside of it in which the precipitate was thicker. This was especially marked in the cases where potassium iodide was the diffusing reagent (the one in the drop). It was found that several of these plates developed a banded structure immediately upon being immersed in a solution of sodium hydroxide, which was used to clean the plates after they had dried. Thus, although the precipitate is present in colloidal form it is arranged in layers or bands, though these are invisible until some such reaction as that described shows their presence.

#### Effect of Different Gelatine Concentration.

The reaction 4N silver nitrate against N/200 potassium chromate was carried out in gelatine of different strengths, obtained by dilution of the one stock. Rings were formed, and the rates of diffusion were measured. The plot of these results confirms the result of Hausmann (loc. cit.) that increase of the gelatine concentration retards the diffusion.

The curves are almost parallel and the rates differ so slightly that the curves only begin to diverge very slightly toward the right. The measurements recorded in these curves are only rough, but they suggest that more careful measurements may be able to detect a numerical relation between the concentration of the gelatine and the amount of retardation.

#### Summary and Conclusions.

After giving a historical account of the work of earlier writers, the results of certain experiments are given, the main points of which may be summarized as follows:

1. The rate of diffusion of a reagent of given strength is retarded by increasing that of the reagent in the gelatine. Also, the total distance to which diffusion takes place is decreased by a similar increase of strength of the reagent in the gelatine.

2. With too close approach of the concentrations of the two reagents, silver nitrate and potassium chromate, a continuous precipitate is formed, but under the microscope, the surface of this is seen to be finely banded. These fine bands follow the same rules as regards spacing as are found with the separated bands.

3. Separated bands are best produced by the diffusion of a strong silver solution against a weak chromate solution. (For other reagents, these conditions may not be universal.) 4. Similar results are obtained by diffusion of a strong

chromate solution against a weak silver solution. But the particles formed are larger in this case.

5. Increase in distance between bands has been held to be due to progressive dilution of the reagents. Rate of diffusion is shown to be an important controlling factor, and that under certain conditions the bands may be equally spaced, or may be spaced at decreasing distances. These conditions are discussed.

6. The rates of diffusion of different reagents in pure gelatine are found to differ; thus potassium chromate diffuses more rapidly than a lead nitrate solution of the same molecular concentration, and a silver nitrate solution more rapidly than a potassium chromate solution. Also, a strong solution of any given reagent diffuses more rapidly than a weak solution.

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# ART. II.—Calorimetry by Combustions with Sodium Peroxide; by W. G. MIXTER.

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

FUSION with sodium peroxide is the only way known for finding the heat of oxidation of elements which do not burn in oxygen and which form oxides insoluble in acids. The method is adapted to the determination of the heat of formation of the oxides of a metal and also the heat of combination of metallic oxides with sodium oxide. The writer has used the method the past ten years and can now describe it more completely than was done in any of his papers.

The method is indirect and the heat effect sought is not the observed effect; hence burning in condensed oxygen is preferable where possible. For example, when carbon is burned with sodium peroxide the observed heat (x) is the result of the following reaction

$$2Na_2O_2 + C = Na_2CO_3 + Na_2O = x$$

and x equals the heat of formation of carbon dioxide plus the heat of combination of carbon dioxide with sodium oxide and less the heat required to separate two atoms of oxygen from two molecules of sodium peroxide, thus

$$x = C + 2O + (Na_{2}O + CO_{2}) - (2Na_{2}O + 2O)$$

and

$$C + 2O = x - (Na_2O + CO_2) + (2Na_2O + 2O)$$

Moreover, many substances do not give with sodium peroxide sufficient heat to fuse the mixture and hence some readily combustible substance, such as sulphur or carbon, must be added, which gives in many cases the larger part of the total heat effect.

As yet we have only a few results obtained by fusion with sodium peroxide to compare with those by other methods. They are

	Sodium peroxide	
	method	Other methods
$C + 2O = CO_{*} +$	96 <b>·4*</b>	94.7*
Ti + 2O = TiO, (amor.	$215.6^{+}$ TiO <sub>2</sub> (c	erys.) 218.44
3Fe + 4O	267.5	265.2
2Na + S + 4O	326.7\$	328.6
3Na + P + 4O	451.4	$452 \cdot 4$
* This Journal, xxix, 130; ibid.	, xix, 434.	
† Ibid., xxvii, 343.	<sup>‡</sup> Ibid., xxxvi, 55.	
§ Ibid., xxvi, 125.	Thomsen.	

The values for  $C + 2O = CO_2 + 94.7$ ,  $Ti + 2O = TiO_2$  crys. + 218.4 and  $3\text{Fe} + 4\text{O} = \text{Fe}_{3}\text{O}_{4}(\text{crys.}) + 265.2$  were obtained by combustion in oxygen. The other values are derived and have the mean error of several experiments. Both values for C + 2O are for acetylene carbon. One reason for the higher value found in the sodium peroxide method is this: The carbon and peroxide were mixed in a mortar, thus allowing the peroxide to absorb a little moisture which added to the heat of the fusion. The amorphous TiO<sub>2</sub> used in the experiments which gave 215.6 was heated to redness for an hour. Apparently it has nearly the same heat of formation as the crystalline form. The value 267.5 for 3Fe + 4O is derived from the results of fusions of iron, ferrous oxide, ferric oxide and the mineral magnetite respectively with sodium peroxide, and 265.2 was the result of burning iron in oxygen. The result for 2Na + S + 4O is derived from the heat of the reaction of sulphur with sodium peroxide and the heats of formation of SO. and Na<sub>2</sub>O. The value 451.4 for 3Na + P + 4O was derived in a similar way. 452.4, given in the Physikalisch-Chemische Tabellen is derived from Berthelot's data.

Sodium peroxide absorbs water rapidly from the air and hence it should be exposed as little as possible as the hydrated peroxide will give more heat with a combustible than the anhydrous. One of two samples which gives off the less oxvgen when fused is the better one. The error from water content is small in good peroxide especially when carbon, for example, is added to make a mixture fuse because the heat effect of the carbon has been found for the carbon and peroxide used. The writer has obtained peroxide in pound packages, containing according to the seller 92 to 95 per cent of Na,O,. To ensure uniformity in composition four or five pounds are mixed thoroughly in a large stoppered jar. Then it is rapidly placed in about half pound lots in flasks with necks which are narrowed to half an inch, and the necks are drawn off and hermetically sealed. The flasks containing peroxide should be stored in a metal box as a precaution against fire in case of breakage. For convenience in using, the peroxide is put into an eight ounce bottle having a smooth, unground neck with a smooth red rubber stopper.

Various substances may be added to a peroxide mixture to increase the temperature of the fusion. The writer has used successively acetylene carbon, sulphur and lampblack. Pure rhombohedral sulphur in fine powder would appear to be the best of the three, but it becomes electrified when shaken in the bomb with the other ingredients and sometimes sticks to the bomb and is not completely oxidized. Sulphide is formed and occasionally free sulphur is left. When the bomb is much blackened by a fusion with sulphur the heat result is low. Acetylene carbon is the ideal substance to use, but difficult to obtain. It is constant in composition after heating to expel hygroscopic moisture, and any unburned is not dissolved when the fusion is treated with water or acid and may be collected on a Gooch filter and weighed. Commercial lampblack nearly ash free is prepared as follows: It is heated for two or three hours to 1000° or higher, sifted when cool and shaken in a large bottle to ensure uniformity in composition. A portion for a calorimetric experiment is heated in a crucible, best in an electric furnace, until the top of it is a faint red to expel moisture, then allowed to cool in a desiccator. Finally it is quickly weighed and placed in a bomb. As the lampblack changes in composition with the intensity and time of heating, care should be taken to heat the different portions used uniformly. Lampblack gives a quicker combustion, often of explosive violence, than acetylene carbon or sulphur. Thus far the writer has found no lampblack left in fusion with sodium peroxide.

One part of carbon requires 13 parts of pure sodium peroxide for combustion and it is best to take about 20 parts in determining the heat effect of the carbon or lampblack. For the combustion of sulphur double the calculated amount of peroxide should be used. Oxygen is often evolved in a combustion from the action of an acidic oxide on the sodium peroxide and the heat required to set it free from the peroxide is added to the observed heat. This correction, 1.73 g-cal. for  $1^{cc}$  of oxygen at 0° and 760<sup>mm</sup>, is derived from Beketoff's Na<sub>2</sub> + O = 100.26 Cal. and de Forcrand's Na<sub>2</sub> + 2O = 119.8 Cal. The writer has tested and found no carbon dioxide in the oxygen given off in considerable quantities from fusions of mixtures of sodium peroxide, an acidic oxide and lampblack.

It is best to use large quantities of substances in calorimetric determinations, not only because the errors are less, but because a large fusion remains liquid longer than a small one and hence the combustion is more likely to be complete. A mixture of 20 to 50 grams giving a heat effect of 10 to 20 Cal. answers well.

The bomb, fig. 1, is sterling silver. It is 3/32 in. in thickness. The inside diameter at the top is 15/8 in., at the bottom 14/8 in., and the length not including the top is 31/4 in. It is slightly conical for convenience in fitting the expanded top of the cup a, to make a dust-tight joint. A fusion in the cup cools more slowly than when in contact with the cold bomb and hence the reaction is more complete. The cup is fine silver and weighs 15 to 30 grams. The top and fittings are brass. The top is 23/4 in. in diameter and 5/8 in. thick



except the rim which is 1/4 in. The gasket slot in the top is 5/32 in. wide and 1/8 in. deep. It should fit the top of the bomb so that the lead gasket will not flow under pressure. The gasket is easily made by placing a disk of lead 1/25 in. in thickness on the bomb and then pressing the top into place by means of the screws. There are eight screws 5/16 in. in diameter. Four are sufficient except for high pressures. The screws should turn easily with the fingers and are best greased with tallow. A 4 in. solid wrench is a convenient one for ' tightening them. The tube b has a length of  $7 \frac{1}{2}$  in., including the screw ends. The narrow part of it is 3/16 in. external and 1/20 in internal diameter. The lower screw joint of b is made tight with soft solder, and for the upper one joining the value shown in the fig. 3 sealing wax answers. The tube c is soldered in the tapering hole in the brass top. It is shown full size in fig. 2. The insulated rod in it has a small short tube on the lower end for the plug which fastens the iron wire d of fig. 1. The upper end of the tube has a glass tube 1/2 in. in length and is packed with dental phosphate cement. The middle of the tube is filled with a flexible cement of caoutchouc and beeswax, and the rest with phosphate dental cement. To prevent the fusion, in case it is thrown against the top of the bomb, from closing the hole in the tube b, it is covered by a thick disk, e, of pure silver, which is held in place by three friction lugs. The ignition wire d should weigh at least 20 mlg. If less is taken it should be weighted with a bit of silver, otherwise the oxide formed when the iron burns will not drop off into the peroxide mixture.

The sterling silver bomb weighed when made 472 grams and after eight years' use 465 grams. The loss is due to corrosion, especially by sulphur, and to polishing. The total weight of the brass work excluding the thick top of the tube c is 397 grams. The lead gasket weighs 10 grams. The writer has two nickel-plated German silver cans for holding the water of the calorimeter. The smaller can measures 5 1/2 in. diameter, has a depth 9 1/4 in., and weighs 50.6 grams. The dimensions of the larger one are 6 1/2 in. and 9 1/4 in., and it weighs 51.2 grams.

The water equivalent of a calorimeter and can may be calculated from the specific heats of the metals in it, or may be determined by the method of specific heat. By the latter way 285 and 281.2 grams were obtained for a steel calorimeter and can; calculated 284.7 grams. The specific heat of the metals are quite accurately known, hence a calculated hydro-thermal equivalent of a calorimeter is likely to be more accurate than an experimental one. The apparatus shown in fig. 3 is designed for use in a room of varying temperature. A is made of very thin tinned iron (sheet tin) or tin foil, and B is a copper tank, holding in the annular space about 20 liters of water. It is tinned on the surface opposite A, and has one hole in the top for the stirrer, one for a thermometer and another for adding water. The



calorimeter can E is supported by the wooden ring F. The cover C is made of two semi-circular pieces of wood. The wooden parts are varnished with shellac. The rod D rests in a cup and is inclined about an inch so that the propeller will give a rotary motion to the water. The bulb G is for collecting gas that may be given off in an experiment. It has a capacity of 500 to 700<sup>cc</sup> and is connected with the bomb by a small, thick-walled rubber tube and with H by a large rubber Both rubber tubes should be securely fastened by wirtube. The lower stop-cock is large so as to allow the water to ing. flow rapidly between the bulbs. If the room and apparatus are colder than desired the latter may be warmed by a lamp flame

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against B while the water in it is stirred. When the jacket water is rapidly raised  $4^{\circ}$  or  $5^{\circ}$  it will be some time before the empty can E is warmed approximately as much. To save time E may be heated by putting into it a closed flask of hot water. If the can E is colder than the water in B when the calorimeter water is cooler than the jacket water, the temperature of the calorimeter may not rise at first and will not rise regularly for some time. And it is better not to let the water in the calorimeter remain long before a combustion on account of loss by evaporation.

Manipulation-The sodium peroxide (weighed in a glassstopped weighing bottle) and the substance to be burned are placed in the open bomb, which is at once covered with a plate glass cover to keep out moisture from the air. Then the cover is clamped to the bomb by two screws and a wooden piece with a bit of rubber under the middle of it. The ingredients are thoroughly mixed by shaking and then the cover is replaced by the top of the bomb. Before tightening the screws the air is displaced by passing about 200<sup>cc</sup> of dry oxygen\* through the tube b, fig. 1. Next the screws are carefully tightened so as not to strain them and the valve is closed. If, however, oxygen from the fusion is to be collected it is left slightly open so that gas may pass slowly. Then the bomb is adjusted as shown in fig. 3, and the required amount of water is poured into the water can. The stirrer is started and the temperature is noted each minute. When it is rising regularly the mixture is ignited by a current passing four 32 candlepower lamps. The temperature usually falls regularly after thirteen minutes and is observed six minutes longer in order to get the rate of fall. Finally the bulb containing the oxygen set free by the fusion is disconnected and the bomb opened and placed in a beaker of water. Rapid evolution of oxygen shows that the mixture contained an excess of peroxide. After the fusion has disintegrated the bomb is removed from the beaker. If an hydroxide insoluble in water is formed it is dissolved by nitric, acetic, or hydrochloric acid as may be best. If some unburned substance remains it is collected on a Gooch filter, washed with water and then ammonia to remove any silver chloride present and its weight is found. If any gas is collected it is brought to atmospheric pressure and known temperature, then the stop-cock of the bulb G, fig. 3, is closed and the rubber tubing removed. The weight of the bulb full of water, less the weight when partly filled with the oxygen collected, equals the number of cubic centimeters of the gas. The weight of the oxygen is found in the usual way.

The silver  $\operatorname{cup} a$ , fig. 1, is usually easily removed from the bomb after an experiment. Sometimes it is necessary to heat

\* Iron wire burned in air does not always ignite the peroxide mixture.

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the bomb in order to loosen it. The bomb and cup are cleaned with strong hydrochloric acid, washed and polished. The top is cleaned in the same way but does not require polishing. The silver cup is often partly melted by a sodium-peroxide combustion and a number should be provided. The top of the cup is easily expanded, if desired, by pressing it against the hemispherical bottom of the bomb.

The following experiments\* illustrate the use of the sodiumperoxide mixture:

Iron	2.550	1.754	1.754	3.000 gr	ms.
Sulphur	1.200	1.200	1.200	1.200	
Sodium peroxide	20.	$19 \cdot$	20.	22.	
Water equivalent of					
system	3080	3078	3188	4108	
Temperature interval	4.016	3.573	3.423	3·180°	
Heat effect	12369	10998	10912	13063°	
Heat effect of sulphur - "ignition	- 7905	- 7905	- 7905	- 7860	
wire	80	- 80	- 60	<u> </u>	
	4384	3013	2947	5158	
Heat effect of 1 grm. Fe	1719	1718	1680	1719	
Ferric oxide		5.403	5.115	5 <sup>.</sup> 296 gra	ams
Sulphur		1.500	1.500	1.200	
Sodium peroxide		20.	19.	20.	
Water equivalent of s	ystem	4112	4137	4149	
Temperature interval.		2.378	2.352	$2.323^{\circ}$	
Heat effect		9778	9730	9762°	
" " of S		-7860	-7860	-7860	
" " Fe wire.		-45		-45	
··· ·· ·· O <sub>2</sub> set f	ree	+80	+31	+82	
Heat effect of Fe <sub>2</sub> O <sub>3</sub> .		1953	1856	1939	
"""lgrame	of Fe <sub>2</sub> O <sub>3</sub>	361	363	366	
Pyrite FeS			4.011	4.059	
Sodium peroxic	le		24	24.	
Water equiv. or	f system _		4045	4085	
Temperature in	terval	·	3.301	3.316	
Heat effect			13352	13545	
" " of ir	on		-40	50	
F	eS,		13312	13496	
·· ·· ·· 1	grm		3318	3325	

The heats of formation of ferric oxide and pyrite may be derived from the foregoing results. The different heat effects of sulphur given in the tables were found by burning it with the two lots of sodium peroxide used.

\* This Journal, xxxvi, 55, 1913.

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# ART. III.—Hébert's Views of 1857 regarding the Periodic Submergence of Europe; by CHARLES SCHUCHERT.

THE geology of France has long been notable for the detailed subdivisions of its periods of time, and much of its terminology has been adopted elsewhere in Europe. Alcide d'Orbigny\* led the way in regard to the terminology, but Edm. Hébert appears to be the one to whom belongs the honor of first clearly pointing out that the oceans periodically but slowly and in an oscillatory manner invade the land—the more or less rhythmic and partial submergence of the continents by the oceans that is destined to give geology a determined and natural chronogenesis. Until recently the writer held that the idea of this resultant of diastrophism had its rise in Suess and Neumayr of Vienna, but the honor apparently goes to Hébert, + dating back to 1857 and thus to pre-Darwinian days. The modernism of his conclusions is striking and hence it is all the more remarkable that they have not been more clearly recognized in the standard text-books of geology. The writer now wishes to call attention to this brilliant paper by a great stratigrapher, and because there are but few copies of it in America, to present here in translation its main conclusions. The translations are by Miss Clara Mae LeVene. The first abstracts below are Hébert's conclusions in regard to some of the formational contacts of the Jurassic, and these are followed by others dealing with the delimitations of his "terrains," by which, as a rule, he means what we know as periods of time or systems of strata.

Previous to 1857, Hébert stated,<sup>‡</sup> the geologists of France held that the periods of time "were the product of epochs of calm separated by cataclysms," believing that "the animals of each period had been destroyed by immense cataclysms which, elevating the mountains, violently agitated the seas and drove them over the continents." These theoretic ideas, Hébert says, are far from true, and adds, "We can boldly state as a principle that the most absolute calm . . . is the distinctive character of the separation of the [Mesozoic] terranes" in France.

In regard to formational contacts, Hébert says :

Lias-Lower Oolite boundary.—We conclude that the physical conditions in the midst of which the sediments were

\*D'Orbigny, Cours élémentaire de paléontologie et de géologie stratigraphiques, 1849-1852. † Hébert, Les mers anciennes et leurs rivages dans le bassin de Paris, ou

† Hébert, Les mers anciennes et leurs rivages dans le bassin de Paris, ou classification des terrains par les oscillations du sol. 1º Partie, 88 pages, Terrain Jurassique. Paris, 1857.

‡ Hébert, Sur les phénomènes qui se sont passés à la séparation des périodes géologiques. Bull. Soc. Géol. de France, (2), xvi, 1859: 596-605. deposited changed in a rather marked manner at the boundary between the two epochs. The beds of the Upper Lias, with their numerous cephalopods, tell of waters which were quite deep. The disappearance of these animals at the base of the Lower Oolite, and the presence of many little polyps in the east, and of rounded pebbles in the west, indicate the nearness of the shore, or waters which were very shallow. There was, then, at the end of the Lias, in the Paris basin, an elevation of the land, and when the waters, which had become deep, were again inhabited by cephalopods, the species were entirely different (page 23).

Lower Oolite-Upper Oolite boundary.—In both east and west we find the Lower Oolite represented by an entirely similar fanna and bearing on its upper surface the traces of denudation and other phenomena indicating a time of arrest in sedimentation and an upward movement of the crust. At either limit, the millet-like oolite is an infallible horizon marker. Between the two formations, in the east, is found the Fuller's Earth, with its maximum thickness. In the west, on the contrary, the absence in the Sarthe of any kind of sediments shows that during a very considerable time—long enough for the accumulation of the thick beds of Ostrea acuminata and other fossils—the land remained emergent (31).

Great Oolite-Oxford boundary.—At the time of the Great Oolite, the seas throughout the Paris basin were constantly shallow, and it happened many times that in one place or another more or less extensive areas were raised so as to be at the level of the sea. But these partial elevations did not hinder the dominantly downward movement, as a result of which the seas rose more and more along the shore of the basin. This movement, whose origin goes back to the Trias, continued to the end of the Great Oolite, interrupted momentarily, either in a general way, as at the end of the Lias, the Lower Oolite or the Great Oolite, or in a local way, of which the Great Oolite offers us numerous examples (33).

On isostasy.—During the first half of the Jurassic [i. e., previous to the Oxfordian] the sediments that accumulated on the bottom of the basin helped by their weight to increase the depth of it [the older idea of isostatic balance]; however, this overloading could not explain the widespread sinking of the shores, accompanied by the intermittent elevations which divided the Jurassic into distinct epochs, each characterized by a particular fauna. Without doubt, although in reality this overloading did produce results which must be taken into account, it was not the principal cause of these movements of the land. That cause is more general (40).

Coral Rag-Kimmeridge boundary.—The characters of the Diceras limestone indicate a shore deposit laid down under similar conditions extending over a lapse of time of a truly prodigious duration. At the time of the deposition of the higher Astarte limestone, the conditions changed almost abruptly, although there is an alternation at the contact. The new causes which brought about the muddy sediments did not at once predominate; there was a struggle, so to speak, but the contrast is none the less striking. Without doubt, like events can be shown within the same stage; but when they are accompanied by a change of fauna as considerable as the one we have shown, there is at this horizon a line of demarcation of a certain importance (59).

On oolite formations.—Let us seek, by examining what takes place to-day in nature, to reconstruct the conditions necessary for the formation of oolitic limestones. Waters not muddy, saturated with carbonate of lime, a warm climate, abundant evaporation [now known to be due to the action of denitrifying bacteria], precipitation of lime at the surface, either around little particles of shells or sand, or even about little crystals of carbonate of lime, immense areas washed periodically by slightly agitated seas, a constant to-and-fro movement to roll the little bodies while they are being encrusted by the lime : we may figure that such conditions were maintained long enough for the accumulation of the oolites to produce masses 100 m. in thickness, not only at restricted places, as can be observed to-day in the Antilles, but over the whole extent of the Paris basin.

Then, all at once, the scene changes, the oolites disappear, the waters become dirty, deposit mud, and nourish an abundance of Panopeas, Pholadomyas, and other molluscs to which the new conditions are more favorable; and these new conditions continue until the end of the Jurassic, long enough for generations of species to succeed each other in the midst of a common fauna (66).

Secondary crustal movements during the period of emergence.—The second period of the Jurassic, which we have named the period of elevation, had for its dominant character a slow elevation of the crust which determined the progressive retreat of the sea, so that the consecutive shores which we can follow to-day with considerable exactness approach more and more the center of the basin. But just as, in the preceding period, the general subsidence of the basin was not the result of a uniform movement, but there were times of arrest and oscillation over more or less extensive areas; so, in this second period, the progressive elevation was subject to the same irregularities, as is proved by the state of the sediments of the epoch.

Thus, the Oxford is a great deposit of clay or more or less marly limestones, i. e., of sediments laid down in a state of mud in quiet waters, wherein lived great numbers of quite large cephalopods for which waters of a certain depth were necessary. That the Coral Rag, from its contact with the Oxford clay, was deposited in shallow waters, under physical conditions altogether different from those of the preceding epoch, is evidenced by the abundance of zoophytes, often in their original places of growth, by the nature of the oolites which make up almost all of its mass, by the pebbles or water-worn fossils which occur so abundantly, and by the almost complete absence in the Paris basin of cephalopods. The Kimmeridge clay, including the Astarte limestone and the Portlandian limestone, has exactly the same character as the Oxford clay. However, it is to the beginning of the Portlandian limestone that the maximum depth of seas must correspond; the end of the Jurassic, on the contrary, marked by the Portlandian oolite and subordinate beds which do not appear to have been as widespread as the preceding formations, saw very shallow waters covering no more than the center of the basin. Soon the sea withdrew completely, and the greatest depression was occupied by fresh waters, whose sediments are quite analogous to the Purbeck beds.

This progressive upward movement terminated in the emergence of the basin, which, though not a state of absolute immobility, lasted during considerable time.

It is to be noted that the same upward movement occurred not only in the basin of Aquitaine, but in the Alps and the Jura as well. There, as in the Paris basin, the Upper Jurassic beds of the Oxfordian stage are superposed, each one "in retreat" with respect to the preceding. The sea withdrew from this region at the end of the Jurassic, and the final depression was occupied by fresh waters before the time of the Neocomian, according to Lory. This shows that the Paris basin took part in a very general movement which affected the Aquitaine basin, the Jura and the Alps, i. e., almost all of France and probably a great part of Europe.

If we seek to fix exactly the secondary movements during the emergent period, we shall see that the depth of water must have increased during the whole of the Oxford clay. With the beginning of the Coral Rag, and probably also after quite a long interruption in sedimentation, the upward movement again predominated. Then appeared a considerable change of fauna without gradual transition. Thus, at the end of Oxford time there was not a polyp left in the Paris gulf; at the beginning of the Coral Rag, on the contrary, zoophytes were widely spread and the mode of sedimentary formation followed altogether different laws. During the deposition of the Coral Rag the waters remained shallow. The crust subsided at the beginning of Kimmeridge time, and another upward movement began at the end of the deposition of the Portland limestone (79-81).

*Hébert's conclusions.*—We have shown that the crustal movements were not at all peculiar to the Paris basin, but that they also affected the ancient rocks which form the circumference of the Paris depression. These movements are so coördinated that we can consider them as being part of a single great oscillation composed of two periods, one during which the crust was slowly and progressively depressed, the other during which it was raised.

Each of these periods was itself divided by secondary oscillations, because of which the land was successively lowered or raised, but in such a way that, during the first period, the sea, in each one of these secondary oscillations, finally gained some land, while, on the contrary, it lost some during the second period.

These movements of the crust had more or less influence on the distribution of the lands and waters, and consequently on the climates, and from this came the changes in the organic realm. These changes can be appreciated to-day only through the remains of marine animals which accompany the sediments of each epoch. They alone, however, are numerous enough to form a sufficient assemblage of facts.

When, as a result of this movement, the change in physical conditions was considerable, the organic modifications were profound. Moreover, it seems evident that the maximum change must correspond to the maximum elevation of the earth and the minimum to the maximum depression. The maximum elevation, when the lands are most emergent, corresponds to the moment when the sea is farthest away from the point under consideration, where there is consequently the longest absence of sedimentation; the two beds nearest to this limit are, then, those which will differ the most.

Let us apply this fact to the present case. In the Jurassic epoch there were two maxima of elevation, one at the beginning, the other at the end. To understand these better, we must investigate the movements which took place during the Triassic and Cretaceous epochs.

During the Triassic epoch, at the time of the deposition of the variegated sandstones, the eastern part of the Paris basin was a shore; the sea occupied it at the time of the Muschelkalk, and left it at the time of the variegated marls. The Triassic was, then, deposited during an oscillation of the crust, which had been depressed up to the time of the Muschelkalk, to rise again at the time of the deposition of the variegated marls. The limit between the Trias and the Lias therefore corresponds to a maximum of elevation. Our countries had been for a long time above the waters of the sea, and when the latter came to occupy them anew, either because of the lapse of time in the interval, or because of the change in physical conditions which was the result of the new order of things, there was also a considerable change in the fauna.

During the Cretaceous epoch, we see the sea again advancing more and more into the Paris basin, the Neocomian strata being deposited in the center of the depression, the Gault exceeding the limits of that stage and extending toward the Meuse, the Ardennes, Boulonnais, Bray and Normandy points that were previously out of water, although remaining a part of the Paris basin; the chloritic chalk and the tuffaceous chalk extend much further and so show that up to this time the waters were rising constantly along the shores of the basin and that they ended by breaking through completely toward the eastern border. The land was therefore more and more depressed during all this part of the Cretaceous period.

The study of the movements of the crust is useful not only for the establishment of the great divisions of the geological classification, i. e., the terranes, but no less so for the secondary divisions or stages. We see, in fact, that it is natural to divide the Jurassic terrane into two corresponding parts, one the period of depression which includes the Lias, the Lower and the Great Oolite, that is, the Lower Jurassic terrane; the other the period of elevation, which is composed of the Oxford clay, the Coral Rag, and the Kimmeridge clay, to which we should add the Portlandian limestone, that is, the Upper Jurassic terrane.

Our two periods can be subdivided very clearly with the aid of secondary oscillations, whose duration, although very short in comparison with that of the great oscillation, was nevertheless immense in each case. We have proved by a great number of facts that the limits of these secondary movements coincide exactly with those of the stages fixed by the most certain characters borrowed from the domain of stratigraphy and paleontology. In this way our stages are distinguished one from another as follows: (1) in that they each belong to a different secondary oscillation, separated from the preceding and the following one by times of arrest corresponding to an emergence of the land and consequently to a break in sedimentation; (2) in that the line of contact is in general broken, often marked by denudation, and always easy to recognize when one includes no very considerable extent of terrane; (3) in that the faunas of these stages, thus limited, differ much more from one another than happens in any other method of classification.

In each of these stages [he names six for the Jurassic] we recognize constant fossiliferous horizons in the whole basin, belonging to systems of beds often easily distinguished by their mineralogical characters, although there may not be between them sharply defined limits, either mineralogical or paleontological; these are the formations which make up the stages. Their characters depend also on the physical and mechanical conditions which presided over their deposition; they differ especially because of the variable depth of the seas, but they pass from one into another because they were formed during the same secondary oscillation. They are themselves subdivided into beds, sometimes very numerous, whose characters may be maintained for great distances, like the bed with Amm. primordialis, or may vary at neighboring points. This fourth method of division, however, although indispensable for local descriptions, cannot enter into the classification of a more extended area.

# ART. IV.-Lawson's Correlation of the Pre-Cambrian Era; by Alfred C. Lane. With Plate I.

A. C. LAWSON has recently issued an addition to his important contributions to "The Correlation of the Pre-Cambrian Rocks of the Region of the Great Lakes" \* which, written in his usual clear and forcible style, with a table of correlations, herewith reproduced modified so as (Plate I) to show my views, is an admirable basis for showing just how and why he differs from many of the others of us who are familiar with the problem.

He assumes that in a region extending from the Adirondacks to the Rainy Lakes, there were two and only two Post-Keewatin periods of batholitic intrusions of granite. With each period there are supposed to go the usual pegmatites, aplites and other dikes, and products magmatic differentiation. That the Keweenawan red rocks would be a third period if they were batholitic, he grants, but assumes that they are ordinarily easily distinguishable from the earlier granites. The Embarrass granite and the ægirite syenite of the Mesabi range, and other cases that seem to contradict his fundamental hypothesis, he might therefore dispose of by saying that these are really exceptional Keweenawan intrusives. Indeed I do not doubt that this is at times a fair explanation. For instance, in the original Animikian slate of Thunder Bay, not far from Loon Lake, is a coarse tourmaline-bearing granite, which some might assoclate with the Presque Isle granite of Michigan, but which I can well believe to be Keweenawan.

Now it may at once be granted that it will be rarely if ever that one will find direct proof in one place of three batholitic granitic invasions. Such invasions alter and shatter the strata too much to leave clear records of the earlier assaults after two later have swept over a region. After double granitic invasions strata of almost any age might be taken for Keewatin. What with the explanation that occasional granites are Keweenawan, and the difficulty of disproving that strata thrice invaded by granite are not Keewatin, it will be hard to prove in a coercive way that his fundamental hypothesis is wrong.

Nevertheless, every case of granite-cutting strata, supposed by Lawson to be later than his later granitic Algoman Revolution, weakens his scheme of correlation.

The facts then of an aplitic dike cutting the Virginia slate, of granite intrusions, like the Embarrass granite, into the Mesabi Range, + Biwabik and later formations, as Wolff and

\*University of California Publications, Bulletin of the Department of Geology, vol. x, No. 1, pp. 1-19, April 27, 1916. †See the October Bulletin of the American Institute of Mining Engineers,

p. 1766.

Allen and Barrett agree as well as Leith and I, and of granite dikes in the Thunder Bay iron formation, make Lawson's hypothesis of less working value.

In the second place, in order to construct his correlation table with only two periods of granitic intrusion he has to correlate Allen's Presque Isle granite with his Algoman granite, and quite disregard Allen's own correlations.\*

In doing this he seems to have accepted without question Allen's work on the eastern Gogebic Range, but assumes that because in his recent able reports Allen has confined himself, except in his correlation tables, pretty much to Michigan, (his own "bailiwick" p. 4) he was not therefore an authority worth considering outside. As a matter of fact I first met Allen in the original Animikie Region near Loon Lake,--he has visited Canada more than once, has written a report for the Ontario Bureau, and his correlation of the Animikie slate of Thunder Bay and the Mesabi with the Gogebic Tyler slate is not a mere echo of the universal opinion of previous writers, but is the deliberate opinion of one familiar with both. If that correlation holds Lawson's scheme falls. Apparently for that reason he rejects it (loc. cit. p. 15), for he accepts Allen's conclusion that the Tyler slate and Ironwood formation of the Gogebic Range is earlier than the Presque Isle granite, and believes in spite of all the facts stated by Leith (and Allen and myself) that the Animikie slates are not cut by granite. Otherwise he thinks his hypothesis would not work. I had rather assume, if I were he, that the granites by which they are cut are Keweenawan.

Why should one imagine, however, that in a region over 1500 miles long, during a time when there were, even according to Lawson, at least three unconformities and seven series of rocks of different character and considerable thickness, only two periods of granite intrusion, especially when Leith and Allen and so many of us who know the ground say there are more? Is it not generally true that in every period of mountain building and igneous intrusion one will find somewhere at the core of the mountain uplift granitic batholitic rocks? I will not go into the question recently raised as to the age of the granite at the Creighton Mine near Sudbury, since I really believe that Lawson favors this hypothesis because with his scientific and unifying mind he wants some wide basis for correlation when fossils fail, not because it is inherently very probable, certainly not because it fits the facts very well, but "faute de miėux."

\*See R. C. Allen and L. P. Barrett, "A revision of the Sequence and Structure of the Pre-Keweenawan Formatione of the Eastern Gogebic Iron Range of Michigan," Journal of Geology, xxiii, Nov.-Dec., 1915; also Pub. 18 of the Michigan Geological and Biological Survey. I have not tried to give full references as Allen and Lawson give them. But if there was the wide continental glaciation for which Coleman and Howe have argued, or if there was a progressive change in the composition of the atmosphere and the ocean recognizable in the character of the rocks as I have argued, these are of as wide range as his granites can be.

Let me then call attention to certain features of Lawson's correlation table.

(1) Outside the Couchiching (which occurs in only one of the 15 columns, and part of which as originally defined he no longer so classes) the oldest formation is the Keewatin, a formation largely of volcanics and volcanic sediments, and markedly devoid of rocks that show primary oxidation (red) or carbonaceous slates, or that concentration of certain elements which Russell has emphasized as one of the great processes of geology and weathering under present conditions. On the whole they deserve the name "Greenstone schists" applied to them by Irving and Williams.

(2) The next formation above does show such concentrated rocks,—quartzites largely composed of  $SiO_2$ , and limestone in which Ca and Mg are concentrated.

(3) The Grenville limestone formation or dolomite, before his first "Laurentian granite gneiss," never occurs in the same column with the eo-Huronian series (or as he calls it, Bruce limestone and dolomite) which comes just after.

There is, therefore, no apparent reason why they might not be the same, if his Laurentian granite is not all of the same time of intrusion, and the Grenville limestones might then be the metamorphic or "granitized" Kona and Bruce dolomites.

(4) Similarly in but two of his 15 columns, Vermilion Lake and Marquette, do we find "Iron Formation" before and after the Algoman granite. And as I have said, to my knowledge, granite does cut the slates he classes as Animikian, in the Thunder Bay and Mesabi ranges. Therefore we are compelled to ask if the separation, for the sake of his theory, of the Virginia and Tyler slate, which all the rest of us correlate, and which seem lithologically and structurally to be two sides of a synclinal, is not an unwarranted divorce.

(5) In all cases there is an extensive slate formation at the very top just under the Keweenaw formation.

(6) Widespread through the region are intrusives or effusives of basaltic magma. And these volcanics except toward the Adirondacks are the latest to occur, and do not cut any rocks that contain any characteristic fossils of the Paleozoic. But these first Paleozoic fossils are Upper Cambrian.

These Keweenawan volcanics appear, therefore, to be deposited during a period of uplift that may have begun before the Olenellus fauna, but certainly lasted (here I am glad to agree with Lawson) into the Paleozoic. When now we use his table (Plate I) and draw lines that express these lithologic correlations, we express the correlations that have been worked out stratigraphically by direct observations in the field, full as well as does Lawson.

Is there an explanation for this lithologic succession which will make it more than a mere accident? It seems to me so. In the first place the source of the oxygen of the atmosphere of which we are sure is the decomposition of carbon dioxide, CO<sub>2</sub>, by means of organisms. Analyses of pure volcanic emanations, of gases given off by igneous rocks in vacuo, and of meteorites, while they show oxides of carbon show no free oxygen, and it is hard to see why it should occur, or, if a little did wander in from empty space, how it could accumulate in the presence of the oxidizable crust of the earth and sunlight and water. Only three hundred feet or so of basalt oxidized as the Medford diabase has been would use up all the oxygen of our present atmosphere. It is, therefore, reasonable to assume that in azoic time there was no atmosphere largely of oxygen. Rocks accumulated under such an atmosphere would be green rather than red as indeed the Keewatin rocks are. Under such an atmosphere the volcanic emanations that went with the volcanic eruptions that are such a dominant feature of the Keewatin could accumulate in the ocean chlorides, not merely of line and magnesium and sodium, but of ferrous iron as well, and though these bases were liable to be precipitated as carbonates considerable quantities might remain in solution as bicarbonate.

On the whole the Keewatin "greenstone schists" are the kinds of rock that we might expect under this hypothesis. Will it not be less hard to explain the occasionally reported exceptional black slates or iron-bearing formations as forerunners of later formations, or as blocks of later formations whose stratigraphic relations have been misunderstood owing to early faulting before the rocks were buried, deeply folded, and metamorphosed, than for Lawson to explain away his difficulties? Good geologists of wide experience have told me flatly that the Keewatin does not contain carbonaceous beds. My experience agrees.

When, however, organic life entered it would naturally be in lower forms like the diatoms, algæ and stone worts. Such life could precipitate the bicarbonates as carbonates, even as Chas. A. Davis has pointed out that at present the thick deposits of "marl" (a nearly pure limestone dough) are formed in the lakes of Michigan and other regions. Thus deposits of cherty iron carbonate and ferrodolomite, and the Grenville limestone would be formed, while at the same time such organisms could be splitting up the CO<sub>2</sub> of the early atmosphere into hydrocarbons and oxygen, supplying a certain amount of oxygen to the air, making way for normal air-breathing animals, and for carbonaceous deposits like some of the graphite in the Grenville limestone, and for oxidized deposits of hematite banded jaspilite.

For a time the early ocean might remain as acid as iron chloride is, and in such an acid or fresh ocean no animals would tend to secrete hard parts until the concentration of salts reached and passed the optimum for some cell activity, when the extra lime would be secreted as a pathological reaction. They would be jelly-like (colloidal) and this would be a Collozoic age,\* but for that very reason might easily and rapidly evolve in various directions.

But while the azoic waters might have been as acid as condensed volcanic emanations would naturally be, they need not have been, even apart from the work of organism. For while the volcanic emanations are acid, volcanic rocks are alkaline, and if exposed to an atmosphere containing CO, would furnish, just as they do now, sodium carbonate and silicate and other alkalines which react with the earthy chlorides of the ocean and accumulate sodium chloride, while the earthy carbonates are thrown down. This goes on now by means of organic life but might go on without it, so that deposits of carbonates might take place even in azoic time. Whether they would take place would depend upon the relative importance of volcanic emanations and volcanic leachings. It seems as though the scarcity of carbonate formations in the Keewatin indicated that volcanic emanations had kept ample pace with the contributions from erosion, though of course + under the pressure of an atmosphere of CO<sub>2</sub> a much larger amount of (Ca, Mg, Fe, etc.) CO, would remain in solution than at present. With the major unconformity that in most places separates the Keewatin from the next overlying formation, however, there must have been a great increase in the rate at which alkaline carbonate was applied to the ocean water. The next formation has quartities that show the effect of leaching and sorting. There are signs of fossils, but the Atikokania lawsoni has not much more structure than a "marl biscuit" made by Schizothrix and may be of similar nature. We have the "Urkalk"-

\*Collozoic is a synonym for Huronian, or Eozoic, nearly, denoting the stratified rocks before the Cambrian in which the existence of life may be inferred, and connoting the supposition that the absence of ordinary fossil remains in them is due to the fact that the animals had not yet developed hard parts, (for the reason as I have supposed that the concentration of base had not passed the physiologic optimum, and the ocean water was soft or acid,) and were yet colloidal or jelly-like.

† The most recent work being that of Johnston, Jour. Am. Chemical Soc., May, 1916, p. 975. the Grenville—Kona dolomite, Randville dolomite, Bad River limestone, which may be a witness to the dominance of forms of vegetation not higher than the Chara.

But this vegetation might rapidly change the atmosphere from one of  $\dot{CO}_2$  to one containing largely oxygen. There is no little graphite in the Grenville, the thickness frequently assigned to it is almost incredible, and the carbon in 100 feet of a limestone with 3 per cent of C would turn our whole atmosphere back into  $CO_2$ .

Not until we get above the "Urkalk" do we find really red quartzite or red rocks that seem to have been originally such or an iron formation that seems to be no leached carbonate or secondary thing, but a primary precipitate formed as suggested by Leith and Mead's experiments when iron chloride or sulphate was broken up by sodium silicate or carbonate and oxygen into  $Fe_2O_3$ ,  $SiO_2$  and NaCl, etc. In the typical jaspilite or banded iron formation the ratio of  $Fe_2O_3$  to  $SiO_2$  is just about that required by such reactions between water-glass and ferrous chloride. But as this reaction went on, the iron accumulated under a non-oxidizing atmosphere would be disposed of, and would be very unlikely to accumulate in such quantities again. The Huronian is as widely associated with iron ore as the Carboniferous with coal. Never again was there an iron ore formation on a world-wide scale.

Not until the air was cleared of most of its  $CO_2$  (as the red character of the Keweenawan shows it then certainly was) and not until the sea was cleared of its ferrous salts, was the world ready for a wide spread of those living forms which may have existed and evolved in nooks and corners, in lakes and rivers, devoid of the hard parts, which were simultaneously evolved in many lines, when the salinity of mother ocean became such as to produce them as a physiological reaction.

Have we not in the correlation of: (1) The ferrous unconcentrated Azoic; (2) The calcareous concentration and precipitation by the first vegetable life; (3) The precipitation of the iron by the oxygenated atmosphere produced by the first vegetable life; (4) The precipitation of skeleton and shell by protoplasm when oceanic concentration reached the point when it became physiologically and chemically necessary,—criteria for Pre-Cambrian or Collozoic Correlation which are more rational à priori and fit the facts full as well as the hypothesis of two and only two granite invasions?

I do not wish to slur over the fact that iron-bearing formations have been found in rocks assigned to the Keewatin and that other objections may be raised, one by one writer one by another. I would only say that they seem to me less difficult to surmount than Lawson's difficulties. In so far, for instance, as an iron formation is due to the alteration of cherty carbonate it might well be formed in azoic. But I have already pointed out that it is extremely easy to include in the azoic masses of rock faulted into it before the whole series was metamorphosed or invaded by granite. And after all, while correlations may differ, it will be found pretty generally that writers have some "greenstone" formation below their jaspilite formation even when they do not class this latter as Huronian.

Nor do I wish to imply that it is at all necessary to adopt all the above suggestions if one rejects Lawson's interesting hypothesis. I have pointed out: first, that Lawson's hypothesis meets fatal objections in the facts (if they are such) presented by other geologists quite as familiar with them as he, whose testimony he is quite willing to accept when it does not conflict with the hypothesis; and secondarily only, that the advantages which it seems to me led him to favor this hypothesis may be obtained by an hypothesis that I favor. But there is no necessary connection between the two hypotheses, so that one or the other must be true. Both might be false, and the best basis of correlation yet awaits exposition.

Barnum Museum, Tufts College, Mass.

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Colle	AN ERA HU	BRUCE (Epoch, Series)		Steeprock Series Volcaaics, lim <u>eston</u> e (fossils), quartzite, conglomerate	Early	(algal?)	limestône		Bad River li <u>mestoae,</u> Sunday quartzito	Randvillo d <u>olom</u> ite, Sturgcon quartzito	Quartzite Raadville dolomite, Sturgeoa quartzito	Wewe slate, Koaa dolomite, Mesaard quartzile	Bruco Sofies Quarizite, h <u>mestono,</u> graywacko, limestono, conglomerato, q <del>ilartzite</del>				
	E	PILAURENTIAN INTERVAL	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Mojor unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity	Major unconformity
	Z [1/	AURENTIAN, REVOLUTION	Granite guelss	Granilo gneiss	Grantle gnetss	Granite gneiss	Granito gneiss	Granile	Grantte gneiss	Granito gneiss	Granito gneiss	Granito gnelsa	Granito gnetas	Granitoj	Granito gneiss	Granito gnoiss	Grantio gneiss
		GRENVILLE (Epoch, Series)												Grenville Qimesco	ne metam.	Greavilla	Grenvillo
010	NTARLAS	WEEWATIN TO (Epoch, Series)	Krewatin	Kcewalia	Keewatin	Keewatin	Keewatin	Keewatia	Keewntia	Greenstone schists.	Keewatia	Keewatia	Keewnlin	Keewalin	Keewalin	Keowalin	an a
Az	°	Courcentening (Epoch, Series)	Contchiching						no aria	ginal red formatic	ns, nor great	chance conc					

## Lawson's correlation of the precambrian on the basis of two and only two granitic invasions marked to show the lithologic correlation

\* Adams (Problems of American Geology, p. 62) takes exception to placing the Laurentian and Algoman granites in the sequence of formations on the ground that they are intensive masses and not members of the stratigraphic succession. It may be urged, however, that the sequence is chromological as well as stratigraphic and in the standard scale we need a term for these two periods of hatholithic development. Perhaps the terms Laurentian Revolution and Algoman Revolution used in the tahuation will meet the objection.

Authorities for the sequence shown in each of the columns of the tabulation :

I and II.--Lawson, Geol. Survey of Canada, Mem. 28, 1912; Mem. 40, 1913; Cong. géol. internat. X11, 1913.

III --Smith, Out. Bur. Mines, 14, 1, 1905. Silver, Ont. Bur. Mines, 15, 1, 1906. Parsons, Cong. géol. internat. XII, Guide Book 8, 1, 1913. III, IV, V. VI, VII, X.-Van Hise and Leith, U. S. G. S. Mou. 52, 1911

VII, VIII, X.-Allen and Barrett, Journ. Geol., vol. 23, 1915.

X1, XII, XIII.-Collins, Geol, Survey of Canala, Mus. Bull. no. 8, 1914, 22, 1916.

XIV.-Miller and Knight, Ont. Bur. Mines, 22, 2, 1911.

XV,-Cushing, this Journal, vol. xxxix, 1915.

C

+ Pebbles in Temiskaulan.



# ART. V.—A Table for Linear and Certain Other Interpolations on Spectrograms; by H. E. MERWIN.

#### METHOD.

In the accompanying table each wave-length,  $\lambda$ , has a definite value for each value of a quantity, n'. On a spectrogram  $\lambda$ for each line has a corresponding value of d, where d is the distance of the line from some chosen line. The relation of the values of n' and d for the same  $\lambda$  is represented more or less approximately by the linear expression  $d_{\lambda} = Kn'_{\lambda} - R$ , where R and K are constants determined for each spectrogram (see equation 8a).

There are three cases to consider: I. Deviations from this linear equation are within the limits of observational error; II. Deviations are small but not negligible; III. Deviations are so large that a plotted deviation curve does not give accurately the required corrections. However, case III can be modified easily so as to come under case I or II.

Case I.—The equation is solved for K and R by using d and n' for the wave-lengths of two comparison lines near the extremities of that portion of the spectrogram to be studied. Then for other values of d values of n' are calculated, and the corresponding wave-lengths read from the table, I.† Values of  $\lambda$  thus obtained agree with values known from other comparison lines on the spectrogram.‡

Case II is like case I except that values of  $\lambda$  for intermediate lines deviate slightly from true values, but the deviations fall on a smooth curve from which proper corrections can be read. This case applies to most work with quartz spectrographs. The deviations are at most a small fraction of the length of the spectrogram, about  $\pm 2$  per cent, even in the extreme case that the whole spectrum ( $\cdot 2$  to  $\cdot 8 \mu$ ) is taken on one plate and lines near the ends are used as standards.

Case III is like case II, but the deviations are too large to handle accurately if the table is used as it stands. But, instead of reading from the table n' corresponding to  $\lambda$  of the spectro-

\*  $n' = \frac{\cdot 01}{\lambda^2 - \cdot 01} - \cdot 01 \lambda^2$ , where  $\lambda$  is expressed in  $\mu$ .

† The table is used like a logarithm table, except that differences are subtracted instead of added.  $\lambda$  corresponds to the number and n' to the log. Thus for  $\lambda = \cdot 18372 \,\mu$ ,  $n' = \cdot 42066$ . The change in scale at  $\lambda = \cdot 33 \,\mu$  should be noted.

 $^{+}$  A plate from a large Hilgar quartz spectrograph size (d) was accurately represented over its entire range,  $^{-}$  4600 to  $^{-}$  30000  $\mu$  of the table.

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**4**9

gram, we read n' for  $\lambda + k$ , where k is small compared with  $\lambda$ . Then the equation is written  $d_{\lambda} = K'n'_{\lambda+k} - R'$  (see equation 8b). The value of k depends upon the type of spectrograph, and in some cases upon the part of the spectrum photographed. The relative positions of the lenses and the photographic plate with respect to the prism seldom if ever affect the deviations sufficiently to necessitate a change in the value of k. Therefore k can be found once for all for a given spectrograph. k can be evaluated in a few minutes by trial and error, by selecting such values of  $\lambda + k$  as will make the deviation for some central line nearly zero. (If the spectrogram includes wave-lengtbs longer than  $\cdot 33 \mu$ , then k need not be determined closer than  $\cdot 01 \mu$ .)

When k has been determined it may be added to the values of  $\lambda$  at the margin of the table, and  $\lambda + k$  written in place of  $\lambda$  in the table. The transformed table can then be used as in cases I and II. For a certain flint glass spectrograph  $k = .09 \mu$ , and for a small quartz spectrograph  $k = -.02 \mu$ .

If great dispersion is obtained by means of a train of prisms the table may not be carried to a sufficient number of figures. A suitable table can, however, be written easily in the same way this table was written.

The departures of the true values of  $\lambda$  from those obtained by means of the linear equation and the table are less than the departures from Cornu's (or Hartmann's) formula.

Suppose there are so few comparison lines (less than 4 or 5) on a spectrogram that a sufficiently accurate departure curve cannot be made. By means of the table a much more accurate interpolation can be made by using the table and the following formula<sup>\*</sup> than can be made by means of Cornu's formula. Suppose we have  $\lambda_1, \lambda_2, \lambda_3, d_1, d_2, d_3$  for 3 lines, we read from the table  $n'_1, n'_2, n'_3$  corresponding to  $\lambda_1$  etc., and write

$$\frac{d_{s} - d_{1}}{n'_{s} - n'_{1}} = \mathbf{N} = \frac{d_{2} - d_{1}}{n'_{2} - n'_{1}} + \mathbf{C}(d_{s} - d_{2})$$

and solve for C.

Then put  $d_4$  (known) and  $n'_4$  (unknown) in place of  $d_2$  and  $n_2$  and we have

$$n'_{4} = n'_{1} + \frac{d_{4} - d_{1}}{N - C(d_{3} - d_{4})}.$$

Finally read off  $\lambda_4$  corresponding to  $n'_4$ .

\*See J. Wash. Acad. Sci., iv, 467, 1914.

λ	. 0	1	2	3	4	5	6	7	8	9	Diff.
·180	·44 610	539	467	396	325	254	184	113	042	$\overline{9}\overline{7}\overline{2}$	72-70
1	$\cdot 43 902$	832	763	694	624	555	486	417	349	280	70-68
2	·43 212	144	076	008	$9\overline{4}\overline{0}$	$\overline{8}\overline{7}\overline{4}$	$\overline{8}\overline{0}\overline{7}$	$\overline{7}\overline{4}\overline{0}$	$\overline{6}\overline{7}\overline{4}$	$\overline{6}\overline{0}\overline{7}$	68-66
3	•42 540	473	407	341	275	210	144	079	014	$\bar{9}\bar{4}\bar{9}$	66 - 65
4	•41 884	820	755	691	627	563	499	435	371	$\frac{308}{2}$	65-63
5	.41 245	182	120	057	995	932	870	808	746	684	63-62
6 17	*40 622		000	439	378	$\frac{317}{577}$	200	190	$\frac{130}{540}$	074 757	61 - 60
0	·40 014	994	890	830	120	191	028	015	040 555	481	00-09 58 57
0	-38 843	786	729	673	616	559	503	447	300	334	57-56
•100	.90 970	999	1.6~	110	010	001	515	201	555	501	56 55
190	-27 726	672	618	564	510	456	9±0 403	340	000 905	241	54-59
2	•37 188	135	010	029	976	923	871	818	765	713	53-52
ã	·36 661	610	558	506	455	403	352	300	249	198	52-51
4	36 147	096	045	$\bar{9}\bar{9}\bar{5}$	$\overline{9}\overline{4}\overline{5}$	891	841	$\overline{7}\overline{9}\overline{4}$	$7\bar{4}\bar{4}$	$\bar{\bar{6}}\bar{9}\bar{4}$	51-50
5	·35 644	594	544	495	446	397	348	299	250	201	50 - 49
6	·35 153	104	056	008	$\bar{9}\bar{6}\bar{0}$	$\bar{9}\bar{1}\bar{2}$	$\overline{8}\overline{6}\overline{4}$	$\bar{8}\bar{1}\bar{6}$	$\overline{7}\overline{6}\overline{8}$	$\overline{7}\overline{2}\overline{0}$	49 - 48
7	$\cdot 34 673$	625	578	530	483	436	389	$\underline{343}$	296	249	48 - 47
8	$\cdot 34 203$	156	110	064	018	972	926	880	834	788	46 - 46
9	33 743	697	652	607	562	517	472	427	382	337	46 - 45
-200	·33 293	249	205	161	116	072	028	984	$94\bar{0}$	896 -	45-44
1	·32 853	809	766	723	680	637	594	551	508	465	44-43
2	422	380	337	295	203	211	168	126	084		43-42
3 1	·52 001	909 5417	918 506	876	830 496	793	792	205	670 964	629	42-41
4 5	·31 184	144	104	064	420	985	945	<u>908</u>	867	897	40-39
6	$\cdot 30788$	749	710	671	632	593	554	515	477	438	39-38
7	400	361	323	284	246	208	170	133	095	057	39-38
8	·30 019	$\overline{9}\overline{8}\overline{1}$	$\bar{9}\bar{4}\bar{4}$	$\overline{9}\overline{0}\overline{\overline{6}}$	$\overline{8}\overline{6}\overline{9}$	$\overline{8}\overline{3}\overline{2}$	$\overline{\overline{7}}\overline{9}\overline{\overline{5}}$	$\overline{7}\overline{5}\overline{7}$	$\overline{7}\overline{2}\overline{0}$	$\bar{6}\bar{8}\bar{3}$	38-37
9	$\cdot 29 \ 647$	610	573	536	499	463	427	390	354	317	37 - 36
·210	$\cdot 29$ 281	245	209	173	137	101	066	030	$\bar{9}\bar{9}\bar{4}$	$\overline{9}\overline{5}\overline{8}$	36
11	$\cdot 28 923$	888	852	817	782	747	712	677	642	607	35
12	572	538	503	468	434	399	365	331	296	262	
13	$\cdot 28 228$	194	160	126	092	058	024	$\bar{9}\bar{9}\bar{1}$	$\bar{9}57$	$\bar{9}\bar{2}\bar{3}$	34
14	·27 890	857	823	790	757	724	691	658	625	592	33
15		521	494	461	429	396	364	331	299	267	90
10	·27 234	202	270	108	100	074	042	011 606	979 664	947	32
18	20 910 602	571	540	509	109	448	417	386	356	325	31
19	$\cdot 26 295$	264	234	204	174	143	113	083	053	023	30
•220	.25 993	963	934	904	874	845	815	786	756	727	00
21	697	668	639	609	580	551	522	493	464	435	29
$\tilde{22}$	406	377	349	320	292	263	235	206	178	149	~0
23	·25 121	093	064	036	008	$\overline{9}\overline{8}\overline{0}$	$\bar{9}\bar{5}\bar{2}$	$\overline{9}\overline{2}\overline{4}$	$\bar{8}\bar{9}\bar{6}$	868	28
24	·24 840	812	785	757	730	702	675	647	620	592	
25	565	538	510	483	456	429	402	375	348	321	27
26	294	267	240	$\underline{214}$	187	161	134	$\underline{108}$	$\underline{081}$	055	
27	24 028	002	.975	949	923	897	871	845	819	793	26
28	23 767	194	110	689	003	038	612	- 080 - 200	001 207	030	
~9 -000	009	404	409	400	408	000 100	006	002	070	202	0.
230	257	232	207	182	$\frac{107}{517}$	$\frac{552}{133}$	108	083	058	033	25
30	20 009 20 765	984	960 716	800	911	644	862	838 506	813	189 540	94
33	22 105 525	501	477	454	430	406	383	359	335	312	24
34	289	265	242	219	196	172	149	126	103	079	
35	22 056	033	011	988	$\tilde{9}\bar{6}\bar{5}$	$\bar{9}\bar{4}\bar{2}$	$\overline{\overline{9}}\overline{\overline{1}}\overline{\overline{9}}$	<u></u>	$\bar{\bar{8}}\bar{7}\bar{4}$	$\bar{8}\bar{5}\bar{1}$	23

TABLE I.

H. E. Merwin—Interpolations on Spectrograms.

λ	0	1	2	3	4	5	6	7	8	9	Diff.
·236 37 38	$ \begin{array}{r} \cdot 21 & 828 \\  & 603 \\  & 382 \\ \cdot 21 & 165 \\ \end{array} $	$805 \\ 581 \\ 360 \\ 142$	783 559 338	$760 \\ 537 \\ 316 \\ 100$	$738 \\ 515 \\ 295 \\ 070$	$715 \\ 492 \\ 273 \\ 057$	693 470 251	$671 \\ 448 \\ 230 \\ 015$	$648 \\ 426 \\ 208 \\ \overline{007}$	$626 \\ 404 \\ 186 \\ \bar{0}\bar{7}\bar{2}$	22
	21 100 20 951 740 720	145 929 719	908 699	100 887 678	866 657	845 636	824 616	803 595	994 782 574	972 761 554	21
$42 \\ 43 \\ 44 \\ 45$	$\begin{array}{r} 533 \\ 329 \\ \cdot 20 \ 128 \\ \cdot 19 \ 930 \end{array}$	$512 \\ 308 \\ 108 \\ 911$	$492 \\ 288 \\ 088 \\ 891$	$471 \\ 268 \\ 068 \\ 871$	$   \begin{array}{r}     451 \\     248 \\     048 \\     852   \end{array} $	$ \begin{array}{r} 430 \\ 228 \\ 028 \\ 832 \end{array} $	$410 \\ 208 \\ 009 \\ 813$	$     \begin{array}{r}       390 \\       188 \\       \overline{989} \\       793     \end{array} $	$     \begin{array}{r}       369 \\       168 \\       \overline{9}\overline{6}\overline{9} \\       774     \end{array} $	$349 \\ 148 \\ \bar{9}\bar{5}\bar{0} \\ 754$	20
$\begin{array}{c} 46\\ 47\\ 48\\ 40\end{array}$	735 543 354	$716 \\ 524 \\ 335 \\ 150$	$696 \\ 505 \\ 317 \\ 122$	$677 \\ 486 \\ 298 \\ 112$	$658 \\ 467 \\ 279 \\ 005$	$639 \\ 449 \\ 261 \\ 077$	$620 \\ 430 \\ 242 \\ 058$	$600 \\ 411 \\ 224 \\ 040$	$581 \\ 392 \\ 205 \\ 021$	$562 \\ 373 \\ 187 \\ 003$	19
		$   \begin{array}{r}     150 \\     967 \\     787 \\     609   \end{array} $	$   \begin{array}{r}     152 \\     949 \\     769 \\     591   \end{array} $	$   \begin{array}{c}     113 \\     931 \\     751 \\     574   \end{array} $	913 733 556	895 715 539	$877 \\ 698 \\ 521$	$859 \\ 680 \\ 504$		$823 \\ 645 \\ 469$	18
53 54 55 56	$\begin{array}{r} 451 \\ 279 \\ \cdot 18 \ 109 \\ \cdot 17 \ 941 \end{array}$	$   \begin{array}{r}     434 \\     261 \\     092 \\     924   \end{array} $	$   \begin{array}{r}     417 \\     244 \\     075 \\     907   \end{array} $	399 227 058 891	$382 \\ 210 \\ 041 \\ 874$	$365 \\ 193 \\ 024 \\ 858$	$347 \\ 176 \\ 008 \\ 841$	$330 \\ 159 \\ \bar{9}\bar{9}\bar{1} \\ 825$	$     \begin{array}{r}       313 \\       142 \\       \overline{974} \\       808     \end{array} $	$     \begin{array}{r}       296 \\       125 \\       957 \\       792     \end{array} $	17
57 58 59	776 613 452	$759 \\ 596 \\ 436$	$743 \\ 580 \\ 420$	727 564 404	710 548 388	$694 \\ 532 \\ 372$	$677 \\ 516 \\ 357$	$662 \\ 500 \\ 341$	$645 \\ 484 \\ 325$	$629 \\ 468 \\ 309$	16
$^{\cdot 260}_{61}$ 62 63 64 65	$\begin{array}{r} 293 \\ \cdot 17 \ 137 \\ \cdot 16 \ 984 \\ 832 \\ 682 \\ 534 \end{array}$	$\begin{array}{c} 278 \\ 122 \\ 968 \\ 817 \\ 668 \\ 520 \end{array}$	$262 \\ 106 \\ 953 \\ 802 \\ 653 \\ 505$	246 091 938 787 638 490	231 075 922 772 623 476	$215 \\ 060 \\ 907 \\ 757 \\ 608 \\ 461$	$200 \\ 045 \\ 892 \\ 742 \\ 594 \\ 447$	$     184 \\     029 \\     877 \\     727 \\     579 \\     432     $	$     168 \\     014 \\     862 \\     712 \\     564 \\     418   $	$     \begin{array}{r}       153 \\       \overline{9}\overline{9}\overline{9} \\       847 \\       697 \\       549 \\       403 \\     \end{array} $	15
66 67 68 69	$388 \\ 245 \\ \cdot 16 \\ 103 \\ \cdot 15 \\ 963$	$374 \\ 231 \\ 089 \\ 949$	$359 \\ 216 \\ 075 \\ 935$	$345 \\ 202 \\ 061 \\ 921$	$331 \\ 188 \\ 047 \\ 907$	$316 \\ 174 \\ 033 \\ 894$	$302 \\ 159 \\ 019 \\ 880$	$288 \\ 145 \\ 005 \\ 866$	$273 \\ 131 \\ \bar{9}\bar{9}\bar{1} \\ 852$	$259 \\ 117 \\ 977 \\ 838$	14
	$\begin{array}{r} 825\\ 689\\ 555\\ 422\\ 292\\ 162\\ \cdot 15\ 035\\ \cdot 14\ 909\\ 785\\ 663\end{array}$	$\begin{array}{c} 811\\ 675\\ 541\\ 409\\ 279\\ 150\\ 022\\ 897\\ 773\\ 650\\ \end{array}$	$797 \\ 662 \\ 528 \\ 396 \\ 266 \\ 137 \\ 009 \\ 884 \\ 761 \\ 638$	$\begin{array}{c} 784 \\ 648 \\ 515 \\ 383 \\ 253 \\ 124 \\ \overline{997} \\ 872 \\ 748 \\ 626 \end{array}$	$\begin{array}{c} 770\\ 635\\ 502\\ 370\\ 240\\ 111\\ \overline{984}\\ 859\\ 736\\ 614 \end{array}$	$\begin{array}{c} 757\\ 622\\ 489\\ 357\\ 227\\ 099\\ \overline{9}\overline{7}\overline{2}\\ 847\\ 724\\ 602 \end{array}$	$\begin{array}{c} 743 \\ 608 \\ 475 \\ 344 \\ 214 \\ 086 \\ \overline{959} \\ 834 \\ 711 \\ 590 \end{array}$	$\begin{array}{c} 730 \\ 595 \\ 462 \\ 331 \\ 201 \\ 073 \\ \overline{9}\overline{46} \\ 822 \\ 699 \\ 578 \end{array}$	$\begin{array}{c} 716\\ 582\\ 449\\ 318\\ 188\\ 060\\ \overline{934}\\ 810\\ 687\\ 566\end{array}$	$\begin{array}{c} 702 \\ 568 \\ 436 \\ 305 \\ 175 \\ 048 \\ \overline{9}\overline{2}\overline{2} \\ 797 \\ 675 \\ 554 \end{array}$	13
	$\begin{array}{r} 542 \\ 422 \\ 304 \\ 187 \\ \cdot 14 \\ 072 \\ \cdot 13 \\ 959 \end{array}$	$530 \\ 410 \\ 292 \\ 176 \\ 061 \\ 947$	518 399 281 164 049 936	$506 \\ 387 \\ 269 \\ 153 \\ 038 \\ 925$	$\begin{array}{c} 014\\ 494\\ 375\\ 257\\ 141\\ 027\\ 914 \end{array}$	482 363 246 130 016 903	$\begin{array}{c} 470 \\ 351 \\ 234 \\ 118 \\ 004 \\ 891 \end{array}$	$\begin{array}{c} 458 \\ 339 \\ 222 \\ 107 \\ \overline{993} \\ 880 \end{array}$	$\begin{array}{c} 446\\ 327\\ 210\\ 095\\ \overline{981}\\ 869 \end{array}$	$\begin{array}{c} 434\\ 316\\ 199\\ 084\\ \bar{9}\bar{7}\bar{0}\\ 858 \end{array}$	12
$86 \\ 87 \\ 88 \\ 89 \\ \cdot 290 \\ 91 \\ 92$	$847 \\ 736 \\ 626 \\ 518 \\ 411 \\ 306 \\ 201$	835 725 615 507 400 295 191	$\begin{array}{c} 824 \\ 714 \\ 604 \\ 496 \\ 390 \\ 285 \\ 180 \end{array}$	813 703 594 485 379 274 170	$802 \\ 692 \\ 583 \\ 475 \\ 369 \\ 264 \\ 160$	$791 \\ 681 \\ 572 \\ 464 \\ 358 \\ 253 \\ 150 \\ $	$780 \\ 670 \\ 561 \\ 454 \\ 348 \\ 243 \\ 139$	$769 \\ 659 \\ 550 \\ 443 \\ 337 \\ 232 \\ 129$	<ul> <li>758</li> <li>648</li> <li>539</li> <li>432</li> <li>327</li> <li>222</li> <li>119</li> </ul>	$747 \\ 637 \\ 528 \\ 421 \\ 316 \\ 212 \\ 108 \\$	11

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H. E. Merwin—Interpolations on Spectrograms.

λ		0	· 1	2	3	4	5	6	7	8	9	Diff.
·293	·13	098	088	077	067	057	047	037	027	017	006	
$94 \\ 22$	$\cdot 12$	996	986	976	966	956	946	936	926	916	906	10
95 06		896	886	876	866	856	846	836	826	816	806	
90 97		698	688	678	669	659	649	640	630	620	610	
98		601	591	581	572	562	553	543	534	524	514	
99		505	495	486	476	467	457	448	438	429	419	
.300		410	400	391	382	372	363	353	344	335	325	
01		316	307	297	288	279	270	260	251	242	233	
02		224	214	205	196	187	178	168	159	150	141	
03	•19	132	123	114 092	100	090	080	077	008 675	009	000	0
05	•11	952	943	934	925	916	907	898	889	880	872	ð
06		863	854	845	837	828	819	810	801	793	784	
07		775	766	757	749	740	732	723	714	706	697	
08		689	680	671	663	654	646	637	629	620	612	
09		603	595	586	578	569	561	552	544	535	527	
-310		518	510	502	493	485	476	468	460	451	443	
11		435	427	419 995	410	402	393	385	377	368	360	
12		270	044 961	ооо 953	531 245	019 237	011 990	50% 220	294	209 204	270 196	
14		188	180	$\frac{200}{172}$	164	156	148	$140^{220}$	132	124	116	8
$\tilde{15}$		108	100	092	084	076	069	061	053	045	037	0
16	•11	029	.021	013	005	$\overline{9}\overline{9}\overline{7}$	$\overline{9}\overline{9}\overline{0}$	$\overline{9}\overline{8}\overline{2}$	$\bar{9}\bar{7}\bar{4}$	$\overline{9}\overline{6}\overline{6}$	$\overline{9}\overline{5}\overline{8}$	
17	·10	950	943	935	927	919	912	904	896	888	880	
18		873	865	807	850	842	834	827	819	811	803	
19		790	700	700	110	700	708	700	745	750	128	
*320		720	628	705	697	690	683	6/75	668 502	660 595	653	
$\frac{21}{22}$		570	563	556	548	541	534	526	519	511	504	
23		497	489	482	475	467	460	453	446	438	431	
24		424	417	409	402	395	388	381	373	366	359	
25		352	344	337	330	323	316	309	302	295	288	
26		281	275	266	259	252	245	238	231	224	217	14
28		210	200 122	190	109	182	$170 \\ 105$	108	101	104	147	.4
$\frac{20}{29}$		071	064	$1.00 \\ 0.57$	050	043	036	030	092	016	010	
*330	•10	002	001	001	000	010	00,0	000	0~00	010	000	
•33	·10	002	$\overline{9}\overline{3}\overline{4}$	$\overline{8}\overline{6}\overline{7}$	$\overline{8}\overline{0}\overline{1}$	$\overline{7}\overline{3}\overline{5}$	$\overline{6}\overline{7}\overline{0}$	$\overline{6}\overline{0}\overline{6}$	$\overline{5}\overline{4}\overline{2}$	$\bar{4}\bar{7}\bar{9}$	$\bar{4}\bar{1}\bar{6}$	68 - 62
•34	$\cdot 09$	354	292	231	172	112	053	$\overline{9}\overline{9}\overline{5}$	$\overline{9}\overline{3}\overline{7}$	$\overline{8}\overline{8}\overline{0}$	$\overline{8}\overline{2}\overline{3}$	62 - 57
•35	•08	766	710	655	601	546	$\underline{493}$	440	387	$\underline{335}$	283	56 - 52
*36 *27	.08	232	181	131	081	031	982	933	885	837	790	51 - 47
-38 -38	-07	745 206	097 253	001 911	000 160	009 197	014 086	470	426	382 565	339 555	40-43
-39	.06	885	846	807	768	$\frac{127}{730}$	692	654	617	580	543	39-37
•40		507	471	435	399	364	328	294	259	225	191	36-34
·41	•06	157	124	091	058	025	$\bar{9}\bar{9}\bar{2}$	$\frac{25}{960}$	$\frac{205}{928}$	$\frac{220}{896}$	$\frac{151}{864}$	34 - 32
$\cdot 42$	$\cdot 05$	833	802	771	741	710	680	650	620	591	562	31-29
*43		533	504	475	447	418	390	362	335	307	280	29 - 27
·44	·05	253	226	199	173	147	120	094	069	043	017	27-25
•46	-04	992 740	907 796	942	917	893	808	844	820	796	772	25-24
•47		521	499	477	455	434	412	391	370	349	328	22 - 22
-48		307	$\tilde{286}$	$\overline{266}$	245	225	205	185	165	145	125	21 - 20
·49	$\cdot 04$	106	086	067	048	029	010	$\overline{9}\overline{9}\overline{1}$	$\bar{9}\bar{7}\bar{2}$	$\overline{9}\overline{5}\overline{4}$	$\overline{9}\overline{3}\overline{5}$	20 - 18
•50	.03	917	898	880	862	844	826	808	791	773	755	18-17
.51		738	721	704	687	670	653	636	619	603	586	17 - 16

H. E. Merwin-Interpolations on Spectrograms.

λ	0	1	2	3	4	5	6	7	8	9	Diff.
$\cdot 52$	·03 570	553	537	521	505	489	473	457	442	426	16-15
.53	410	394	379	364	349	334	319	304	289	274	15 - 14
•54	259	244	230	216	201	187	172	158	144	130	15 - 14
.55	$\cdot 03 116$	102	088	075	061	047	033	020	007	$\overline{9}\overline{9}\overline{3}$	14 - 13
$\cdot 56$	$\cdot 02 980$	967	954	941	928	915	902	889	876	863	13
.57	851	838	826	813	801	789	776	764	752	740	
.28	727	715	703	691	680	668	656	644	633	621	12
$\cdot 59$	610	599	587	575	564	553	542	531	519	508	
.60	497	486	475	465	454	443	432	421	411	400	11
.61	390	380	369	359	349	338	328	318	307	297	
$\cdot 62$	287	277	- 267	257	247	237	227	218	208	198	10
$\cdot 63$	188	179	169	160	150	140	131	121	112	102	
$\cdot 64$	093	084	075	065	056	047	038	029	020	011	
.65	$\cdot 02 \ \ 002$	$\overline{9}\overline{9}\overline{3}$	$\bar{9}\bar{8}\bar{4}$	$\overline{9}\overline{7}\overline{6}$	$\overline{9}\overline{6}\overline{7}$	$\overline{9}\overline{5}\overline{8}$	$\bar{9}\bar{4}\bar{9}$	$\bar{9}\bar{4}\bar{1}$	$\bar{9}\bar{3}\bar{2}$	$\bar{9}\bar{2}\bar{3}$	9
$\cdot 66$	$\cdot 01 914$	906	897	889	880	872	863	855	846	838	
-67	830	822	813	805	797	789	781	772	764	756	
$\cdot 68$	748	740	732	724	716	708	701	693	685	677	8
$\cdot 69$	669	661	653	646	638	631	623	616	608	601	
.70	593	586	578	571	563	556	549	541	534	527	
.71	520	513	506	498	491	484	477	470	463	456	
.72	449	442	435	428	421	414	407	400	393	386	7
.73	380	373	366	359	352	346	339	332	326	319	
.74	313	306	299	293	286	280	273	267	260	254	
.75	247	241	235	228	222	216	209	203	196	190	
.76	184	178	172	165	159	153	147	141	135	129	
.77	123	117	111	105	099	093	087	081	075	069	6
.78	063	057	051	045	039	033	027	022	016	010	
$\cdot 79$	$\cdot 01 \ 004$	$\overline{9}\overline{9}\overline{8}$	$\overline{9}\overline{9}\overline{2}$	$\bar{9}\bar{8}\bar{7}$	$\overline{9}\overline{8}\overline{1}$	$\overline{9}\overline{7}\overline{6}$	$\bar{9}\bar{7}\bar{0}$	$\bar{9}\bar{6}\bar{4}$	$\overline{9}\overline{5}\overline{9}$	$\overline{9}\overline{5}\overline{3}$	
.80	$\cdot 00 947$	942	936	931	925	920	914	909	903	898	

## DEVELOPMENT OF THE FORMULA.

Consider a narrow beam of light bent twice in the same direction and dispersed by a very small prism and formed into a spectrum which is photographed without intervening lenses on a flat plate. Then if *i* is the angle of incidence upon the prism, *r* the angle of refraction from the prism,  $\Delta$  the angle of the prism, *n* the refractive index of the prism, *i'* and *r'* the angles of incidence and refraction within the prism,  $\beta$  the angle the emergent ray makes with the photographic plate, *d* the distance on the plate from the normal to the back face of the prism to the image of the emergent ray, A etc., constants,

Then 
$$\sin r = n \sin i'$$
, and  $i' = \Delta - r'$   
Then  $\sin r = n \sin (\Delta - r')$   
Or  $\sin r = n(\sin \Delta \cos r' - \cos \Delta \sin r')$   
But  $\sin r' = \frac{\sin i}{n}$ , and  $\cos r' = \sqrt{1 - \frac{\sin^2 i'}{n^2}}$   
Then  $\sin r = \sin \Delta(\sqrt{n^2 - \sin^2 i'} - \sin i \cot \Delta)$  (1)  
Also  $\sin r = \frac{d \sin \beta}{A}$  (2)

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Therefore 
$$d = A \frac{(\sin \Delta)}{\sin \beta} \sqrt{n^2 - \sin^2 i} - \sin i \cot \Delta)$$
 (3)

which may be written 
$$d = \frac{A'}{\sin\beta} (\sqrt{n^2 - B} - C)$$
 (4)

There are three conditions which obtain in the practical application of equation 4 to spectrograms: first,  $\beta$  is not far from a right angle (80° to 100°); second,  $n^2$  is between about 2.4 and 3.0; third, the ideal relations assumed in obtaining equation 4 are not significantly violated by the optical system of a spectrograph. Then we may write as a first approximation\*

$$\sin \beta = 1, \text{ and } \sqrt{n^2 - B} = Fn^2 - G$$
  
which gives  $d = A'(Fn^2 - G - C)$   
or  $d = Hn^2 - K$  (5)

The relation between refractive index and wave-length for wave-lengths that are freely transmitted is given by the equation

$$n^2 = a + \frac{b}{\lambda^2 - c} - e\lambda^2 \tag{6}$$

Then from 5 and 6  $d = -R + K\left(\frac{b}{\lambda^2 - c} - e\lambda^2\right)$  (7)

The quantity in parenthesis, call it n', can be evaluated and tabulated for various values of  $\lambda$  by taking the constants already known.

Then we may write 
$$d = Kn' - R$$
 (8)

That is,

$$d_{\lambda} = Kn'_{\lambda} - R \tag{8a}$$

However, as shown later, not the exact values of b, c and e, but such approximate values as are best adapted to the easy calculation of values of n' need be used. For quartz each of these constants is nearly  $\cdot 01$ . This value was used in computing the accompanying table by means of Barlow's tables of squares and reciprocals. These values of n' are so near those for flint glass that the tables may be used in interpolating spectrograms from glass prisms.

In most cases interpolations made by using formula 8 in connection with the tabulated values of  $\lambda$  and n' will be as exact as desired, especially if one or more comparison lines besides the two required for the determination of K and R are used to determine a deviation curve.

\*  $n^2 - B$  is very nearly equal to Ln - M, so that an equation, 6a, may be written d = Nn - P. The error introduced by assuming  $\sin \beta = 1$  is much larger than the error from either of the other assumptions.

But in some cases, e. g., III. ante, a second approximation is required. The resulting formula also is a straight line and is used with the same table. The second approximation is based upon the considerations which follow. The graph of n' against  $\lambda$  has gradually changing curvature. We may make use of this fact in applying formula 8 if we simply increase or decrease by the same amount all the values of  $\lambda$  along the margin

of the table. Thus in the table  $n' = \frac{\cdot 01}{\lambda^2 - \cdot 01} - \cdot 01\lambda^2$ . But

we may write  $n' = \frac{f}{(\lambda + k)^2 - g} - h(\lambda + k)^2$  and reproduce the

values of n' provided k is small compared with  $\lambda$ . Trials have shown that a small value of k is all that is required to make the deviations from formula 8 very small or negligible; f, gand h do not require evaluation.

Then 
$$d_{\lambda} = K' n'_{\lambda + k} - R' \tag{8b}$$

Formulas 8a and 8b apply to a spectrum from a single prism. If a train of prisms is used in producing the spectrogram, equation 3 is still a true equation if *i* is the angle of incidence upon the second and each succeeding prism. But *i* is not constant, as in the case of a single prism, but it decreases with  $\lambda$ . This has the effect of slightly changing the relative values of *d* and  $\lambda$ . But the changes are taken care of (if necessary) in equation 8b.

Geophysical Laboratory, Carnegie Institution of Washing

Carnegie Institution of Washington, Washington, D. C., October 9, 1916.

# ART. VI. — On the Preparation and Ionization of the Dialkylphosphoric and Benzenedisulphonic Acids; by W. A. DRUSHEL and A. R. FELTY.

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

THE acids studied in this investigation are the lower dialkylphosphoric acids of the general type  $R_2HPO_4$ , simple monobasic acids, and the three unsubstituted, dibasic, isomeric benzenedisulphonic acids of the formula  $C_6H_4(SO_3H)_2$ . Ionization measurements of only one of the dialkylphosphoric acids have been reported in the literature.\*

Preparation of materials.—(a) The dialkylphosphoric acids and their alkali salts. For making conductivity measurements the free dialkylphosphoric acids and their sodium salts were The trialkyl phosphates<sup>†</sup> were prepared by the action used. of the proper sodium alcoholate upon phosphorus oxychloride in the presence of ether according to the equation: 3RONa  $+ POCl_{3} = R_{3}PO_{4} + 3NaCl$ . The precipitated sodium chloride was filtered off and washed with ether. The ether was distilled off from the filtrate and the trialkyl phosphate was recovered from the residue and purified by fractional distillation, using diminished pressure for the tripropyl phosphate. The trialkyl phosphates were decomposed by concentrated aqueous barium hydroxide and the barium tetra-alkyl phosphates were purified by crystallization from water. The anhydrous barium salts dried to constant weight were decomposed by the theoretical amount of sulphuric acid, taking care to avoid an excess, and the aqueous acid solutions were exactly neutralized with pure sodium hydroxide. The aqueous solutions of the three dialkyl sodium phosphates were evaporated in platinum. The sodium salt of dimethylphosphoric acid was recrystallized and dried to constant weight at  $110-120^{\circ}$ . The sodium salts of the diethyl- and dipropylphosphoric acids could not be recrystallized but were prepared by evaporating their aqueous solutions in platinum and drying to constant weight at 140-150°. These two salts are hygroscopic and must be weighed from weighing bottles. The three sodium dialkyl phosphates were made up in N/8 solutions for conductivity work.

The dimethyl-, diethyl- and dipropylphosphoric acids were prepared for conductivity work by treating weighed amounts of the pure barium salts with the theoretical quantities of sulphuric acid and making up the solutions to the proper normality, verifying the normality of each solution by titration

> \* Van Hove, Bull. Acad. Roy. Belg., 1909, 282-294. † Limpricht, Ann. d. Chem., cxxxiv, 347, 1865.

with standard sodium hydroxide. The dipropylphosphoric acid was also prepared from the sodium salt by adding the theoretical amount of sulphuric acid, evaporating the solution on the steam bath and extracting the free acid from the residue with absolute alcohol, the alcoholic solution was diluted with water, concentrated in platinum on the steam bath and finally made up to the proper normality with distilled water. The solution was found to be free from sulphate and its normality was checked up by making a titration with standard sodium hydroxide solution.

(b) The isomeric benzenedisulphonic acids and their alkali For the preparation of these acids and their potassium salts. salts methods were chosen which give each acid and its salt entirely free from the acid or salt of either of its two isomers. This is important in the present investigation, for in order to compare the strengths of the three isomeric benzenedisulphonic acids it is necessary that each acid should be prepared entirely free from its two isomers. The *m*-benzenedisulphonic acid is the only one of the acids prepared by the direct sulphonation of benzene. When benzene is sulphonated benzenemonosulphonic, m-benzenedisulphonic, s-benzenetrisulphonic, and possibly under special conditions, a little *p*-benzenedisulphonic acid may be formed; but by properly regulating the temperature and concentration of the sulphuric acid the only products. are the monosulphonic acid, the *m*-disulphonic acid, a little excess of sulphuric acid and a trace of benzene. The benzene was removed by water, the excess of sulphuric acid as barium sulphate, and the strongly acid aqueous filtrate was then converted to the potassium salt by exact neutralization with potassium hydroxide or carbonate, and evaporation to crystallization. By a number of recrystallizations the pure potassium *m*-benzenedisulphonate was obtained in good yield, the monosulphonate tending always to remain in the mother liquor. Potassium *m*-benzenedisulphonate was readily converted into the pure acid by the following procedure. The potassium salt was dried at 200°-220° to remove the molecule of water of crystallization and the anhydrous salt was then mixed with the theoretical amount of powdered phosphorus pentachloride and warmed. After the reaction was over the mixture was treated with cold water to remove the sodium chloride formed in the reaction, the insoluble diacid chloride was filtered off, dried and purified by recrystallization from ether. The diacid chloride was obtained in quantitative yield and was converted to the acid by heating for an hour with distilled water. This acid solution was then treated with a little more than the theoretical amount of pure silver oxide necessary to remove the hydrochloric acid formed in the hydrolysis. Care was exercised

in preparing the silver oxide to wash it thoroughly and repeatedly with boiling distilled water in order to remove every trace of alkali and sodium nitrate resulting from the precipitation of the silver oxide by the action of sodium hydroxide upon a dilute hot solution of silver nitrate. The free disulphonic acid containing a little silver disulphonate was separated by filtration from the silver chloride and treated with hydrogen sulphide in excess. The precipitated silver sulphide was filtered off and the filtrate heated to boiling to remove the excess of hydrogen sulphide. The solution was tested for silver and for halogen and was found to be free from both. It was an aqueous solution of pure *m*-benzenedisulphonic acid of about N/5 concentration. The solution was standardized against decinormal sodium hydroxide and then diluted with freshly distilled water to N/8 concentration for beginning the conductivity measurements.

For the introduction of the sulphonic acid group (SO<sub>3</sub>H) into the benzene ring in positions other than meta to acid groups already in the ring several methods have been proposed. P. Klason\* acted upon the diazo salt of sulphanilic acid with alcoholic potassium sulphide to introduce sulphur in the para position to the sulphonic acid group. He obtained the potassium salt of p-thiophenolsulphonic acid (KSC, H, SO, K, 1, 4) which on oxidation with potassium permanganate gave potassium *p*-benzenedisulphonate. C. J. Blanksma<sup>+</sup> and J. J. Polak<sup>+</sup> prepared the ortho- and paranitrobenzenedisulphides by the action of sodium disulphide upon the corresponding chlornitrobenzenes. These disulphides (NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S.SC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>) on oxidation gave the corresponding nitrobenzenesulphonic acids (C, H, NO, SO, H). In 1890 the xanthate method of R. Leuckart§ was published. This was shown by Erhardt, Ruhnau¶ and others to be a general method of preparing various sulphonic acids free from their isomers. Polak,\*\* Walter++ and Armstrong and Worley ## used this method for the preparation of o- and p-benzenedisulphonic acids. None of these investigators, however, described the xanthate method with sufficient particularity to make a fair yield of the disulphonic acids possible without further experimentation. Since the disulphonic acids can be obtained entirely free from their isomers it was deemed desirable to determine more closely the

> \* Klason, Ber. d. d. Chem. Gesell, xx, 350, 1887. + Blanksma, Rec. trav. chim. Pays-Bas, xix, 111, 1900.

Polak, Rec. trav. chim. Pays-Bas, xxix, 419, 1910.
S Leuckart, J. pr. Chem., xli, 179, 1890.
Ehrhardt, J. pr. Chem., xli, 184, 1890.
Ruhnau, J. pr. Chem., xli, 184, 1890.

\*\* Polak, l. c.

++ L. E. Walter, Proc. Chem. Scc., xi, 141, 1895.

#Armstrong and Worley, Proc. Roy. Soc., xc, 86-7, 1914.

conditions which give the best yield of these acids. The xanthate method uses as starting out material in each case the corresponding amidobenzenesulphonic acid, and involves the following steps to obtain the potassium salt of the benzenedisulphonic acid: (1) diazotization of the amidosulphonic acid, (2) action of the diazo compound with potassium xanthate to form the xanthate ester, (3) hydrolysis of the xanthate ester to form the potassium salt of thiophenolsulphonic acid and its oxidation to the disulphide of potassium benzenesulphonate, and finally (4) oxidation of the disulphide to potassium benzenedisulphonate by means of potassium permanganate. The steps and conditions for the formation of the potassium o- and p-benzenedisulphonates are essentially the same, starting with o- and p-amidobenzenesulphonic acids.

Several points are of importance in carrying out the processes previously mentioned. Diazotization of the amidobenzenesulphonic acids by passing N2O3 gas through a suspension of the amidosulphonic acids in cold water is unsatisfactory since the amidobenzenesulphonic acids as well as their diazo compounds are only slightly soluble in cold water, and an attempt to diazotize in this way results merely in the superficial diazotization of the solid particles, and rarely results in the diazotization of more than 20 per cent of the amidobenzenesulphonic acid, even after passing the N<sub>2</sub>O<sub>3</sub> for several hours. The most satisfactory method proved to be a slight modification of Fischer's process. The amidosulphonic acid was treated with about an equal weight of water and to this was added a cold saturated solution of the theoretical amount of sodium nitrite, resulting in immediate diazotization with of heat, probably according to the equation: evolution  $C_{s}H_{4}NH_{s}SO_{3}H + NaNO_{s} = C_{s}H_{4}N_{s}OHSO_{3}Na + H_{s}O.$ The mixture was at once treated at room temperature with the calculated amount of concentrated hydrochloric acid with stirring. Reaction took place at once with the separation of the diazo compound:  $C_{6}H_{4}N_{2}OH.SO_{3}Na + HCl = C_{6}H_{4}N_{2}SO_{3} + NaCl$ + H.O. To make the separation of the diazo compound as complete as possible the mixture was chilled in an ice bath, then quickly filtered on a porcelain funnel with suction and washed with a little ice-water. The diazo compound was made into a thin mush with water and added in small portions to the calculated amount of potassium xanthate dissolved in about ten times its weight of water and heated on the steam bath to 65° or 70°. Vigorous reaction took place at once with copious evolution of nitrogen after the addition of each portion of diazo compound. At the temperature used the xanthate ester formed was immediately hydrolyzed chiefly to the corresponding thiophenolsulphonate. These reactions may be

expressed by the following equations:  $C_6H_4N_2SO_3 + KS.CS.OEt = C_6H_4SO_3K.SCSOEt + N_2$ , and  $C_6H_4SO_3K.SCSOEt + H_2O = C_6H_4SH.SO_3K + COS + EtOH$ . Hydrolysis was completed by evaporating the reaction mixture to dryness on the steam bath, during which process the thiophenolsulphonate was oxidized by the air chiefly to the disulphide,  $KSO_3C_6H_4S.SC_6H_4SO_3K$ .

The disulphide prepared as described always contained an orange-red dye resulting from the diazo reaction. This dye is soluble in alcohol while the disulphide is not. The disulphide was therefore purified from the dye by twice precipitating the disulphide from its saturated aqueous solution by the addition of alcohol. The trace of color still remaining could be removed later by means of animal charcoal. On oxidation the disulphide yields the corresponding benzenedisulphonate. The oxidation was best effected by the use of hot saturated aqueous potassium permanganate, which was added in about theoretical amount in small portions in the course of 20 to 30 minutes to the cold dilute aqueous solution of the disulphide. The reaction evolved considerable heat but the temperature was not at any time allowed to rise above 60°. Toward the end of the oxidation the solution retained the purple color of the permanganate for 10 to 15 minutes on the steam bath. This slight excess of permanganate was finally destroyed by the addition of a few drops of alcohol. The reaction mixture was somewhat diluted by the addition of water and allowed to stand on the steam bath until the hydrated oxide of manganese had well settled out. The oxide of manganese was then easily removed by filtration with suction and was well washed with hot water on the porcelain The combined filtrates were concentrated on the funnel. steam bath to crystallization and allowed to stand over night for the potassium benzenedisulphonate to crystallize out. If any of the reddish dye persisted at this stage it was removed by animal charcoal. The p-benzenedisulphonate was further purified by recrystallization from water. A 60 per cent yield of potassium p-benzenedisulphonate may be obtained from sulphanilic acid by the xanthate process under favorable conditions. A convenient method for the purification of the o-benzenedisulphonic acid is to convert the potassium salt into the barium salt by the action of saturated aqueous barium chloride, and recrystallization of the barium salt from hot water. This method was described by J. J. Polak.\*

The *o*-benzenedisulphonic acid was prepared from *o*-amidobenzenesulphonic acid by the xanthate method. The amidosulphonic not being obtainable in the market, it became

\* Polak, Rec. trav. chim. Pays-Bas, xxix, 418, 1910.

necessary to prepare it in the laboratory. In its preparation from aniline a few important points must be observed in order to obtain the final product in pure condition and in good yield. Several modifications were introduced into the processes described in the literature, increasing the yield and improving the purity of the products. Parabromacetanilide was prepared from aniline by a modification of Hübner's\* method. One mol of aniline, one mol of acetic anhydride and two mols of glacial acetic acid were mixed and allowed to stand until cold. To this mixture one mol of bromine was added in small portions with cooling. When the last portion of bromine was added crystals began to separate out and the mixture was immediately poured into a liter of cold water with stirring. On recrystallizing the precipitate from alcohol snow white *p*-bromacetanilide was obtained in almost quantitative yield. The *p*-bromacetanilide was converted to *p*-bromaniline-o-sulphonic acid by heating at 170°-180° with the theoretical amount of sulphuric acid of specific gravity of 2.0 in an oil bath until the acetic acid was completely eliminated, instead of heating the mixture directly over a free flame as suggested by Kreis.<sup>+</sup> In this way charring was entirely avoided and the yield was practically quantitative. The method of removing the bromine from *p*-bromaniline-*o*-sulphonic acid suggested by Kreis<sup>‡</sup> was also modified in an important point, shortening the time required and improving the quality of the product. Under the conditions described by Kreis boiling with zinc dust in alkaline solution for nine hours was found insufficient to remove completely the brownine from 60 grue. of p-bromanilineo-sulphonic acid. A 60 grm. portion of this sulphonic acid was boiled for three hours with 600<sup>cm<sup>3</sup></sup> of sodium hydroxide solution containing 15 grm. excess of sodium hydroxide and 25 grm. of zinc dust. At the end of three hours a titration of  $5^{\text{cm}^3}$  of the solution showed that over 70 per cent. of the bromine had been removed from the benzene ring. Fifteen grams more of sodium hydroxide and 10 grm. of zinc dust were now added and the boiling continued for two and a half hours, when a titration showed that the bromine was removed quantitatively from the benzene ring. In other particulars the method was carried out as described by Kreis, obtaining a good yield of pure o-amidobenzenesulphonic acid.

The *p*-benzenedisulphonic acid was prepared from its purified potassium salt by the procedure described for the *m*-benzenedisulphonic acid. The o-benzenedisulphonic acid was prepared directly from its purified barium salt by the action of the theo-

\* Hübner, Ann. d. Chem., ccix, 355, 1881.

† Kreis, Ann. d. Chem., cclxxxvi, 377, 1895.
‡ Ibid., cclxxxvi, 379, 1895.

retical amount of sulphuric acid. The purity of the three disulphonic acids was determined by converting portions of their purified potassium salts into the acid chlorides and taking the melting points of the acid chlorides\* recrystallized from ether, and by converting the acid chlorides to the acid amides and taking their melting points. For beginning conductivity measurements the three isomeric disulphonic acids were made up in N/8 solutions with freshly distilled water, and for the determination of the strengths of the acids as catalytic agents in the hydrolysis of ethyl acetate they were made up in N/10solutions. The normality of the acids was checked up in every case by making titrations with standard sodium hydroxide.

### Conductivity and hydrolysis measurements.

The apparatus used in this work was the usual conductivity apparatus, a Wheatstone bridge previously calibrated, an ordinary Ostwald cell whose constant was determined with N/50potassium chloride, an alternating induction coil with high frequency vibrator and telephone receiver, a standard plug resistance box, a pair of carefully calibrated 10<sup>cm<sup>3</sup></sup> pipettes and a thermostat kept at 25°.

(a) Ionization of dialkylphosphoric acids.—The molecular conductivities of the sodium salts of the dialkylphosphoric acids were first determined at different dilutions starting with N/8 solutions. From these measurements the values of  $\mu_{\infty}$ were determined by the method of graphic extrapolation described in Ostwald–Luther.<sup>+</sup> To obtain the values of  $\mu_{00}$ for the acids the corrected values of the sodium salts were diminished by the ionic conductivity of the Na ion (51) and increased by that of the H ion (347). The molecular conductivity of the dimenthylphosphoric and dipropylphosphoric acids were determined in this way. In attempting to dehydrate the sodium diethylphosphate slight decomposition occurred giving a value for  $\mu_{\infty}$  abnormally high. This value was therefore rejected and the value of  $\mu_{\infty}$  for the correspond-ing acid determined by Van Hove; was used. The molecular conductivities of the three homologous dialkylphosphoric acids were measured for dilutions ranging from N/8 to N/1024. The value of  $\mu_{\infty}$  for dipropylphosphoric acid obtained by the graphic method was verified by direct measurement at high dilution. The mean of the two values (389.5) was used in

\* Ortho-, 143°. Meta-, 63°. Para-, 139°. † Ostwald-Luther, Physiko-Chemische Messungen, (2d ed.), 414. ‡ Van Hove, Bull. Acad. Roy. Belg., 1909, 282-294. Van Hove determined by the conductivity method the dissociation of diethylphosphoric acid, but no previous work is reported on the dissociation of its homologues. His average value for k was  $10.03 \times 10^{-2}$ .

# Drushel and Felty-Preparation, etc., of

the calculations. From the values obtained by direct measurement and calculation the degrees of ionization of the acids expressed in per cent were found, also the affinity constants of the acids were calculated from the formula of Ostwald,  $k = a^2/(l-a)v$ . The values found for the dialkylphosphoric acids are recorded in Table I.

#### TABLE I.

A.	. Degrees of	f ionization	of dialkylpl	hosphoric aci	ds. 25°.	
Dilu- tion v	Μe μυ	e₂HPC₄ per cent dissociated	$\mu v$	t₂HPO₄ per cent dissociated	${ m P}$ $\mu v$	r₂HPO₄ per cent dissociated
8	262.6	69.3	236.8	62.2	227.2	58.25
16	292.3	77.1	274.4	72.1	266.7	68.4
32	317.0	83.7	304.6	80.0	296.9	76.1
64	335.0	88.4	328.5	86.26	325.9	83.26
128	348.0	91.85	344.7	90.51	342.0	87.68
256	356.0	93.95	354.9	93.50	354.2	88.70
512	362.7	95.7	362.5	95.20	366.1	93.86
1024	367.8	97.05	365.7	96.03	379.9	95.20
	$\mu_{\infty}$		$\mu_{\infty}$		$\mu_{\infty}$	
	379.0		379.0		389.5	
	(Graphic)	(	Van Hov	e) (388	3 - ora	phic)

B. Affinity constants of the dialkylphosporic acids. 25°.

Dilution	${ m Me_{2}HPO_{4}}$	$\mathrm{Et}_{2}\mathrm{HPO}_{4}$	$\mathrm{Pr}_{2}\mathrm{HPO}_{4}$
	k	k	k
8	$19.5 \times 10^{-2}$	$12.8 \times 10^{-2}$	$10.1 \times 10^{-2}$
16	$17.0 \times 10^{-2}$	$11.6 \times 10^{-2}$	$9.2 \times 10^{-2}$
32	$13.1 \times 10^{-2}$	$10 \times 10^{-2}$	$8 \times 10^{-2}$

(391 – direct)

(b) Ionization of the isomeric benzenedisulphonic acids.— The benzenedisulphonic acids represented by the general formula  $C_6H_4(SO_3H)_2$  are dibasic and are dissociated similarly to sulphuric acid at different dilutions into the ions  $\overset{+}{H}$ , and  $\overline{C_6H_4(SO_3H)SO_3}$ , and finally into  $\overset{+}{H}$ ,  $\overset{+}{H}$  and  $\overline{C_6H_4(SO_3)_2}$ . That is, at moderate concentration one H ion splits off and on dilution the second H ion is formed.

Considerable work has been done on the sulphonic acids of benzene derivatives, but conductivity measurements of the simple unsubstituted benzenedisulphonic acids have apparently not been previously reported. Ebersbach and Ostwald\* determined the conductivities of ortho- and meta-toluidinsulphonic

\* Ebersbach and Ostwald, Zeitschr. phys. Chem., xi, 617-8, 1893.

acids  $(C_{e}H_{2}NH_{2}CH_{s}(SO_{s}H)_{2})$  in order to ascertain the effect of the different positions of the methyl group on the dissociation of the acids. Armstrong and Worley<sup>\*</sup> studied a number of sulphonic derivatives but their work on the simple benzenedisulphonic acids was confined to the use of the three isomeric acids as catalytic agents in the hydrolysis of cane sugar in order to determine their relative strengths. They found the metaacid slightly stronger than the para-acid and both very much stronger than the ortho-acid. Our results obtained both by the conductivity method and the hydrolysis method are only partially in agreement with the results of Armstrong and Worley. Both methods of measurement gave concordant results and show the para-acid to be a little stronger than the meta-acid and both very much stronger than the ortho-acid. Our results are really in better agreement with Armstrong and Worley's structure theory for the explanation of the catalytic action of the three isomeric benzenedisulphonic acids than their results, although these acids, as shown by our conductivity measurements, require no special structure theory to explain their catalytic activity. The general ionization theory amply covers the case of the three isomeric benzenedisulphonic acids. The results of our conductivity measurements are given in Table II.

#### TABLE II

Conductivities and degrees of dissociation of the isomeric benzenedisulphonic acids. 25°.

Dilu-	C	ortho-acid	I	Aeta-acid	Par	a-acid
v	$\mu v$	dissociated	l μv	dissociated	$\mu v$	dissociated
8	$317 \cdot 2$	83.09	339.2	88.64	343 <b>·3</b>	89.47
16	329.4	86.28	351.5	91.63	353.8	92.21
32	341.3	89.39	359.3	93.66	361.6	94.24
64	351.9	92.17	367.3	95.75	370.5	96.56
1 <b>2</b> 8	361.1	94.59	374.2	97.52	$375 \cdot 2$	97.78
256	367.5	96.79	380.1	99.09	380.1	99.06
512	374.7	98.06	383.6	100.	383.1	99.84
1024	377.5	98.90			383.7	100.
2048	381.7	$100 \cdot$				
2048	381.6	100.	By single	dilution.		

(c) Catalytic action of the isomeric benzenedisulphonic acids in the hydrolysis of ethyl acetate.—The ionization of these acids as determined by the conductivity method was confirmed by using them in decinormal concentration in the hydrolysis of ethyl acetate at 25°. In order to determine positively the relative strength of the meta- and para-acids dupli-

#### \* Armstrong and Worley, l. c.

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# Drushel and Felty-Preparation of Acids.

cate measurements were made for these two acids. For the purpose of comparison hydrochloric acid in decinormal strength was also used for the hydrolysis of ethyl acetate. Titrations were made in the usual way and the constants were calculated from the usual titration formula for reactions of the first order. The results obtained with these acids are given in Table III.

#### TABLE III

Isomeric benzenedisulphonic acids as catalytic agents in the hydrolysis of ethyl acetate. Acids used in decinormal solutions at 25°.

HCl	Ortho-acid	Meta-acid	Para-acid
$10^{5}\mathrm{K}$	$10^{5}\mathrm{K}$	$10^{5}$ K	105K
64.4	67.2	(76.0)	73.8
65.0	65.2	72.4	74.8
63•3		72.2	73.7
65.4	$65 \cdot 1$	72.0	75.6
64.0	64.0	73.9	75.1
63.6		72.4	73.1
62.2	64.6	75.5	(77.3)
64.0	65.2	73.0	74.35
		72.9 duplicate	74.50 duplicate

#### Summary.

1. The lower homologous dialkylphosphoric acids may be prepared by the action of barium hydroxide upon the trialkyl esters, and the decomposition of the barium salts with sulphuric acid.

2. The degree of dissociation of the dialkylphosphoric acids decreases regularly with the increase in the molecular weight of the alkyl groups.

3. The isomeric benzenedisulphonic acids may be prepared, each entirely free from its isomeric forms, by a proper choice of methods. In this connection the xanthate method of converting amidobenzenesulphonic acids into the corresponding benzenedisulphonic acids gives good results under favorable conditions.

4. The catalytic activity of the isomeric benzenedisulphonic acids is in the order ortho-, meta-, and para-. The relative catalytic activity of the three acids requires no special explanation based upon a structure theory, but is in agreement with the general ionization theory.

# ART. VII.—On the Double Salts of Casium Chloride with Calcium and Strontium Chlorides; by George S. JAMIE-SON.

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

THE object of this work was to investigate the double salts of cæsium chloride in combination with the alkali earths metals. It should be observed that no barium double salt was obtained, but this was not surprising since barium generally shows little tendency to form double salts. Many attempts were made to obtain double cæsium alkali earth bromides, but without success.

The double salts to be described are as follows:

## 2CsCl.CaCl<sub>2</sub>.2H<sub>2</sub>O 5CsCl.2SrCl<sub>2</sub>.8H<sub>2</sub>O.

Cæsium-Calcium Chloride.—This salt was obtained readily from concentrations of 1-4 molecules of cæsium chloride to 1-4 molecules of calcium chloride.

80 grams of cæsium chloride and 40 grams of anhydrous calcium chloride were dissolved in 100<sup>cc</sup> of hot water. During the night a crop of colorless slender prisms separated. The crystals were filtered by suction, pressed thoroughly on filter paper, and allowed to stand in a desiccator over calcium chloride for about 4 hours before making the analysis. This double salt was found to be very soluble in water. After the removal of the first crop of crystals, 40 grams more of anhydrous calcium chloride, previously dissolved in 50<sup>cc</sup> of water, were added to the solution. A second crop of the double salt was obtained. Some of these crystals were 2.5<sup>cm</sup> long. Another 40 grams of calcium chloride in 50<sup>cc</sup> of water were added to the solution and a third crop of the double salt was obtained. The three preparations gave the following results by analysis:

	Calculated for 2CsCl.CaCl <sub>2</sub> .2H <sub>2</sub> O	1	Found 2	3
Н"О	7.44%			
Cl	29.34			
Са	8.26	8.43	8.46	8.60
Cs	54.96			

Cæsium-Strontium Chloride.—A solution containing 2 molecules of cæsium chloride to 1 of strontium chloride yielded the double salt. When the concentration was one molecule of cæsium chloride to one of strontium chloride, only strontium chloride crystallized, and when the concentration of the solution was in the proportion of 3 molecules of cæsium chloride to one of strontium chloride, cæsium chloride separated from the solution.

100 grams of cæsium chloride and 79 grams of crystallized strontium chloride were dissolved in about 150<sup>cc</sup> of hot water and allowed to cool slowly. After the solution had stood for some hours, a crop of very thin leaf-like crystals with a pearly luster was obtained. Two other crops of this double salt were obtained by concentrating the solution slightly each time after the previous crop of crystals had been removed.

The following results were obtained by analysis:

Calc 5CsCl.2	Calculated for 5CsCl.2SrCl <sub>2</sub> .8H <sub>2</sub> O			2	3
		$\mathbf{A}$	В		
H <sub>0</sub>	11.03%	10.66			10.88%
Cl	24.50	24.48	24.33		24.13
Sr	13.43	13.36	13.36	13.24	13.20
Cs	51.00		51.28		

The analyses agree well with the calculated formula, and as the crops were carefully examined under the microscope and appeared to be homogeneous, there seems to be no doubt as to this formula, which is unusual for double halogen salts, and which does not agree with the type shown by the cæsium calcium salt.

# ART. VIII. — Crandallite, a New Mineral; by G. F. LOUGHLIN and W. T. SCHALLER.\*

Introduction.—To the long list of unusual minerals in the Tintic mining district, Utah, which has recently been augmented by A. H. Means<sup>†</sup>, another is here added-crandallite, named after Mr. M. L. Crandall, until recently engineer for the Knight Syndicate of Provo, Utah, who did much to aid in the recent study of the district by the U.S. Geological Survey.

Occurrence.--Crandallite is a hydrated phosphate of aluminum and calcium, and has apparently resulted from the alteration of a pre-existing non-fibrous mineral similar to goyazite; (hamlinite). The new mineral was found by Mr. Loughlin in vein material on the dump of the Brooklyn mine, in the monzonite area of the district  $1\frac{1}{4}$  miles east of Silver City. The mine workings were inaccessible and only a small amount of ore was available for study on the dump. In this ore the new mineral was very scarce.

Crandallite occurs in compact to cleavable masses without distinct crystal outline, and partly fills irregular-shaped cavities in a quartz-barite ore aggregate, resting indifferently on any of these minerals and to a minor extent replacing them. The cavities, some of which are almost completely filled by crandallite, measure from a few millimeters to six centimeters in diameter. The ore minerals of the vein include principally pyrite with considerable enargite and small amounts of galena and zinc blende. The crandallite is covered by a crust of tenorite half a millimeter thick (partial analysis of impure sample gave: CuO, 80.12; H<sub>2</sub>O, 4.02; P<sub>2</sub>O<sub>5</sub>, 1.44; insol., 2.94), which in turn is coated by a film of greenish copper minerals.

According to these relations crandallite is later than the undoubted primary (hypogene) minerals of the vein, and earlier than the common secondary (supergene) minerals. So far as its composition is concerned it may be either the latest of the primary or the earliest of the secondary minerals.

The hand specimen suggests that crandallite has a platy structure, yielding smooth cleavage surfaces, but when any of

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

<sup>&</sup>lt;sup>4</sup> Means, A. H., Some new mineral occurrences of the Tintic mining district, Utah, this Journal (4), xli, 125-130, 1916.
<sup>‡</sup> The suggestion was made by W. T. Schaller (ibid., (3), xxxii, 359, 1911;
U. S. Geol. Survey, Bull. 509, p. 70, 1912) that hamlinite was probably identical with goyazite. The name goyazite (1884) has priority over the perhaps better known name hamlinite (1890); Farrington (ibid., xli, 358, 1916) has recently questioned this proposed identity. See parer in the following the follow 1916) has recently questioned this proposed identity. See paper in the following number.

these plates are crushed and examined microscopically it is seen that they are composed of fibrous aggregates, the fibers, extremely fine, being generally in radiated groups. The conclusion reached is that crandallite is a fibrous mineral, resulting from the alteration of a pre-existing mineral of similar chemical composition to which belong the platy structure and smooth cleavage surface.

Description. The exterior surface of the crandallite lining, which is about a millimeter thick, is uneven to imperfect botryoidal, but the cross sections of the lining show a distinct straight lamellar structure, the individual plates being about a fourth of a millimeter across and considerably less in thickness. The part of the lining next to the rock is compact and waxy looking whereas the last formed part of the lining seems to be more distinctly and coarsely crystallized and somewhat whiter in color. When crushed and examined under the microscope, however, the two parts appear the same and the apparent differences seen in the hand specimen can no longer be noted. The crushed fragments, observed under the microscope, have no regular boundaries and are irregular in shape with only a faint suggestion of the lamellar structure seen on the hand specimen. The new mineral on the hand specimen closely resembles a crust of very fine-grained dolomite or calcite; in thin section or in crushed fragments, with nicols crossed, a striking resemblance to some chalcedony is noted.

The color is white to light gray with shadings into yellow and brown. The streak is white. The luster is dull, somewhat greasy in the more compact, and somewhat pearly in the coarser lamellar variety. Almost opaque on the hand specimen, the crushed fragments are transparent to opaque under the microscope, the opacity being caused by minute indeterminate inclusions, many of them apparently unreplaced ore The mineral, free from any inclusions, is colorless minerals. and transparent in thin pieces. The cleavage on the hand specimen is distinct and the cleavage faces have a decidedly pearly luster. The direction of the cleavage is basal, such fragments, which are unaltered, being isotropic and yielding a uniaxial positive interference figure. This basal cleavage is believed to be the cleavage of the original mineral (goyazite?), whose alteration has yielded crandallite. The cleavage of crandallite could not be determined. The density was not determined, on account of the scarcity of the material and because of the many impurities. The brittle mineral has a hardness of about 4.

Optical properties.—The white or gray crandallite is colorless and non-pleochroic under the microscope. The material analyzed contained a considerable amount of impurities, chiefly quartz, with a little barite and traces of sulphides. The crandallite was in irregular granular or cryptocrystalline masses, many of which showed distinctly on high magnification a fibrous structure in large part radiating. The individual fibers are very minute and it was not possible to isolate on the glass slide a fragment or fiber which was composed of only one unit. The refractive indices of the mineral showed a minimum of 1.585 and a maximum of 1.595, the birefringence of the material ranging from zero to a maximum of about 0.01. Some of the material appears amorphous, but it may be very

FIG. 2.





FIG. 1. A portion of a hexagonal crystal, basal section, showing concentric, radiating fibrous structure. A pseudomorph of crandallite (fibrous) after goyazite (?).

FIG. 2. A crystal plate showing fibrous structure, and with a birefracting center with isotropic rim. A pseudomorph of crandallite (fibrous) after goyazite (?).

finely cryptocrystalline. The fibers apparently have parallel extinction and the elongation is negative.

Some of the crandallite on the hand specimen which appeared better crystallized than the material analyzed, was crushed and examined optically. In this crushed material were found several irregularly shaped to poorly defined hexagonal plates which were isotropic, uniaxial, positive, and which on edge gave parallel extinction and a moderate birefringence (estimated as about 0.01-0.02). The refractive index varied from about  $1.605\pm.005$  to 1.62. Some of these plates were uniform in structure and isotropic; others showed a concentric, radiating, fibrous structure (fig. 1), and were either isotropic (index about  $1.605\pm.005$ ) or else feebly birefracting. A single crystal plate showed an inside area which was feebly birefracting, the fibers giving parallel extinction while the outside rim was isotropic, although both parts showed a distinct fibrous structure as shown in fig. 2.

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*Pyrognostics.*—Heated in a blowpipe flame, crandallite decrepitates somewhat, then exfoliates slightly and fuses to an opaque white enamel, coloring the flame intermittently a pale green (phosphorous) with occasional flashes of red (calcium, strontium). In a closed tube decrepitation occurs with the liberation of water. Soluble in acids.

Chemical composition.—The results of the analysis are as follows, the material being dissolved in acids and the insoluble residue filtered off and weighed. The insoluble residue consisted of 97 per cent  $SiO_2$ , the remainder being barite with traces of sulphides.

Analysis of Crandallite. [W. T. Schaller, analyst.]

	Analysis	Same with insoluble deducted			Ratios
Insol.	35.13				
Al <sub>2</sub> O <sub>3</sub>	25.16	38.71	0.379	0.379	1.96 or $2 \times 0.98$
CaO	4.88	7.50	·134)		
$\operatorname{SrO}$	1.44	2.21	$\cdot 021 \}$	·178	$\cdot 92 \text{ or } 1 \times 0.92$
MgO	0.61	0.94	•023)		
$P_2 O_5$	17.61	27.09	·191)	•915	$1.11 \text{ or } 1 \times 1.11$
SO <sub>3</sub>	2.47	3.80	·047 ∫	210	111011/111
$H_2O -$	0.84	1.29	.072		
$H_2O +$	12.26	18.86	1.048	1.048	5.43 or $5 \times 1.09$
-					
	100.40	100.40			

An inconclusive test for rare earths (probably cerium) seemed to show their presence to a slight extent but the identification was not verified. Barium could not be detected in the acid-soluble part, neither was any barium sulphate precipitated on solution of the mineral. The barium sulphate in the insoluble residue was in relatively large cleavage plates, plainly derived from the mineral barite.

Genetic relations.—The ratios of the analysis yield the formula CaO.2Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O with slight replacement of CaO by SrO and MgO, and of P<sub>2</sub>O<sub>5</sub> by SO<sub>3</sub> [or more exactly of  $(\text{HPO}_4)''$  by  $(\text{SO}_4)''$ ].

This type of formula is slightly different from that of goyazite (hamlinite),

Crandallite	2CaO.4Al <sub>2</sub> O <sub>3</sub> .2P <sub>2</sub> O <sub>5</sub> .10H <sub>2</sub> O
Goyazite	2SrO.3Al <sub>2</sub> O <sub>3</sub> .2P <sub>2</sub> O <sub>5</sub> .7H <sub>2</sub> O

but is of the same type as that of gorceixite.

Crandallite	$CaO.2Al_0O_3P_0O_5.5H_0O$
Gorceixite	$BaO.2Al_0, P_0, B_0, 5H_0$

In an earlier paper it was suggested\* that gorceixite was the barium equivalent of goyazite (hamlinite) and that its formula should be written 2BaO.3Al, O. 2P, O. 7H, O. The original analysis gives ratios which do not support this suggestion but lead to the formula BaO.2Al, O, P, O, 5H, O. Thin sections of gorceixite are stated to have shown an aggregate of minute, colorless, irregular grains, therefore, apparently not fibrous. The question thus arises : What is the systematic position of gorceixite? Does it belong in the alunite-beudantite group with goyazite (hamlinite), plumbogummite, and florencite, and would another analysis on pure material agree better with the type formula, 2RO.3Al<sub>2</sub>O<sub>3</sub>.2P<sub>2</sub>O<sub>5</sub>.7H<sub>2</sub>O; or is gorceixite, with the formula BaO.2Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O, a fibrous alteration product of a pre-existing unknown mineral of the goyazite type of formula; or is gorceixite a non-fibrous mineral, with the formula BaO.2Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O, as independent genetically as goyazite and not a fibrous alteration product of some preexisting mineral of a similar chemical composition?

The formulas of goyazite and gorceixite have been discussed by Farrington<sup>+</sup> in a recent paper. The three analyses (by H. W. Nichols) of Brazilian favas given by Farrington represent well the composition of the favas but are of no value for the elucidation of the composition of any mineral. His material was not examined optically to see if it was homogeneous or free from impurities. The analysis of Fava No. 2 baffled interpretation so that Farrington concluded that "this fava was evidently a mixture." Of Fava No. 3 he finally states : "Of its optical properties nothing can be stated since, unfortunately, all the substance of the fava was used for the chemical analysis."

The homogeneity and character of transparent minerals can be so easily and quickly determined by the present day facilities for microscopic examination (imbedding in oils of known index) that it is a matter of regret that mineralogical papers are still published with detailed and careful chemical analyses of material which has not been first submitted to microscopic examination.

The fibrous plumbogummite, described by Lacroix<sup>‡</sup> (hitchcockite?), may represent a distinct species related to plumbogummite as crandallite is to goyazite.

A sulphate mineral possibly related to crandallite was described

\* Schaller, W. T., The alunite-beudantite group, this Journal, (3), xxxii, 359, 1911. In Mineralogical Notes, Series 2, U. S. Geol. Survey, Bull. 509, p. 76, 1912.

<sup>+</sup> Farrington, O. C., Studies of Brazilian favas, this Journal, (4), xli, 355, 1916.

‡ Lacroix, A., Minéralogie de la France, vol. IV, p. 586, 1910.

by Lindgren<sup>\*</sup> as a basic hydrous strontium sulphate which occurs as an impalpable white powder covering granular celestite, in a vein on level 7 of the Ironclad Mine, Cripple Creek, Colorado. Under the microscope the mineral was seen to consist of short and extremely delicate white fibers of very feeble double refraction and an extinction which is probably parallel. An analysis by W. T. Schaller of a very small quantity gave: SrO, 25<sup>.1</sup>; CaO, 15<sup>.1</sup>; Al<sub>2</sub>O<sub>3</sub>, 13<sup>.9</sup>; MgO, 2<sup>.5</sup>; SO<sub>3</sub>, 13<sup>.9</sup>; H<sub>2</sub>O (107<sup>°</sup>), 0; H<sub>2</sub>O (ignition), 24<sup>.1</sup>; total, 94<sup>.6</sup>. No water was lost at 100<sup>°</sup> and at 260<sup>°</sup> only 1<sup>.4</sup>9 per cent H<sub>2</sub>O was driven off. No test for phosphoric acid was made and the material was too limited in quantity and of too undetermined purity for these figures to have much more than a qualitative value.

The relations of these minerals, especially of the fibrous ones to those not fibrous (those of the alunite-beudantite group), are not at all clear, but the composition of crandallite seems to indicate that there is a definite group of fibrous minerals which are closely related in the type of formula to those of the alunite-beudantite group and yet seem to be very distinct therefrom and to probably result from their alteration.

\*Lindgren, W., and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado. U. S. Geol. Survey, Prof. Paper 54, p. 125, 286, 1906. ART. IX.—A Titaniferous Augite from Ice River, British Columbia; by CHARLES H. WARREN and JOHN A. ALLAN, with a Chemical Analysis by M. F. CONNER.

In the course of an extended study of the nephelite-syenites and their associated rocks, occurring in the Ice River District of British Columbia,<sup>\*</sup> one of the authors (Allan) has described several melanocratic types of rock, occurring as basic differentiates from the nephelite-syenite magma, particularly near the contacts. In several of these (jacupirangites, etc.), a rather strongly pleochroic pyroxene, containing abundant, rod-like, black inclusions, was noted. On study, it was found to be an augite of somewhat unusual characteristics, and it has accordingly been thought well to publish a brief description of it.

In several specimens, representing the melanocratic types, this augite was noted, frequently associated with a pale green, augitic pyroxene.<sup>†</sup> It was also commonly associated with a brown, barkevikitic hornblende, biotite, nephelite, apatite, sphene and ilmenite. Fortunately, one specimen was found which consisted very largely of the augite—an augitite, in fact—and from this specimen material, suitable for microscopic study and chemical analysis, was obtained.

In the specimen alluded to, the augite was associated with a small amount of apatite, occurring as rounded or elongated grains between the augite crystals, with ilmenite, as irregular grains, sometimes in the augite, sometimes about its margins, with a little biotite, and with a little original, brown hornblende. In places a little alteration of the augite to hornblende was noted, and occasionally small amounts of other alteration products were seen, among them calcite. On the whole the material was quite fresh.

In the hand specimen the augite is black in color and of rather irregular habit, although there is a well-marked tendency toward the prismatic development. The grain is rather fine, the length of the prisms rarely exceeding 2<sup>mm</sup>. The cleavage, while distinct, is rather poorly developed. There is perhaps a suggestion of a schistose texture present.

In thin-section, the grains have, in general, irregular forms, although the tendency to elongation in the direction of the vertical axis is obvious. The cleavage is poorly developed. The majority of the grains show minute, black, rod-like inclusions arranged in two distinct series. In many of the grains the inclusions are very abundant, and are a striking characteristic; in other grains they are less numerous, or almost absent.

\*Geology of the Ice River District, B. C., Thesis for the Degree of Doctor of Philosophy, Massachusetts Institute of Technology, 1912.

<sup>&</sup>lt;sup>†</sup> Attempts were made to isolate this green pyroxene for chemical analysis, but without entirely satisfactory results with the material at the time available.

One of the series of rods lies parallel to the vertical crystallographic axis; the other follows a direction which makes an angle of about 74° with the first series (on sections parallel to (010)) and appears, therefore, to follow the direction of the edge, 001-010. In the absence of well-defined cleavage lines, the first set of inclusions can be used very well to measure the extinction directions on. In view of the black color and opacity of the inclusions, and the very high titanium content of the augite, it seems pretty certain that the inclusions are ilmenite. It may be noted, that when some of the inclusions are viewed on end, they appear to be minute tubes, filled with some transparent material. The augite grains also contain some minute black inclusions which lie at random, and also a few larger, irregular or rounded masses of what seems to be also ilmenite.

- a =reddish or pinkish-brown (with a violet shade in thick fragments).
- $\beta$  = reddish or pinkish-brown (with a violet shade in thick fragments).
- $\gamma$  = pale, bright yellow (a little brownish shade in thick fragments).
- The absorption is :-  $\alpha \equiv \beta > \gamma$ .

The extinction was measured against the series of black inclusions lying parallel to the vertical axis in several thinsections of grains showing a maximum double refraction, and was found to range for  $\gamma \wedge c'$  from 41.9° to 42.6°, or an average of 42.3°. This value was obtained by measuring from the direction of the lines of inclusions to the position of maximum darkness in white light. Like many titaniferous augites this pyroxene has a very strong dispersion of the bisectrices, and anomalous interference colors appear on either side of the position of maximum darkness. In the present case, the change was quite sharp, and experiment showed that the results obtained in this way were more consistent than were those obtained by using monochromatic lights.

The interference figures, obtained in convergent light, show a very strong, inclined dispersion;—red greater than blue. One of the hyperbolas appears black, while the other consists of a strong, red, inner band (convex side) and an equally strong, blue band on the concave side. The width of the two colored curves covers together about five divisions on the micrometer scale used, which is equivalent to about 9° angular. Two sections were found which were nearly normal to the acute, positive bisectrix, and with these sections the optic angle in the air was measured under the microscope using the Wright micrometer scale. On account of the breadth and lack of sharpness of the hyperbolæ, both in white light and also in monochromatic light, no great accuracy can be claimed for this measurement, and it was deemed sufficient to measure it in white light alone, taking the readings from the middle of the black brush passing through the one optic axis to the division between the strong red and blue parts of the other brush, this division being fairly well marked-the sharpest thing about the interference figure in fact. One section gave  $2E = 58.5^{\circ}$ , the other, 59.5°, or an average of 59°. In sections near the optic axis A, the interference color as seen in parallel light between crossed nicols is a peculiar dull, deep blue or bluish gray; in those almost perpendicular to the axis, the color is still more dull and has a gray or brownish tint. The sections nearly normal to the acute bisectrix have also a peculiar dull brownish- or purplish-gray color. These interference colors are, as a matter of fact, quite characteristic of the thin-slices of the rocks carrying this augite.

Two of the indices of refraction were determined by the immersion method, and were found to be, for sodium light, a = 1.725,  $\gamma = 1.746$ . This makes the double-refraction equal to 0.021. This is agreement with the value estimated from the thin-slice, which was about 0.020.

A very careful separation of the augite from the minerals accompanying it was carried out by means of the bariummercuric-iodide solution. The final product, examined under the microscope, showed a very satisfactory degree of purity, there being very little attached or included hornblende or biotite present, and only traces of other incidental impurities. The mineral thus prepared was analyzed by Mr. M. F. Conner, of Ottawa, with the following results :---

Augite Ice River S	e from venite. B.	C.	Augite Monchiqu Rio de J	from a uite dike, aneiro.
Conner,	Analyst.		Hunter,	Analyst.
,	%	Ratio.	%	Ratio.
SiO,	41.80	0.692	44.55	0.742
Al,Ó,	9.30	·091	7.86	.077
Fe <sub>0</sub> O <sub>2</sub>	5.44	•034	3.81	.024
FeO	3.30	·046	4.53	•063
MgO	10.82	·238	12.71	•318
CaO	<b>2</b> 2·89	•409	20.84	.372
H <sub>0</sub> -	0.16			
H <sub>0</sub> +	1.10	·060		
TiO	4.84	•060	2.85	·035
MnÓ	0.10	.002	•38	•006
	99.75		Na <sub>1</sub> 0 1.29	·021
			K <sub>2</sub> 0 ·49	.005
Sp. Gr. $= 3.39$			99.31	
<b>.</b>			Sn $Gr - 3.284$	

A search of the literature relative to the chemical composition of the augites has so far failed to find any which are very close to the one under consideration. The nearest approach is found in an augite from near R10 de Janeiro, analyzed by Hunter and described by Rosenbusch.\* The latter gives its properties as follows:—Extinction  $\gamma$  on c', 40°; dispersion strong; pleochrism,  $\beta = \gamma =$  reddish-violet, a = yellow-rose.

While the Ice River augite is much higher in titanium and contains no alkalies, there is otherwise considerable similarity in the composition of the two. In both, the silica is rather low, the alumina, ferric iron and lime are high, as is also the titanium. The latter is very high in the Ice River variety, although it is true, that some part of the titanium is present in the form of the rod-like inclusions, and not in the augite itself. It is impossible to say how much  $TiO_2$  should be deducted from the augite, but if it amounts to as much as one or even two per cent, which is not improbable, it would still leave the titanium high. A combination of the various oxides into groups yields the following :—

Ice River Augite.Rio de Janeiro Augite. $SiO_2 + TiO_2 = 0.757$ 0.777 $RO + H_2O = 0.755$  $0.785 (+R_2O)$  $R_2O_3 = 0.125$ 0.101 $SiO_2 + TiO_2: R_2O_3: RO + H_2O =$  $SiO_2 + TiO_2: R_2O_3: RO + R_2O =$ 6: 0.99 : 5.9177: 7.08 : 0.91

The titanium has all been included, which in the case of the Ice River augite unquestionably makes it somewhat too high. The water and alkalies are here included with the RO. It is noticeable that, as might be expected, the relative proportions of the RO<sub>2</sub> and RO are about equal. The ratio of the RO<sub>2</sub> in the one augite is 6:1, and in the other, 7:1, or nearly so, thus bringing out a rather sharp distinction between them.

It has occurred to the authors, that at the time of crystallization of the augite, the ilmenite molecule,  $\text{RTiO}_3$ , analogous to the metasilicate molecule,  $\text{RSiO}_3$ , may have crystallized isomorphously with it, and subsequently becoming unstable in that state, have separated out—unmixed. In any case the titanium would be combined with the RO (FeO), and hence would not affect the relative values of the ratio,  $\text{RO}_2$ : RO, as calculated. It would still leave the excess of  $\text{R}_2\text{O}_3$  in the Ice River mineral, as compared with the other, as marked as before.

In conclusion it may be said that the augite described above differs in its microscopic and chemical characteristics from any augite known to the writers and is believed to be of interest in extending somewhat our knowledge of the titaniferous augites.

Geological Department, Massachusetts Institute of Technology,

Cambridge, Mass., August, 1916.

\*Tsch. Min. Petr. Mitt., xi, p. 460. This augite occurred in a monchiquite dike in gneiss at Rio de Duro, Sera de Tingua, near Rio de Janeiro.

## SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. The Determination of the Density of Solids.—HENRY LE CHATELIER and F. BOGITCH observe that the determination of the specific gravity of solids is one of the simplest of physical measurements, but that this determination is usually made in an inexact way, so that it is unusual that the density of a solid is known with an accuracy of one part in 100. The treatises on chemistry hardly ever give exact numbers for densities. For example, in Moissan's large treatise we find for common substances occurring frequently in a state of great purity the following statements in regard to densities :

> Quartz, between 2.55 and 2.74 Natural galena, varying from 7.26 to 7.70 Artificial galena, varying from 6.9 to 7.5 Natural blende, varying from 3.5 to 4.2.

Now, in regard to quartz, deLépinay and Buisson have shown that its specific gravity is absolutely fixed, and is 2.6507 with an uncertainty of only one unit in the fourth decimal.

The authors discuss the probable cause of our shocking ignorance in connection with these constants, and they conclude that while impure substances and insufficient weights of samples may sometimes cause errors, the principal cause of inaccuracy is the adhesion of a thin layer of air to the surface of the solid. They observe that this effect is well known to be enormous, as in the "flotation" processes of separating sulphides from other minerals. Upon experimenting with various liquids, they have found that carbon tetrachloride, benzol and petroleum ether do not give this difficulty, and they recommend that water should never be employed for the purpose. They have devised a very simple and convenient apparatus for determining specific gravities. It consists of a glass tube of about 5<sup>mm</sup> interior diameter, graduated in cubic centimeters and their tenths, with a bulb at its lower extremity and placed upright. The tube is charged with the liquid, the level is read, either by the eye alone or by means of a cathetometer, and the weighed solid, thoroughly freed from dust by sifting, is introduced by means of a long funnel. The increase in volume, which should amount to at least about 3<sup>cc</sup>, is determined by reading the new level of the liquid. Using carbon tetrachloride, with coarse and fine material in each case, galena gave the results 7.584 and 7.590, while zinc blende gave 4.079 and 4.079. When water was employed, even in cases where it was attempted to remove the adhering air by exhausting the air above the liquid, the results were very unsatisfactory.- Comptes Rendus, clxv, 459. H. L. W.

2. A New Reagent for Free Chlorine.—The detection and determination of active chlorine in public water supplies has become important on account of the frequent use of hypochlorites in purifying such waters. The classical reagent potassium iodide with starch paste is generally used for this examination, but G. A. LEROY proposes the employment of the chlorhydrate of hexamethyl-triparaminotriphenylmethane for the purpose. When this reagent is added to the extent of a few thousandths to a potable water containing traces of free chlorine, a violet coloration is formed immediately and this varies in proportion to the amount present. The reagent will show about 3 hundredmillionths of chlorine, while potassium iodide and starch show only about one ten-millionth.—Comptes Rendus, clxv, 226.

H. L. W.

3. The Right Honourable Sir Henry Enfield Roscoe, A Biographical Sketch, by SIR EDWARD THORPE. 8vo, pp. 208. London, 1916 (Longmans, Green & Co. Price \$2.50 net).-The distinguished author of this biography, who calls himself "a grateful pupil, an attached co-worker, and a lifelong friend " of the eminent subject of his essay, has produced a book of unusual interest. Roscoe's name is well known to chemists on account of his text-books, and his chemical researches, particularly his investigations dealing with the compounds of vanadium, and his explanation of constant-boiling acid solutions. But this story of his life shows that his activities were important in many directions. He did effective service in the development of Owens College, Manchester, he was active in scientific societies and in public service, and gave much time to the advancement of popular and technical education. After teaching for nearly 30 years at Owens College he was elected a Member of Parliament in 1885 and held his seat for 10 years. He died in 1915 at the age of 83 years. His biographer characterizes him as a strenuous highminded man, of large aims and generous impulses, who spent his abilities and energies unstintingly in promoting the welfare of science and the good of his kind. The book contains a fine portrait of Roscoe as an elderly man. H. L. W.

4. A Text-book of Inorganic Chemistry; by A. F. HOLLEMAN, Issued in English in Coöperation with H. C. COOPER. 8vo, pp. 521. New York, 1916. (John Wiley & Sons, Inc.)—This is the fifth edition in English, the first of which appeared 15 years ago, of an excellent and widely-used text-book. The present issue has been thoroughly revised and many parts have been rewritten by the American collaborator, so that the recent achievements in chemical science receive consideration. For instance, the results of T. W. Richards on the atomic weight of radioactive lead isotopes are mentioned. There is no doubt that the book presents the whole subject in a very satisfactory way. However, it is decidedly advanced in its treatment of physico-chemical topics from a mathematical standpoint, but it is stated that notwithstanding the appearance of differential formulæ in the book, it is believed that a student who is unfamiliar with the calculus should have little difficulty in understanding the meaning and use of such formulæ, provided he is willing to take the author's word for the solution of the equations. H. L. W.

5. Organic Chemistry for the Laboratory, by W. A. NOYES. 8vo, pp. 292. Easton, Pa., 1916 (The Chemical Publishing Co.). —This guide for organic preparations now appears in its third edition, revised and slightly enlarged. As is well-known, the book presents a liberal number of classified and well-selected preparations, with full and clear directions and abundant references to the literature. There are 132 numbered exercises, many of which involve several operations, from which more or less extensive courses of laboratory work may be selected. H. L. W.

6. Note on the Electrolysis of Gallium; by H. S. UHLER (communicated).-After the article by Philip E. Browning and myself had appeared (vol. xlii, p. 389, November, 1916), I met with a difficulty in the electrolysis of gallium which caused me to lose much time, and hence it seems desirable to present this brief note of warning for the benefit of other investigators who may be working in the same field. In order to increase the purity of some gallium which had been obtained by the electrolytic method outlined in the above mentioned paper, the metal was dissolved in a hot solution made from equal volumes of concentrated nitric acid and water. The resulting solution was then made strongly alkaline by the addition of caustic soda so that the gallium hydroxide was thoroughly dissolved. An attempt to electrolyze this solution was unsuccessful, from the practical point of view, for only an insignificant mass of gallium deposited on the cathode in the course of several days. The addition to the electrolyte of several times its volume of a very concentrated aqueous solution of sodium hydroxide increased the rate of deposition to some extent but not enough to be comparable with the rate obtained with alkaline solutions containing no nitrates. To prove that no blunder had been made, the solution was neutralized with hydrochloric acid and the precipitated gallium hydroxide was thoroughly washed and thus freed from soluble compounds. The precipitate was then dissolved in an excess of caustic soda, after which treatment the solution electrolyzed with great facility. The entire experiment was repeated, commencing with 1.05 grams of metallic gallium. Only 4.5mg were deposited on the cathode in 112.75 hours. After neutralization, and so forth, the metal was recovered with promptness. It is certain, therefore, that the presence of sodium nitrate greatly retards the electrolytic deposition of gallium. Although no quantitative comparisons were made, the rates of deposition with and without the presence of chlorides seemed to be about the same. The warning is,—avoid nitrates. H. S. U.

7. The Condensation of Gas Molecules. -- By using cadmium instead of mercury vapor R. W. Wood has performed some very interesting and instructive preliminary experiments on the con-

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 253.—JANUARY, 1917.

densation and reflection of gas molecules. The advantage of cadmium over mercury consists in the fact that films of the former metal remain solid and *in situ* at room temperature whereas films of the latter liquefy and form globules at temperatures convenient for making observations. We shall omit the experiments relating to the cosine law of reflection because they are not as delicate as those of Knudsen (vide in/ra).

A long glass tube was sealed off at one end and blown out into a relatively large bulb at the opposite end. Near the bulb the tube was constricted for a length sufficient to ensure the transmission of an approximately one-dimensional flow of vapor molecules into the bulb. The cadmium was placed in the small end of the glass system and was heated by a gas-flame 3 or  $4^{mms}$  high, burning at the orifice of a glass tube drawn down to a fine capillary The tube and associated bulb were kept in communication with a Gaede pump during the experiments, since a good vacuum is necessary.

When the bulb is kept at room temperature no trace of a deposit appears, but when the wall of the bulb opposite the inlet is cooled with a pad of cotton wet with liquid air a small deposit of metal begins to form at once. If the degree of exhaustion is sufficiently high, prolonging the experiment for 15 or 20 minutes causes no sensible increase in the diameter of the circular zone of condensed metal, whereas if the vacuum is inferior the diameter of the spot increases due to the deflection of the cadmium vapor by the residual gas molecules. It is evident, therefore, that with a high vacuum the molecules of the vapor shoot across the bulb without spreading laterally. If, at the beginning of the experiment the cold pad is placed against the bulb at any point 90° from the inlet a large deposit of irregular shape forms immediately, showing that the bulb is filled with cadmium vapor having three-dimensional motion. Even if the cold cotton wad is held against the bulb for only a second or two the deposit starts to form and continues to build up indefinitely after the pad has been removed. Hence, the chance of reflection at room temperature of cadmium vapor from a cadmium surface is zero, that is, condensation occurs at the first collision. If the surface of the bulb opposite the inlet is subsequently cooled with liquid air the small circular spot mentioned above forms at once and increases in thickness after removal of the cotton wad. No further deposition of cadmium molecules occurs on the metal at the side of the bulb, for the polar deposit, when once formed, serves as a trap for the incident parallel stream of molecules.

The fact that molecules of cadmium vapor can experience a large number of reflections from glass without condensation was neatly shown in the following manner. A glass tube was bent at right angles in a number of places and blown out as a thin-walled bulb at the end remote from the source of vapor. Condensation took place in the bulb when it was cooled with liquid air. Tubes with more than a dozen bends were used, proving that a large number of reflections are possible, since the number of bends gives the minimum number of reflections suffered by a molecule before reaching the condensation bulb. The greater the number of bends the longer was the time required to produce in the bulb a film of definite thickness. Consequently a certain fraction of the total number of molecules in the column of vapor must have fallen by the wayside. In a particular tube deposits of equal density were obtained in the bulb, at a chosen bend, and at a bend still nearer the source, in 15 mins., 2 mins., and 10 secs., respectively. Although the density of the cadmium vapor is considerably decreased by its passage along the bent tube, no visible deposit can be detected on the uncooled walls. Microscopic examination of a bulb which had been kept at room temperature and in communication with the source of vapor for 40 mins. showed discrete aggregates of metal which seemed to be clusters of very minute The temperature necessary for the formation on glass crystals. of a homogeneous film of cadmium was found experimentally to be in the neighborhood of -100 °C. The corresponding "critical" temperatures for iodine and mercury are roughly  $-60^{\circ}$  and  $-140^{\circ}$ , respectively.-Phil. Mag., xxxii, p. 364, October, 1916.

H. S. U.

8. The Cosine Law in the Kinetic Theory.—From his earlier experiments on the flow of gases through capillary tubes Knudsen concluded that all of the n molecules which strike an element of surface from a solid angle do' leave this surface in such a manner as to have their velocities uniformly distributed over every azimuth. More precisely  $dn = \pi^{-1} n \cos \chi d\omega$ , where  $\chi$  denotes the angle between the normal to the surface and the direction of the This is equivalent to putting a certain fraction f, axis of  $d\omega$ . which occurs in Maxwell's original theory, equal to unity. Later simultaneous and independent experiments by Knudsen and R. W. Wood have apparently confirmed Knudsen's cosine law. Since, however, these investigations involved the comparison of different surface densities, which cannot be determined with ease and accuracy, a more recent and conclusive method of attacking the problem, devised and employed by MARTIN KNUDSEN, deserves notice.

The innovation consists in assuming the validity of the cosine law and then finding the form of surface over which the distribution of condensed vapor would be uniform. This method is very sensitive because any appreciable departure from constant surface density can be readily detected. It can be shown by very simple analysis that if the molecules obey the cosine law and are reflected from one portion of the inner surface of a spherical cavity they will be uniformly distributed over the rest of the same spherical surface. Accordingly a glass bulb was blown in as nearly a spherical shape as possible and was drawn out at one point in the form of a tube which communicated with the source of mercury vapor, with the air pump, etc. The lateral tube and the auxiliary apparatus were designed in such a way as to cause a narrow stream of mercury vapor to enter the bulb diagonally and then strike the spherical surface obliquely at the other end of the chord. To prevent condensation the region of reflection was kept warm by means of an electrically heated metal trough the lower end of which fitted the outside of the glass bulb very closely. The temperature of the water in the trough was maintained at 30° C. so that the temperature of the glass reflecting surface was probably between 0° and 20°. Below the zone of contact of the heating trough the rest of the bulb and a portion of the auxiliary apparatus were kept immersed in liquid oxygen. This liquid was contained in a glass vessel with unsilvered walls to enable the making of visual observations without changing the temperature of the bulb and its accessories.

When the mercury in the auxiliary system had been warmed for a very short time the layer of condensed mercury on the walls of the inlet tube became completely opaque and, after a few minutes, the condensed vapor in the bulb became visible. The layer in the bulb appeared to be uniformly distributed from the instant when it first became discernible until it had attained almost complete opacity. "It was not possible to detect anywhere a structure or a difference in transmissive or reflective power, save at a zone about 1<sup>mm</sup> wide which surrounded the heating vessel and which remained absolutely clear and transparent." After the experiment had continued for "a good 20 minutes" the mercury deposit was so dense that an incandescent lamp could barely be seen through it. The heating currents were then broken, the liquid oxygen and frost removed, air was admitted to the bulb, and the apparatus was allowed to come to room temperature. The film of mercury, now liquid, had a very characteristic and uniform opalescence. At the expiration of 24 hours the diffraction rings formed by the mercury droplets, when the bulb was illuminated by a distant electric light, were examined and found to have the same appearance for all parts of the bulb which had been previously frozen.

In order to obtain quantitative measurements the experiment was repeated and continued until a thicker deposit of mercury had formed. By skilfully manipulating the bulb the mercury layer was collected from definite spherical zones by causing an auxiliary globule to run around over the region in question. By weighing the mercury and measuring the corresponding areas the surface density of the selected regions was obtained directly. The zones were chosen at such azimuths, with respect to the direction of the incident stream of mercury vapor and the warmed spot, as might be expected to produce the greatest differences in surface density in case the cosine law did not hold true. The numbers found, however, were constant within the limits of experimental error. Consequently the cosine law is valid even when there is no temperature equilibrium, for the temperature of the reflecting surface was below 20° C. while that of the incident mercury vapor was above 80°.-Ann. d. Physik, vol. xlviii, p. 1113, Feb., 1916.

## Geology.

## II. GEOLOGY.

1. A preliminary paper on the origin and classification of intraformational conglomerates and breccias; by RICHARD M. FIELD. Ottawa Nat., Vol. XXX, 1916, 23 pages.—An interesting paper explaining the origin of several kinds of intraformational conglomerates. The author also defines conglomerates, glomerates, tectibreccias, and bioglomerates. Phenoclasts are defined as the fragments and rocks of which the foregoing are composed. "Intraformational conglomerates and breccias seen at Chambersburg, Bellefonte and Tyrone, Pennsylvania, are of extremely shallow water origin; in fact, their formation postulates an emergence from the sea such as is common under tidal action. . . Mud-cracked beds and intraformational breccias are in certain cases one and the same thing." C. S.

2. Florida Geological Survey, Eighth Annual Report; E. H. SELLARDS, State Geologist. Pp. 168, pls. 31, text figs. 14, 1916.— Besides the administrative report and an account of the mineral industries of Florida during 1915, this volume has three memoirs treating of Cenozoic vertebrates. O. P. Hay describes twentytwo species, of which nineteen are turtles; E. H. Sellards describes a new Miocene fauna of five species, and four vertebrates from the Pliocene, and discusses the Pleistocene vertebrates from the state. He also presents a bibliography of the literature treating of Floridian fossil vertebrates. The last paper, also by the state geologist, describes in greater detail the human remains and associated fossils from the Pleistocene of Florida first announced in this Journal last July. c. s.

3. A study of the Morrison formation; by CHARLES CRAIG MOOK. Ann. N. Y. Acad. Sci., Vol. XXVII, 1916, pp. 39-191, pl. 6.—The Morrison formation originally "had an extremely wide distribution, which may have amounted to four or five hundred thousand square miles," and is celebrated for its many and striking dinosaurs, among them the largest of all land animals. The author here brings together our knowledge of the Morrison deposits and their distribution east of the Rocky Mountains, and seeks to determine whether they are of Jurassic or Comauchian age. His conclusions are as follows : "It appears, then, that the Morrison commenced as a continental deposit in the western areas of its occurrence in early Comanchean time (or possibly latest Jurassic), and that it spread outward as it was built up, the uppermost and easternmost beds being laid down in [later] Comanchean time . . . If the above interpretation of the Morrison be anything like the truth, it seems probable that the Morrison merged into the marine [Comanchian] deposits in the southeastern areas, such as Texas, and that the Morrison in its southeastern and eastern areas consisted of true delta deposits" (172).C. S.

4. Notes on the geology of Nelson and Hayes Rivers; by J. B. TYRRELL. Trans. Roy. Soc. Canada, Ser. III, Vol. X, 1916, pp. 1-27, pls. 1-5, 2 text figs.—An interesting address, particu5. Sixth Annual Report of the Director of the Bureau of Mines, VAN. H. MANNING, for the year ending June 30, 1916.— As will be remembered, Dr. Joseph A. Holmes, under whose direction the United States Bureau of Mines took shape and was developed to a high degree of efficiency, died on July 13, 1915, and his place was taken by the present Director, Dr. Van. H. Manning, who now presents the annual report for the year ending June 30, 1916. The work of the Bureau, as heretofore, is concerned perhaps first of all with efforts to insure the health and safety of the miners. It is stated that during the year, 8,400 miners were trained in mine rescue and first aid; numerous accidents were investigated and a large number of men rescued. Further, the health conditions in mining towns have been investigated, as regards, for example, the presence of the hookworm in California mines, and the prevalence of tuberculosis in Montana, and pathological conditions elsewhere.

The Bureau is also actively engaged in endeavoring to accomplish a greater degree of economy in the various mining and metallurgical processes. Perhaps the most important of these are concerned with the fuel supply of the country. It is shown that the petroleum industry, which in 1915 produced over 281,000,000 barrels, valued at about \$180,000,000, or over 65 per cent of the total for the world, needs a most thorough investigation as to the economy of production and elimination of waste, since it is estimated that the known supply is likely to be exhausted in less than thirty years, at the present rate of produc-Economy in coal mining is not less important, as well as tion. the attainment of the most efficient results in the use of the fuels. Much is being done now in these directions, but a more liberal supply of funds is called for, in order to accomplish the best results. As another example of the activity of the Bureau to be mentioned is the extraction of several grams of radium from carnotite ore at the Denver plant, this being accomplished at an estimated cost of \$40,000 per gram.

The publications of the year include a large number of bulletins, technical papers, and miners circulars. The following bulletins have been received since the last list published (see vol. xli, pp. 83, 84):

No. 105. Black damp in mines; by G. A. BURRELL; I. W. ROBERTSON, and G. G. OBERFELL. Pp. 88.

No. 106. The technology of marble quarrying, by OLIVER BowLes, 1916. Pp. 174, 12 pls., 33 figs.

No. 108. Melting aluminum chips, by H. W. GILLETT and G. M. JAMES, 1916. Pp. 88.

No. 116. Methods of sampling delivered coal, and specifications for the purchase of coal for the Government, by G. S. POPE. Pp. 64; 5 pls., 2 figs. No. 118. Abstracts of current decisions on mines and mining, reported from October to December, 1915, by J. W. THOMPSON. Pp. 74. No. 126; the same from January to April, 1916, by J. W. THOMPSON. Pp. 90.

No. 134. The use of mud-laden fluid in oil and gas wells, by J. O. LEWIS and W. F. MCMURRAY. Pp. 86; 3 pls., 18 figs. 6. An Introduction to Historical Geology; by WILLIAM J.

MILLER. Pp. xvi, 399, with 238 figures. New York, 1916 (D. Van Nostrand Company).-In 1915 appeared the Historical Geology by Schuchert, earlier in 1916, Cleland's Geology, Physical and Historical, and now a third book on the earth's history by Miller of Smith College. While the subject is handled differently by each of these authors, there is a similarity of treatment that is most marked in the first two books. Miller's book is unlike the other two in that it is not accompanied by a text treating of dynamic and structural geology. He aims at using a small number of technical terms, especially the names of fossils. As a rule, only the ordinal and class terms of organisms are given in the text, but the legends of the illustrations of fossils all have their specific names "in the interest of scientific accuracy [the names are not always correct] with no thought that these are to be remembered by the student." The paleogeographic maps are those of Willis and De Lapparent. The book looks well, and the illustrations as a rule are good, adequate, and up to date. general, it may be said that a great deal of information is here compacted into small space, and that the book is one of facts, unadorned to stimulate interest on the part of the undergraduate student.

## III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Report of the Secretary of the Smithsonian Institution, CHARLES D. WALCOTT, for the year ending June 30, 1916.—The most interesting announcement contained in Dr. Walcott's report is the record of the gift, by Mr. Charles L. Freer, of a sum of \$1,000,000 in cash, for the immediate erection of a building for the permanent preservation of the collection of art objects presented by him to the Institution in 1906, and since increased by further gifts. The building will be of granite and located at the southwestern corner of the Smithsonian reservation ; it is expected that the work of construction will soon begin. The original collection consisted of about 2,300 paintings and other objects of art, and has since been increased to 5,346 items, including American paintings and sculptures, the Whistler collection, and Oriental paintings, pottery, bronzes, and jades from China, Korea, Japan, and other Asiatic countries.

During the past year the Institution has carried on the usual series of explorations and researches in the different lines of science. These include the work of the Secretary in the Yellowstone Park and from there north in the Belt Mountains east of Helena. The work in the former area had to do with the investigation of the depositions from the geysers and hot springs as influenced by algæ and possible bacteria; also the collection of specimens of these deposits and of silicified wood for the National Museum. The investigations also include the study of the Paleozoic deposits of the Mississippi valley by Dr. Ulrich, work in the Ohio valley by Mr. Springer, and in Pennsylvania and Virginia by Dr. Wherry. Zoological and botanical explorations have also been carried on in St. Thomas, South America, and at several points in the Far East. Of the grants from the Hodgkins fund, the most important is that to Professor Angström for the study of nocturnal radiation. Earlier results were published in 1915, and later ones have been extended to the Far North during the arctic night.

The work of the Institution in its regular departments has gone forward as usual, except so far as the war has interfered with the Bureau of International Exchanges; this work is summarized by the Secretary and the same subjects are discussed at length by the various gentlemen in charge in Appendixes I–VIII. As to the work of the Astrophysical Observatory, it may be noted that Messrs: Abbot and Aldrich have designed an instrument called the pyranometer, so constructed as to measure accurately the intensity of skylight by day and the radiation from the whole sky at night. The tests which have been made with it prove its accuracy and general use, and further indicate that it may be snitable even for measurement of radiation in deep shade, as in forests and greenhouses.

2. Field Museum of Natural History; FREDERICK J. V. SKIFF, Director. Annual Report of the Director to the Board of Trustees for the Year 1915. Pp. 74; 14 pls.

Botanical Series. Vol. II, No. 11. I. Contributions to North American Euphorbiaceæ—VI; II. Vegetation of Alacran Reef; by CHARLES F. MILLSPAUGH. Pp. 401-431; maps and illustrations.

Geological Series. Vol. III, No. 10. Catalogue of the Collection of Meteorites; by O. C. FARRINGTON.

Since the earlier catalogue of 1903 (see vol. xvii, p. 329) the Field Museum has acquired the Ward-Coonley collection of 620 falls and an aggregate weight of 2,495 kilograms, bringing the total of the Chicago collection up to the impressive total of 657 falls and 7,560 kilograms.

#### OBITUARY.

PROFESSOR HENRY H. W. PEARSON, the able botanist of Cape Town, South Africa, died on November 3 at the age of forty-six years.

PROFESSOR HENRIK MOHN, for many years director of the Norwegian Meteorological Service and an active contributor to the subject of meteorology, died in Christiania on September 12 at the age of eighty-one years.
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# [FOURTH SERIES.]

ART. X.—The Water Content of Coal, with Some Ideas on the Genesis and Nature of Coal; by Edward Mack and G. A. HULETT.

# PART I. Water Content of Coal in relation to its Origin and Constitution.

At the present time our understanding of the nature of coal is largely limited to a knowledge of the chemical elements present in the coal substance, while there is little known about the chemical compounds present, or about the physical properties of coal. Since the economic utilization of coal depends mainly on destructive distillation, it is of first importance to have definite information about the constitution of the various kinds of coal, and much attention has been given to this subject, especially during the past few years, from the standpoint of distillation at low temperatures and pressures and by the use of extractive solvents.

Commercially it has been found desirable to know the moisture content of coals and chemists adopted the usual analytical method for moisture, namely, drying the sample in an oven at 105° C. But it soon developed that the results were not concordant or reproducible, and for that reason several committees have been appointed to look into the question. Among these committees was one which reported to the Eighth International Congress of Applied Chemistry in 1912.\* At that time it was recommended that in making moisture analyses a special oven be used which would provide proper temperature control, since there is sometimes a variation of 15° C., or more, in dif-

\*Holloway and Coste, Report of Sub-Committee 10 of the International Commission on Analysis. Also, Hillebrand and Badger, Proc. 8th Intern. Cong. Appl. Chem., vol. x, 187.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 254.—FEBRUARY, 1917. 7 ferent parts of an ordinary air oven. Furthermore the moisture of the air passing through the oven was found to be a factor as well as the depth of the coal in the crucible, the drying agent used in the desiccator in which the coal and crucible were cooled, etc. In short it was found necessary to specify numerous empirical details of manipulation, and even when these were strictly adhered to, it seemed impossible to obtain very satisfactory checks.

Indeed, in this connection Hillebrand and Badger have emphasized the fact that loss of moisture is not the only change which occurs on heating a sample of coal at 105° C. in a drying oven. Other factors which may operate to cause a change of weight are: the sensitiveness of the powdered coal to the atmospheric conditions; the loss of volatile matter other than water; the taking up of oxygen which may be either oxygen added directly to the coal substance, or oxygen combined with carbon or with hydrogen, and split off to form respectively carbon dioxide and water. Some coals are very easily oxidized, e.g. Archibald and Lawrence\* have showed that the error introduced into the value of the moisture determination by the effect of oxidation may in extreme cases be very large. Moreover it can readily be seen that with different coals the modifying factors may assume the most varying values with respect to each other, and it is therefore desirable that as many as possible of them be eliminated. Yet, in spite of all its defects the present method will likely be retained for trade purposes in the commercial examination of coals.

The fact remains that there is still a very decided need for a method which would give the real moisture content of coal and which would serve as a standard of reference. This would be of importance in research, especially in connection with the study of the constitution of coal.

On account of the scientific importance of a definite knowledge of the moisture content of coal, many methods have been proposed, in which any effect due to oxygen is excluded, e. g.: drying in a vacuum over sulphuric acid or phosphorus pentoxide for several days, heating the coal sample in a stream of dry nitrogen, hydrogen, or carbon dioxide; treatment of coal with calcium carbide and measurement of volume of acetylene gas generated; heating in boiling xylol, toluol, and similar liquids with measurement of the volume of water which distils over with the oil; collection of water given off by absorbing it in anhydrous calcium chloride or hot lime; using the reaction of water with the Grignard reagents; and several others. It is not necessary to discuss the advantages and disadvantages of

\* Determination of Water in Coals, by E. H. Archibald and J. H. Lawrence in J. Ind. Eng. Chem., iv, 258-62. these various methods here, as they have been treated at length in the literature.\*

We will, however, consider at this place the method by which coal is dried in a vacuum over such dehydrating agents as concentrated sulphuric acid or phosphorus pentoxide. This method has been regarded as most reliable, since there is no oxygen in contact with the coal and also since it gives higher results than most other analytical methods. But it does not follow that it really gives the true water content of coal, for it is based on the assumption that by dehydrating coal in a vacuum at room temperature all of the water may be removed by these reagents in experimental time. This, however, involves a fundamental point in this problem; as a matter of fact, we have found that dehydration at room temperature still leaves with the coal a considerable portion of its water content. The following experiments, in which we used widely different kinds of coal, were made to test this point.

The samples were powdered (20-30 mesh), weighed out in crucibles and permitted to stand in large vacuum desiccators (2-3<sup>mm</sup> pressure) over fresh phosphorus pentoxide for 7-14 days or until repeated weighings from day to day showed constant weight to  $\pm 0.2$  milligram. The desiccator was provided with a small electric heater into which the coal crucible just fitted so that the coal could be heated inside the desiccator when desired. A very short thermometer (from a set) was adjusted so that the bulb was imbedded in the coal. After the coal had been desiccated until it showed no further loss, it was warmed up gradually and maintained finally at a definite temperature for a few minutes. In every case there was a marked loss of water from the coal which had apparently attained equilibrium with the first hydrate of phosphorus pentoxide at ordinary temperature. The accompanying table gives the results.

None of the above losses resulting from the application of heat was due to the evolution of gases (other than water) since the amount of these was determined and corrections made. This was done as follows: Previous to heating, each of the samples had been run in duplicate, one crucible with its contents being placed in the electric heater just described, the other being heated to the same temperature (or  $10^{\circ}-30^{\circ}$ higher) in an apparatus where the gas was collected and its volume and weight measured. The weight of the gas evolved in each case was subtracted from the total loss on heating and the amount of water lost by each of the six samples was thus obtained. The corrections were small, lying between the

\* For example, see Huntly and Coste, The Determination of Moisture, Jour. Soc. Chem. Ind., xxxii, p. 62.

### TABLE I.

Powdered coal dried in vacuum desiccator over phosphorus pentoxide with percentage loss of water :

	New River	Pitts- burgh	Illi- nois	Wyo- ming	Lignite	Peat
Weight of each sample	1.6623	1.6131	1.3704	1.5853	1.7465	1.2875
Time :						
1 hr.						45.98%
3 hrs.		1.75%	6•40%			20 0070
5 hrs.	1.26%		7-		40.09%	
2nd day	$1.52^{'}$	1.29	7.66	9.17%	40.76	55.80
3rd "	1.63	1.48	7.86	12.63	41.01	55.96
4th "	1.69	1.61	7.93	12.85		
5th "			7.97	12.92	41.20	56.15
6th "	1.72	1.70				
7th "	1.74	1.76	8.03	12.93		5 <b>6</b> .16
8th "	1.74	1.78	8.04			
9th "			8.02			
10th "				12.92	41.32	56.18
13th "					41.38	
14th "					41.39	
On heating	3 min up	13 min	4 min	12 min	26 min	10 min
gradually	to $125^{\circ}$	up to	up to	up to	up to	up to
for		2 <b>3</b> 0°	115°	170°	$190^{\circ}$	115°
	2.13%	2.10%	8.58%	13.20%	42.91%	<b>56</b> .63%
			15 more	11 more		11 more
			min up	min up		min up
			to 205°	to 200°		to 170°
			10.200	13.360		56.010
			10 29%	10 00%		00 01%

NOTE—Weighings on successive days were made only roughly at 24 hour intervals.

limits of 0.09 per cent. for New River and 0.61 per cent. for lignite.

It has been shown\* that there is not a measurable decomposition of these kinds of coals when heated in a vacuum to 250° for several hours—a point we will consider more in detail below. Since none of the additional water expelled by heating above room temperature could come from a synthesis of water from oxygen and hydrogen, and since it did not behave like combined water or water of crystallization but showed a typical solution or adsorption curve,† the water must, there-

\* H. C. Porter and G. B. Taylor, The mode of Decomposition of Coal by Heat, Proc. Amer. Gas. Inst., vol. ix, 234, 1914.

† Porter and Ralston.

fore, have been present as such. Later work indicates that, even by heating in the manner just described, we did not get all the water out. In our definition of the water content of coal this water must be included, consequently the method of drying over phosphorus pentoxide does not give the true water content, nor do any of the other methods which have been used, so far as we know.

There does not appear to have been any attempt by workers in this field to state the problem clearly, that is to consider what is the precise significance of the term "the water content of coal." In order to get a working definition of the water content of coals let us consider the problem from the standpoint of the origin of coal.

It has been fairly well established that the starting point of coal in the natural process of its making was peat. There is considerable evidence which indicates that this peat was formed in a manner somewhat analogous to the peat of the present age, though on a much vaster scale.<sup>\*</sup> From year to year the decaying vegetable matter accumulated at the bottom of the swamp, and as it gradually sank below the surface of the water, it was protected from the oxygen of the air, and from certain ferment organisms which, together with the oxygen, were the active agents in the chemical changes that transformed the vegetable matter to peat. The rate of accumulation depended on the rate of the vegetable growth, and the efficiency of its preservation. As the deposit grew, the deeper portions became more dense, and according to a rough estimate, it required something like a century to form a thickness of one foot of such dense peat.

With regard to the changes taking place in the transformation of peat to coal our knowledge is still largely speculative. One of the most favored ideas at present is that pressure plays the most important rôle in these changes—a pressure due to the overlying weight of debris and rock which covered up the swamp; or due to a metamorphic change such as a compression in the earth's crust. According to this view, the peat subjected to compression gradually became in successive stages lignite, sub-bituminous, bituminous and finally anthracite coal and graphite. Starting with peat and going down the series, chemical analyses show that extensive chemical changes have taken place,<sup>†</sup> the net result of which was a progressive elimination of volatile matter such as carbon dioxide, carbon monoxide, methane and water, and in such relative pro-

\* White and Thiessen, The Origin of Coal (page 53), Bulletin 38, Bureau of Mines, 1913.

†O. C. Ralston, Graphical Studies of the Ultimate Analysis of Coal. Paper presented at Cincinnati meeting of Amer. Chem. Soc., and published as a Bulletin of the Bureau of Mines.

portions that there was a continuous diminution in the percentage of oxygen present in the substances which make up the coal.

It must, however, be noted that water cannot be removed from peat or coal to any great extent by pressure, but as a result of the *chemical reaction* involved in the transformation of peat to coal the physical properties of the mass changed so that it was possible for the water partially to escape. We may question whether too much importance has not been assigned to the influence of pressure as a factor in the change from peat to coal; for pressure plays little, if any, rôle in the chemical reactions which take place in a condensed system, either as regards the kind of the reaction or the rate. However if the pressure causes a rise in temperature then the rates of the chemical reactions taking place are markedly accelerated. Pressure has undoubtedly aided somewhat in the mechanical elimination of the more volatile and liquid products of the chemical reactions, and has been a factor in giving coal its firm, compact qualities.

The possibility that pressure may have caused a rise in the temperature of the peat-like substance has been suggested. It is, however, to be remembered that the mere subjection of a body to a pressure strain will not generate heat unless there is an actual decrease in the volume of the substance compressed, in accordance with the energy equation :

### $P \times V = 2T$ calories.

Heat is produced by the action of pressure through a distance, represented here by a volume change. And in the case of peat, coal and the intermediate substances, the deposit (from the old swamp) either yielded suddenly to an enormous pressure, breaking or crumpling, in which case the heat produced would be dissipated or conducted off fairly rapidly by surrounding rock; or the deposit and the rock above and below it were pressed in such a way that they were not forced to yield suddenly, but remained under the strain for a long time.\* For this latter case we may make an approximate calculation.

Assume that we have a deposit of dense peat 5 meters thick and that it is compressed at the rate of about one-half a meter a century, i. e. one-tenth of its volume the first hundred years. Suppose the peat layer to be buried one kilometer beneath the surface, under a mass of debris, which had an average specific gravity of 3.0. Then the pressure on the peat per square centimeter would have been,

# 1000 (m) $\times$ 100 (cm) $\times$ 3 grams = 300 kilograms

1000 (grams)

<sup>\*</sup> White and Thiessen, The Origin of Coal, pages 106 and 128 of the chapter "Regional Metamorphism of Coal."

or about two tons per square inch. The amount of heat developed in a hundred years in each cubic centimeter of the peat substance would have been :

 $\frac{1000 \text{ (m)} \times 100 \text{ (cm)} \times 3 \text{ gm.} \times 0.5 \text{ meter}}{4.5 \text{ (m)} \times 100 \text{ (cm)} \times 424 \text{ (mech. equiv. of heat)}} = 79 \text{ calories.}$ 

If the specific heat of the deposit was 4, the heat produced during a hundred years would have been sufficient to raise the temperature of the deposit only 2°. Even assuming that the peat was subjected to a continuous prodigious pressure a thousand times as great as that here calculated, still the increase in temperature would have been only about 2° a month, even with perfect insulation : but peat and the adjacent material saturated with water are quite good heat conductors. Therefore, the heat must have been conducted off almost as fast as it was developed and it is difficult to see how the prospective coal bed could have been kept above the temperature of the surrounding rock strata for any considerable length of time. If, however, as a result either of folding or slipping of strata (friction), a higher temperature was maintained locally, there might have been a sufficient increase in the rate of the chemical reactions taking place to have caused a comparatively rapid alteration of peat to coal. But this would be local in its effects and could be detected. Igneous intrusions do not appear to have played any great rôle. (See The Origin of Coal, p. 101.)

The foregoing considerations are supported by the experiments of Dr. F. Bergius,\* who actually succeeded in the laboratory in transforming cellulose or peat into a product very much resembling, and having the composition of, coal. Hitherto all attempts in this direction had failed because, when the peat or other raw material was heated in a closed vessel with the object of making it into coal, it was found impossible to control the temperature of the reacting particles, that is, to avoid a superheating of the materials due to the exothermic reactions, and for this reason the final products resembled charcoal or coke rather than coal, all the volatile and resinous substances having been driven out or decomposed by exposure to too high a temperature. In Bergius' experiments this difficulty was overcome by heating peat together with a large amount of water, where the heat capacity of the liquid water was such that it served to absorb the excess heat from the reacting peat particles which otherwise would have been superheated. Thus the water acted as an excellent thermostat, making it possible to control the temperature at which the chemical re-

\* Jour. Soc. Chem. Ind., xxxii, p. 462, 1913.

actions in the peat were taking place. In working above 100° C. it was of course necessary to maintain the pressure at or above that of the vapor pressure of the water in order to keep the water in the liquid state, but we fail to see that the pressure played any rôle in the chemical reactions.

The interesting point of Bergius' work is that he showed that the same product was obtained by heating for 8 hours at 340°, as for heating 64 hours at 310°. In other words the rate of reaction was doubled for every rise of 10°, which is the characteristic increase of rate for chemical reactions. On this basis, assuming that the chemical changes involved in the transformation of peat to coal in the natural process took place at the average temperature of 10° C., Bergius calculated that to form bituminous coal from peat,  $2^{i_3} \times 8$  hours was the time required, or about 8 million years, an estimate in good-enough agreement with the calculations of the geologists. Bergius gives this figure with all "due reserve," but it will readily be seen that this line of evidence, while perhaps not absolutely conclusive, gives very strong support to the idea that the transformation of peat to coal was the result of a series of slow chemical changes proceeding at about the same temperature as the earth's surface, and quite independent of the presence or absence of pressure.

Bergius showed that vegetable matter or peat could be changed to a residue having the same composition as bituminous coal, by reactions which require a definite "temperature-time" interval, but the product was an amorphous powder when separated from the water. Bergius further showed that this residue could be transformed to a substance having not only the chemical composition but also the texture and properties of anthracite, by subjecting it to a temperature of 340° and a pressure of 5000 atmospheres for some time. At this temperature the chemical changes were quite rapid and the residues were compressed to a substance with the hardness of anthracite. It is quite possible that both a great pressure and a high temperature, considerably above ordinary rock temperature, have played a rôle in the formation of our anthracite coals. The comparative suddenness in the change, from a chemical standpoint, from bituminous to anthracite coal, is indicated in the graphical studies of the Ultimate Analyses of Coal,\* and is in line with these results of Bergius.

It is not necessary to assume either pressure or any higher temperature than ordinary rock temperature for the transformation of peat through the various forms of coal to bituminous coal. The cellulose and protein substances of the original vegetable matter are gradually changed by the action

\* Ralston, Tech. Paper, 93, U. S. Bureau of Mines, 1915.

of fungus bacterial ferments to so-called "humus" substances, while at the same time, but more slowly, the wax and resinlike matter decomposes, giving rise to hydrocarbons. The microscopic examination of peat and coals by Thiessen (l. c.) has revealed a fine spongy structure made up of a mat of resin granules, spores, and pollen exines, humic and woody remains. The original plant cells having been collapsed, there remains a mass which has passed through various colloidal stages.

In the first stages peat may be largely a hydrosol. Accompanying the slow chemical changes, reactions which take place of themselves with a decrease in free energy, there is an elimination of water, carbon dioxide, methane, etc., and the mass becomes more largely a hydrogel which by the further loss of water and volatile products can harden to bituminous coal. The chemical reactions involved are generally of the nature of the formation of small molecules from larger ones, a change almost invariably accompanied by an increase in volume, and the effect of pressure in such cases is rather to oppose than aid the chemical reactions.

The foregoing considerations indicate the importance of the "water content of a coal" in questions concerning its present status and constitution. In addition to the water originally present, the slow chemical reactions continually form water as one of the decomposition products, and consequently there must be an elimination of water from the coal beds during the slow transformations from peat to anthracite. Nevertheless coals are normally dry. We may dismiss any idea that hydrocarbons, resinous bodies, waxes, carbon residues and humus substances combine with water in any such way as water of crystallization, but if these substances form a colloidal solution with water as one of the phases the matter is entirely comprehensible. The organic substances from peat to anthracite are in an exceedingly finely divided state and present an enormous surface for the water phase. It is generally recognized that at the surface of heterogenous phases there is a concentration layer, and in the case of a colloid the total surface is so great that the actual amount of water concentrated in the film may be a considerable percent of the total mass. Some interesting estimates have been made of the thickness and density of such films. For the thickness Lewis<sup>\*</sup> assigns  $5 \times 10^{-6}$  cm.

This seems rather large, for taking the diameter of the water molecule as  $0.2 - 1.0 \times 10^{-8}$  cm., two have a film 500-2500 times as thick as a water molecule. A more reasonable figure is that of Taylor,  $\ddagger 0.6 \times 10^{-8}$  cm. Sutherland gives

\*W. C. McC. Lewis, On the Nature of the Transition Layer between Two Adjacent Phases, Phil. Mag., xx, p. 509, 1910. †W. Sutherland, The Molecular Constitution of Water, Phil. Mag., Nov. 1900, p. 473; and W. Ostwald, Grundriss der Kolloidchemie, 1912, p. 32. ‡ W. W. Taylor, The Chemistry of Colloids, 1915, p. 225.

 $1.26 \times 10^{-8}$  cm. If these latter values are to be regarded as probably nearer the truth, then the film cannot be more than a few molecules thick. The density of the film has been put (for 25° C.) at about twice that of water, namely at 2.  $\cdot$  It is to be noted, however, that the first few layers of molecules next to the colloidal surface represent a greater density than the layers more removed, which in fact probably grade off imperceptibly into the bulk water, making it hard to say just exactly where the "film" really begins.

If we consider one cubic centimeter of the organic substances which make up coal, free from water and ash, it would have a density of not much over 1. If the cube were divided into little cubes 10<sup>-6</sup> cm. on each edge—a particle readily detected by the ultra-microscope—the area of the faces of these little cubes would be 600 square meters. If we suppose that they are covered with a layer of water molecules say  $1 \times 10^{-8}$ cm. thick with a density of 1, although it is probably greater than that, there would be '06<sup>ce</sup> of water on these faces in a condensed condition such that it would show little or no vapor pressure. If the layer of water were 1/10 of the thickness of the cube or 10 molecules thick with the increased size of the cubes, there would be about .7<sup>cc</sup> or 60 per cent water intimately associated with this original cubic centimeter of coal substance and the vapor pressure of this water would undoubtedly be much below that of a plane surface of water at the same tem-The substance would no doubt take up water from perature. ordinary air and "feel dry."

Some of the particles of coal are probably as small or smaller than we have assumed—others larger, the humus material in general being in the colloidal condition outlined. In the progress of the transformation of peat to bituminous coal, as the chemical reactions slowly result in the disappearance of the humus, the waxes, resins, etc. forming carbon residue (composition of anthracite), carbon dioxide, volatile hydrocarbons, water, and the various other products, there results a gradual but marked *decrease* in the water content proportional to the *decreased* colloidal surface.

The true water content of any coal might thus be taken as a rough measure of its humus content, and vice versa.\*

The condition of water on "adsorption" surfaces was first studied by Van Bemmelen<sup>†</sup> who experimented in particular with silicic acid and ferric oxide gels. The method used was to place weighed amounts of the gels in desiccators where a definite vapor pressure was maintained by sulphuric acid of a

\* John Harger, Jour. Soc. Chem. Ind., xxxii, p. 460, 1913, suggested that the humus material contained most of the water found in coal.

+ J. M. Van Bemmelen, Die Adsorption, 1910.

suitable density. There was no evidence of a combination between the water and gels. The results showed that the water was continuously removed as the surrounding water vapor pressure was lowered, and in general when the vapor pressure was increased the gel would take on water; but this "hydration" curve fell above the dehydration curve, that is, the vapor pressure of a gel with a given amount of water had different values depending on its previous history and on whether it was being dehydrated or hydrated. Porter and Ralston\* have found this same phenomena with different varieties of coal, so that in this respect also coal behaves like a colloid. Whether or not there is here a coagulation of colloidal particles during dehydration of such a nature that there is less surface available when hydrating, the fact is that the process is not reversible, and if we allow a coal sample to lose or gain water we are not in a position to return it to the original condition and water content, with a definite vapor pressure. These facts and considerations make it necessary to fix some base line or starting point in determining the moisture content of a coal.

There seems to be no evidence that extraneous water penetrates the coal beds or coal. It would be only locally that spring water, or an unusually warm zone, might alter the normal content of a coal bed. In the main the water content would depend on the per cent and texture of the humus and colloidal matter in the coal, both of which are determined by its previous history. It would seem therefore entirely satisfactory to define the water content of coal as the amount of water present in that coal as it is found in the bed. Care must be taken that the sample is from a fresh break, and that it does not lose or gain water during the subsequent handling and preparation of the analytical sample.

On exposure to air coal begins to lose or gain moisture depending on the kind of coal, the temperature, and the moisture content of the surrounding air. In view of the foregoing considerations we could not expect attainment of a condition of equilibrium even with fixed air conditions or even attainment of a "steady" state. If the air is saturated with moisture any coal takes on moisture, the amount and rate depending on the nature and thickness of the water layer on the humus and colloidal particles and on the per cent of humus present. If this absorbed layer is very thin it has a very low vapor pressure, increasing with the thickness of this layer, and approaching but never reaching the vapor pressure of a plane water surface. Under ordinary conditions air is generally not saturated with water vapor and for the most part is far from it, so that generally a coal loses water on exposure to air. As

\* Tech. Paper 113, U. S. Bureau of Mines, 1915.

the rate of loss of water is dependent on the thickness of the film and surface available we find the loss most pronounced in the lignites,<sup>\*</sup> where ordinary moisture determinations are quite useless unless the sample has been properly collected and handled. As we approach the anthracite end of the coal series the adsorption surface and moisture content are small and vapor pressure such that there is relatively little loss or gain under ordinary conditions.

In removing water from coal by the use of such drying agents as sulphuric acid or phosphorus pentoxide, time is gained by reducing the coal to a fine state of division, and by using a vacuum. The rate of loss is a maximum at first, falling off rapidly as the adsorbed water film becomes thinner and finally ceasing when the adsorbed film has been reduced to a vapor pressure about equal to that of the dehydrating agent. With our best dehydrating agents such as  $H_{a}SO_{4}$  and  $P_{a}O_{5}$  it would seem to be impossible to remove the films of water which are only a few molecules in thickness. Lewest considers that a certain sub-bituminous coal which loses 15 per cent of moisture at 105° is composed of humus 35 per cent, hydrocarbons and resinous matter 30 per cent, carbon residue 20 per cent,—or over 50 per cent of this coal might be considered as colloidal and according to the approximate calculation previously made the adsorption surface is sufficient to retain some 3 per cent of water in a layer one or two molecules thick, so that it would not be removed by vacuum desiccation with our best dehydrating agents. Many assumptions were necessary in making the calculations but they should give an idea of the order of magnitude and in fact they agree satisfactorily with our experimental results in Table I.

It was to be expected from the first that a rise of temperature would increase the vapor pressure of the adsorbed film, thus yielding more water. For it is well known that the condensation of water on fine materials is accompanied by an evolution of heat, i. e., the process by which water in mass passes into a film having a greater density, is exothermic. Consequently, according to the law of Le Chatelier, the application of heat to such a film as that on the colloidal humus must result in diminishing the density and the surface tension of the film, with a corresponding increase in the vapor pres-In fact it has been shown that the density of film water sure. approaches that of water in "bulk" as the temperature of both is raised the same amount, and of course at the critical temperature 365° the density of both become equal to that of water vapor.

> \* G. H. Frankforter, Jour. Amer. Chem. Soc., xxix, p. 1488. † Lewes, The Carbonisation of Coal, p. 48.

These considerations gave us a fairly definite conception of the water content of coal and also indicated the line of attack which promised a successful solution of the problem of determining the water. We cannot determine the water content of a sample of coal by vacuum desiccation at ordinary temperatures on account of the difficulty of maintaining a sufficiently low vapor pressure in the desiccator and especially on account of the slowness of the escape of the last but considerable part of the water from the coal. If, however, we keep the vapor pressure low but heat the coal, we increase the vapor pressure of the film of adsorbed water, and so may make the time required for its removal as short as we wish. Oxygen must of course be excluded and in a vacuum the rate of loss of water is somewhat greater. We have devised several satisfactory methods for accomplishing the desired results, but have studied particularly some questions raised by such procedures.

Our preliminary experiments, Table I, showed that vacuum desiccation, with reagents which maintained the vapor pressure of water at about  $01^{\text{mm}}$ , still left very considerable portions of the water in the coal, which however came off rapidly when the coal was raised some 100° in temperature, and while it was concluded that this probably removed most of the water from the coal we recognized the possibility that some water could be retained until a temperature approaching the critical temperature of water was employed—but it was necessary to consider another result of heating coal. Coal is a conglomerate of constituents, some of which at least are decomposing as outlined above, and forming among other products water. The rate of these reactions at ordinary temperatures is immeasurably slow, but Bergius' work shows that the rate doubles for each increase of 10°. Therefore we must avoid the conditions of temperature and time at which the reactions are capable of yielding measurable amounts of water. The problem was then to find out whether we could heat the coal for a "temperature-time" interval such that the water film could be decreased to negligible amount, without accelerating the decomposition reactions of coal substances to an extent such that a measurable amount of water would be formed.

For the question of the preliminary decomposition of coal substances we have some data from the work of H. C. Porter and G. B. Taylor.\* These workers determined the amount and nature of the volatile products obtained from coal at 250°, 350° and 450° when maintained at these temperatures from 7 to 13 hours and at very low pressure. The following table shows some of the results which are of interest here. Four types of coal were used.

\* Proc. Amer. Gas. Assn., vol. ix, p. 234, 1914.

	New River	Pittsburgh	Illinois	Wyoming
Per cent gas liberate	d			•
at 250°	- •12	•10	•35	1.04
Per cent $CO_2 + CO$ in	1			
the gas	- •49	•70	•71	•85
Per cent gas liberate	d			
at 350°	- •33	•50	1.2	· 3·16
Per cent $CO_2 + CO$ in	1	10		
the gas	- •49	•21	•45	•64



At higher temperatures the amounts and rate of formation of gas increase rapidly. In addition to the above, "tar" and water were volatilized, but they may have been present as such in part or largely, and in view of the large percentage of CO<sub>2</sub> and CO in these first gaseous products it may well be that they also were largely present as such in the surface film, held much as is the water. This would be particularly true of the CO<sub>2</sub>. The moisture contents of these four kinds of coal increase, from the New River to Wyoming, in the same ratio as do the gas losses at these temperatures. So we may consider that the adsorption surfaces vary in about the same ratio, and it is entirely probable that these first gases were largely adsorbed along with the water film. There is no doubt that there is some decomposition of coal constituents at 250° but it is very slow and small in amount for a period of 6-7 hours, while for an hour at this temperature there would be formed only a trace of water, but at 350° for a comparatively short time we would have measurable amounts of water formed by decomposition of coal substances. Our work confirms these

observations and shows that a temperature even less than 250° for a reasonable time is sufficient for our purpose.

Our first experiments were carried out with a very simple apparatus. A glass "alembic" of the form shown in fig. 1 was weighed, and after the lower bulb (5<sup>cc</sup> capacity) was filled with coal, it was reweighed to get the weight of coal. The tube was now evacuated to about 2<sup>mm</sup> pressure and sealed off. A split cork just below the alembic bulb served to hold the lower



FIG. 2.

bulb and tube in a vapor bath,-where the condensation of vapor on the coal bulb not only rapidly brought it to the tem-perature of the bath, but maintained the temperature accu-The moisture from the coal rapidly rately and easily. evaporated and condensed in the alembic bulb, which was cooled by ice or a jacket with ice-salt mixtures. After a sample of coal had been heated for a definite time, the apparatus was removed from the bath, the tube was cut just below the alembic bulb and by weighing, removing the water and again weighing, the water was determined. A little glass-blowing permitted of using the same tubes again. It was found to be necessary to cool the coal bulb in a freezing mixture to prevent loss of moisture on evacuating; at  $-20^{\circ}$  the loss was negligible. When all these precautions were taken it was found possible to duplicate a result to 0.2 to 0.5 per cent of the amount of water determined.

With this apparatus we studied the per cent of water lost by a given coal for different periods of heating, obtaining an isothermal with percentage of water as a function of time, the curve showing a flattening when the loss of water finally in



FIG. 4.



the last intervals became no longer measurable. Then other isothermals at successively higher temperatures were determined, until we reached a condition where there were indications of a decomposition of the coal substances. The vapor baths were as follows: "95 per cent" alcohol for 82°, water for 100°, toluol for 111°, xylol for 140°, aniline for 184°, naph-thalene for 218°, and thymol for 230°. Figs. 2, 3, and 4 show the time curves for the three coals, New River, Pittsburgh and Illinois. It must be noted that the form of the tube in which the coal was heated and also the conduction of heat through the coal, are factors in determining the slope of the first part of each curve. With regard to the form of the apparatus, we made blank tests by placing weighed amounts of water in the bulb at the bottom, and determining the time required to collect all the water in the alembic at the top. For example, 0.1156 gm. water was heated at 111° and after two minutes the amount which had been driven into the upper bulb was 0.1152 gm. Furthermore, the small mass of coal in the bulb which is in direct contact with a hot condensing vapor is soon brought to the same temperature throughout its entire body. Consequently we are justified in looking on these time curves as really affording a good idea of the actual rate at which the water is given off from the coal at the respective temperatures.

The coals used in our investigation were samples secured by engineers of the U. S. Bureau of Mines and analyzed in the Bureau of Mines Laboratory. These samples were stored in large bottles with paraffined stoppers and kept in a cool room. As needed, smaller samples were powdered and kept in small rubber-stoppered bottles. The question of loss in sampling and powdering was considered and observations made on 8-20 mesh grains, on 20-30 and on 60 mesh powder of the same coal (fig. 5). It was concluded that rapid powdering to 20-30 mesh did not cause a measurable loss of moisture due to exposure to air or to the dehydrating effect of crushing.\*

A second method differing somewhat from the first, was used to obtain the time curves, a method which possessed the additional advantage that it afforded means by which the gas evolved from the coal could be determined along with the water. It consisted in heating the coal in the glass bulb (fig. 6) attached to a capillary glass tube of about  $\cdot 5^{mm}$  bore by the ground glass joint C. The capillary led through a threeway stop-cock to a measuring burette having a large bulb at its lower end, which was connected to a rubber tube and a leveling bulb, both containing mercury, in such a way that by lowering and raising the level of the mercury and at the same time opening and closing the cock, the air could be driven out

\* R. Mauzelius, Sveriges Geol. Undersökning, 1907.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 254.—FEBRUARY, 1917.



Fig. 6.





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of the large bulb and the burette and a vacuum created. The mercury, after this, was adjusted to the level L, and the coal which had been cooled and evacuated by connection with the pump through the three-way cock, was then joined to the burette by turning the cock. The gas from the heated coal collected in the large bulb and could be measured at any time in the burette by closing the cock and raising the leveling bulb. The coal bulb was heated in the vapor bath up to the point C, and the water from the coal condensed at the opening of the capillary tube and was rapidly forced by the slight pressure in The water collected on the coal bulb to traverse the capillary. the top of the mercury, but a measurement of the volume of the water was not very satisfactory. We obtained the weight of the gas by transferring it from the burette by means of the mercury into a partially evacuate tube which had been weighed. The weight of the gas was subtracted from the total loss from the coal bulb to give the weight of water. The determinations made on the three coals with the alembic method were repeated, using the second method, the two sets of results agreeing very well, as fig. 7, with the results at 184°, will show. During the first few minutes water was removed more rapidly from the coal bulb of the second apparatus than from the first, but the flat portions of the curves are almost identical.

If the final values represented by the flat portions of the time curves in figs. 2, 3, and 4, are plotted as ordinates against the temperatures to which the coal was heated, as abscissæ, the curves shown in figs. 8, 9 and 10 are obtained. The marked flattening of the curve at the higher temperatures indicates that very little more water could be removed from the coal by any further heating, though some water probably still remains on the adsorption surfaces even at the highest temperature, especially since pressure of the water in the alembic tube is appreciable, even when the alembic bulb is cooled.

Below 250° very little gas indeed came from the coals used and, as we have pointed out, it is probable that a considerable portion of this gas was merely adsorbed on the large surfaces of the colloidal coal. We were not particularly concerned with the gases evolved during the heating of the sample coal, except in so far as it enabled us to know whether or not decomposition of the coal was taking place. We did however make determinations of the amounts of gas liberated in the various experiments and the work of Porter and Taylor on these coals give us sufficient information on their composition.

#### Summary.

We have attempted to define the true moisture content of coals and have made some determinations on three typical coals,

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by a method which should give a close approximation to the true moisture content of these coals.

This work has suggested several ideas on the nature and genesis of coal. It is evident that there is practically no definite information about the relation of moisture to such substances as coal and in fact to all organic and colloidal substances.

Laboratory of Physical Chemistry, Princeton University, June, 1916.

# ART. XI.—An Apparatus for Determining Freezing Point Lowering; by R. G. VAN NAME and W. G. BROWN.

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

THE apparatus here described and figured operates, like the familiar Beckmann method, on the undercooling principle. It differs from others of its type both in the manner of effecting the undercooling, and in the fact that the whole process, undercooling, inoculating, freezing, and remelting in preparation for a new determination, is carried out in a vacuum walled container (Dewar tube).

With any type of freezing point apparatus the need of effective heat insulation of the mixture of solid solvent and solution during the period of temperature observation is self-evident, and the use of a Dewar tube as container is a recognized feature of at least one well-known method, that of Richards. The convenience and accuracy of the Richards method are unquestioned, but it has the disadvantage shared by others of its type, that the concentration of the solution whose freezing point is measured cannot be definitely fixed beforehand. For this and other reasons methods of the undercooling type are in certain cases to be preferred, both for very exact measurements and for those of lower accuracy.

The form of apparatus which we have used is represented in fig. 1, which shows all the important parts, but omits the mechanism for operating the stirrer, and a few other minor details. The Dewar tube, of about one-half liter capacity, is surrounded by a projecting jacket of tin, AA, and is closed by a cork stopper, B, perforated in four places to admit (1) the Beckmann thermometer, (2) the stem of the glass stirrer C, (3) a short tube, not shown in the figure, ordinarily kept stoppered, .through which inoculation is effected, and (4) the cooling device D. This cooling device, consisting of two concentric



glass tubes through which cold brine<sup>\*</sup> is circulated, is the essential feature of the apparatus.

As the brine enters by the inner tube its temperature is shown by a small thermometer. At the beginning of a determination the inner tube is drawn up slightly so that there is a free passage between the two tubes at the bottom. The brine passes down the inner tube, rises between the inner and outer tubes, thus exerting its cooling effect on the liquid outside, and finally escapes through the side tube. When the desired degree of undercooling has been obtained, the inner tube is lowered until in close contact with the outer tube at the bottom, where it has been ground to a fit, thus stopping the circulation through the lower part of the cooling system. This is the position shown in fig. 1. The lowering of the inner tube uncovers a hole in that tube, previously covered by the rubber stopper E, and the brine now circulates only through the upper portion of the cooling tube which projects from the apparatus. So long as the inner tube is in this lower position the upper part of the cooling device is thus kept at a temperature below that of the solution, and by an amount which is easily regulated. This is an important point since it insures that such transfer of heat as occurs through the cooling tube shall be outward rather than inward, so that instead of promoting leakage of heat into the apparatus, as it might otherwise do, the cooling device actually tends to compensate for such leakage as occurs elsewhere.

Fig. 2 shows the details of the cooling device, though without its thermometer. The inner tube is here shown raised, in the position for undercooling. All the upper part of the cooling tube, down to a point below the level of the liquid into which it dips, is surrounded by a narrow vacuum jacket, so that the cooling effect is exerted only below the surface of the liquid. This prevents accumulation of frost on the cooling tube above the liquid, which would be apt to cause premature freezing, and therefore permits the use of a much colder brine, making the whole determination a great deal more rapid. An unjacketed cooling tube can be used with equally accurate results, but only at a considerable sacrifice in convenience.

The brine is drawn through a strainer of fine wire gauze from a large ice and salt mixture placed slightly above the level of the apparatus, and circulates through the system by gravity, the rate of flow being regulated by screw pinch-cocks on the rubber connecting tubes. It is collected in another

<sup>\*</sup> It is assumed here and in what follows that we are dealing with the measurement of freezing point of water solutions, since this is by far the commonest and most important case, and is the one to which our practical experience with the apparatus has been confined. The adaptability of the method for other solvents, of widely differing melting points, is, however, quite obvious.

receiver and from time to time returned by hand to the freezing mixture.

A side branch in the tube which conveys the brine to the apparatus is connected with the water main so that when desired the brine temperature may be raised by admitting water in regulated amounts. To insure thorough mixing of the two liquids they pass, just beyond their point of meeting, through a roll of fine wire gauze, so arranged as to be easily accessible for cleaning (fig. 2, G). After each determination, the ice which has separated is melted by shutting off the brine altogether and permitting water alone to flow through the cooling tube for a short time.

The stirrer is driven by a motor, and except for a brief interval at the time of inoculation, is kept in motion throughout the experiment. The successive steps in determining the freezing point of a solution are as follows: The solution (of known concentration) is placed in the apparatus, the stirrer set in motion and the flow of brine started. When the desired degree of undercooling has been reached the inner tube of the cooling device is lowered to the position shown in fig. 1. After waiting a short time for temperature equilibrium the thermometer is read (this reading is used only in calculating the degree of undercooling) and the inoculation effected in the usual way, whereupon the temperature rises and becomes constant at the freezing point. Owing to the good heat insulation the constancy of the freezing point is almost as perfect when working with a solution as it is with pure water. This eliminates the necessity for considering the so-called " convergence temperature," and makes the calculation of the correction for undercooling simple and free from uncertainty.\*

The effective heat insulation is due not only to the use of the Dewar vessel but also to the fact, mentioned above, that the flow of brine through the upper part of the cooling tube tends to compensate for the heat leakage and the heat generated by stirring.

With regard to the possibility of using this form of apparatus for very accurate measurements we would call attention to the fact that by suitable provision for a closer regulation of the temperature, rate of flow, and path of the brine, this compensation could be made approximately complete, thus permitting the temperature readings to be made under practically ideal conditions. The accuracy would then be limited only by that of the temperature measurements.

<sup>\*</sup> This correction is based on the degree of undercooling, the heat of fusion of the solvent, and the heat capacities (a) of the liquid, and (b) of the container, stirrer, thermometer, etc. In practice (a) is so large compared with (b) that a rough estimate of the latter is generally amply sufficient for the purpose.

For most purposes, however, a comparatively rough compensation is all that is needed. With our apparatus as at first used there was a tendency, under ordinary working conditions, for the compensation to be incomplete, an unfrozen liquid showing a slow rise in temperature. This was corrected in a sufficiently effective manner by filing a small notch in the lower edge of the inner tube of the cooling device, thus permitting a very slight flow of brine at this point even when the ground surfaces were in contact.

We have put the method to a practical test in an extended series of determinations of the freezing points of water solutions. A Beckmann thermometer with a 5° scale was used throughout so that it was impossible to observe temperature differences of less than  $0.001^\circ$ , but within the limits of accuracy so imposed the results were very concordant and satisfactory. A few results obtained with two different solutions prepared from a carefully purified sample of cane sugar are given below by way of illustration :

Gms. sugar per 100gms. H <sub>2</sub> O	Observed f. p. lowering	Under- cooling	Corrected f. p. lowering	Av.	Molecular lowering
4·274 ‹‹ ‹‹	0·239° 0·236 0·235	1·81° 0·94 0·67	0·234° 0·233 0·233	0 <b>·</b> 233°	1.865
8·521 " "	$0.487 \\ 0.489 \\ 0.485 \\ 0.488$	1·10 1·48 0·88 1·27	0.481 0.480 0.480 0.480	0.480	1.92 <sub>6</sub>

The thermometer used had been carefully compared with a similar one certified by the U. S. Bureau of Standards, and the observed freezing point lowerings as given in the second column of the table have been corrected for the errors of the thermometer. Those in the fourth column have been further corrected for the undercooling. Considering the lack of sensitiveness of the thermometer employed, and the fact that it was not kept in ice-water when not in use so as to avoid the effect of slow volume changes in the glass, the values found for the molecular lowering agree about as well as could be expected with the best available values for such solutions, as determined by Raoult and others.

## ART. XII.—The Sodium-Potassium Nephelites; by N. L. Bowen.

#### INTRODUCTION.

Among rock-forming minerals, especially those of the interesting alkaline rocks, nephelite takes a prominent place and for this reason has attracted considerable study on the part of mineralogists and petrologists. This study has revealed in nephelite considerable chemical complexity the explanation of which has been and, to some extent, still is a matter of controversy. The simple compound NaAlSiO<sub>4</sub> is now rather generally regarded as the fundamental molecule of nephelite, but the composition of the natural mineral always departs from this markedly, showing a large content of potash, often considerable lime, and a variable excess of silica above the orthosilicate ratio. A study of the fundamental compound and of the lime content of nephelite has already been made at this laboratory.\* The present paper describes the continuance of this work in the study of the potash-bearing nephelites or the binary system,  $NaAlSiO_4$ -KAlSiO<sub>4</sub>.

#### The End Members.

 $NaAlSiO_4$ .—The compound NaAlSiO<sub>4</sub> can be prepared by sintering together Na<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in the proper proportions at a low temperature (about 800°) to prevent loss of Sintering must be repeated several times with intersoda. mediate grindings and then the whole may be raised above the melting temperature. The product is a clear homogeneous glass of the appropriate composition. † This glass crystallizes at low temperatures to the hexagonal form, nephelite, and at high temperatures to the triclinic (?) form, carnegieite. The inversion temperature of  $1248^{\circ} \pm 5$  obtained in the earlier work was confirmed during the present investigation, as was also the melting temperature of carnegiete, 1526°.

Pure sodium nephelite is hexagonal and negative. The refractive indices are  $\omega = 1.537 \pm .002$ ;  $\epsilon = 1.533 \pm .002$ . The density is 2.619 at 21°.

Carnegieite always shows a complicated polysynthetic twinning. There are often two intersecting sets of lamellæ suggesting the microcline twinning and again three sets giving an hexagonal aspect. It has been considered triclinic, though it could be, perhaps, orthorhombic or monoclinic. The refractive

\* N. L. Bowen, this Journal, xxxiii, 551, 1912. † The reasons for this procedure are given in the former paper, this Journal, xxxiii, 552, 1912.

indices are  $\gamma = 1.514 \pm .002$ ,  $a = 1.509 \pm .002$ . It is biaxial, with negative optical character and  $2V = 12^{\circ}-15^{\circ}$ . The density is 2.513 at 21°.

Glass of composition NaAlSiO<sub>4</sub> has a refractive index  $1.510 \pm .002$ .

KAlSiO,.--The preparation of the pure potash compound is not so readily accomplished. The same precautions of sintering at a low temperature before raising above the melting point are not adequate in this case to prevent volatilization of the alkali, partly because the potash is much more volatile than soda and partly because of the high melting-temperature of the potash compound. In raising the charge to this temperature which is somewhat above the melting-point of platinum, considerable potash is lost. The pure compound cannot, then, be prepared in the dry way simply by mixing the components and melting them, though its preparation by this method has been claimed. Especially should one not attempt to prepare it by fusion in a platinum crucible, for the crucible melts and runs away when the sintered charge is still intact. In a poorly mixed charge melting can be obtained at comparatively low temperatures, silica and potash fluxing together and leaving much alumina undissolved, but this is not melting of kaliophilite. Nevertheless one can obtain a product with only a moderate deficiency in potash by sintering at a low temperature as described and then rapidly raising to the melting temperature in an iridium furnace. The glass so obtained is apparently not very different in viscosity from the nephelite glass and crystallizes about as readily when not too rapidly cooled. In this way one obtains crystals which correspond in properties with the natural mineral kaliophilite, always, however, with a little foreign material since the composition does not lie exactly at the compound KAlSiO<sub>4</sub>.

The artificial kaliophilite so obtained is hexagonal and negative,  $\omega = 1.532 \pm .002$ ,  $\epsilon = 1.527 \pm .002$ . The prism and base are predominant with only an occasional truncation of the edge by a pyramidal face. One sees, then, the hexagonal basal sections and quadratic prismatic sections precisely as in nephelite.

With the aid of potassium tungstate as a flux good crystals of kaliophilite were prepared at about 1300°. The largest of these were somewhat contaminated with the flux and showed higher indices of refraction than those given above, but the smallest crystals were found to agree exactly in all their properties.

Small crystals of kaliophilite were prepared hydrothermally by Morey in this laboratory. Kahlbaum's potassium aluminate and potassium silicate were used. These were placed with water in a gold crucible in a steel bomb after the usual method.\* The temperature was kept at 600° and the pressure of water vapor at about 1000 atmospheres for 24 hours.

An analysis of the kaliophilite crystals obtained is stated below.

T	11
38.0	38.07
32.0	32.21
29.8	29.72
$\cdot 12$	
99.9	100.00
	$   \begin{array}{r}     1 \\     38.0 \\     32.0 \\     29.8 \\     \cdot 12 \\     \overline{99.9}   \end{array} $

I. Artificial kaliophilite. Analyst N. L. Bowen.

II. Theoretical composition, KAlSiO<sub>4</sub>.

The optical properties were exactly as given above.

Formation of leucite.—In attempting to prepare kaliophilite by heating glass of composition KAlSiO<sub>4</sub> at about 800° with potassium tungstate occasional crystals of kaliophilite were obtained but the great bulk of the product was a material of weak double refraction and conspicuous polysynthetic twinning. The refractive index was 1.509. This value, together with the polysynthetic twinning, gave the impression, at first, that a form of the potash compound corresponding with carnegieite had been obtained. These properties agree, however, with those of leucite and an occasional crystal suggested the typical icositetrahedron of that mineral though the majority of them were in branching forms. The amount of material was insufficient for analysis so a small portion was converted to glass in the oxy-hydrogen flame and the refractive index of the glass determined. The index was found to be about 1:490 and to correspond with that of glass made by melting leucite from Vesuvius whereas the index of glass of composition KAlSiO<sub>4</sub> is 1.508. The crystals were thus proved to be leucite and not a new form of KAlSiO,. At 800° with potassium tungstate as a flux, then, KAlSiO<sub>4</sub> glass is largely converted to leucite crystals whereas at 1300° it crystallizes as kaliophilite.

Orthorhombic form of  $KAlSiO_4$ .—In the charges heated in the iridium furnace occasional crystals were seen with polysynthetic twinning. These were thought to be kaliophilite twinned on a pyramidal face because the indices were sensibly those of kaliophilite. In the later work on intermediate mixtures it was found that those rich in kaliophilite always showed this twinned form when quenched from high temperatures. These better crystals were found to be biaxial. The crystals are usually interpenetration twins giving an hexagonal section

\* G. W. Morey, Jour. Am. Chem. Soc., xxxvi, 217, 1914.

divided into six sextants that extinguish together in opposite pairs. Occasionally polysynthetic twinning similar to that in albite is shown, but this appears to follow the same law as the previous case with the same prism face acting repeatedly as composition face instead of adjacent faces as in the case of penetration twins.

Crystals of this orthorhombic form were made by fusing together silica, alumina and potassium fluoride over a Bunsen burner after the method of Duboine.<sup>\*</sup> The twinning was not so frequently developed as in the crystals obtained at high temperatures but occasionally appeared in typical form. The refractive indices are  $\gamma = 1.536$ , a = 1.528,  $2V = 39 \pm 3^{\circ}$  negative.

The product obtained by this method is not strictly pure but contains an amount of foreign material estimated under the microscope to be about 5 per cent. This consists of isotropic octahedra whose refractive index is about 1.540. The correspondence with the compound  $K_2Al_2SiO_6$  as described by Weyberg<sup>+</sup> is complete.

Analysis of this mixture resulted as follows:

SiO	36.7	38.07
Al <sub>2</sub> Õ <sub>3</sub>	32.8	32.21
K Ö	30.3	29.72
*		**************************************
·	99.8	100.00

- I Product obtained from fusion with KF. Analyst N. L. Bowen.
- II KAlSiO<sub>4</sub>, theoretical composition.

It will be noted that the analyzed material is low in silica and high in alumina and potash and calculation shows that it corresponds with a mixture of 93 per cent KAlSiO<sub>4</sub> with 7 per cent K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub>. The analysis and the microscopic examination together may therefore be regarded as definitely proving that the foreign material is K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> present to the extent of about 5–7 per cent and that the twinned material corresponds with kaliophilite in composition.

Glass of composition  $\text{KAlSiO}_4$  (approximately) has a refractive index for sodium light of  $1.508 \pm .002$ .

A number of supposed other forms of  $KAlSiO_4$  have been encountered by various investigators, but the material was always poorly crystallized and the measured properties were hardly sufficient to individualize them as species. No crystalline forms of  $KAlSiO_4$  other than the two described were encountered during the course of the present work. The

\* Bull. Soc. Min. Fr., xv, 191, 1892.

† "In Canada-balsam sehr schwer sichtbar," Weyberg, Centralblatt Min. 1908, p. 329. alteration product obtained by Stephenson is very similar to if not identical with the twinned form of KAlSiO4.\*

### Intermediate Mixtures.

By mixing the alkaline carbonates, silica and alumina, in the proper proportion, sintering and then fusing, the intermediate mixtures containing up to 40 per cent of the potash compound were made satisfactorily. In mixtures richer in potash, however, the temperature which must be reached to obtain a homogeneous melt is higher so that a little alkali is lost. The loss increases as the potash end is approached. An attempt was made to avoid this difficulty by using kaliophilite made hydrothermally by Morey, and nephelite made in the ordinary way as the ingredients of the mixtures. Even with this method the same loss of potash was encountered in those mixtures whose melting required a high temperature. The results from the potash-rich mixtures are, therefore, to some extent unsatisfactory. This loss of potash is not, however, so serious as to obscure the relationships involved, though it does interfere with the accurate fixing of temperatures.

A study of equilibrium in these mixtures was made in the ordinary way by the method of quenching. Besides the loss of potash noted above certain difficulties were encountered in the optical determinations which are, perhaps, worthy of note. The hexagonal forms of the two components nephelite and kaliophilite are so nearly identical in properties that when obtained as small crystals embedded in glass, as they are in quenchings, it is impossible to determine whether the crystals are kaliophilite or nephelite or of an intermediate composition. As a rule in such a case one can obtain a clue to the composition of the crystals by determining the composition of the glass, but in the present instance the extreme glasses and all intermediate glasses have nearly the same refractive indices and the composition cannot, therefore, be determined by such a method. To determine optically the question of solid solution between the components, and its limits, one crystallizes a glass of intermediate composition and examines the product to see whether it is homogeneous or not. In the present system, however, one cannot determine whether the fine-grained product so obtained consists of homogeneous mix-crystals or whether kaliophilite and nephelite are present as distinct phases.

Studies of equilibrium are often made in systems of various kinds with little observation of the phases themselves. The work is almost entirely a measurement of the temperatures at which changes of phase take place in various compositions, the change being recorded, say, thermally or dilatometrically. When these temperatures are plotted against composition it is

\* Jour. Geol. xxiv, 197, 1916.

<sup>119</sup> 

usually possible to deduce a complete equilibrium diagram. Dependence had to be placed on this method to a considerable extent in the present case. The temperatures at which beginning of melting and inversion and completion of melting and inversion take place were measured by the quenching method. These, when plotted against composition, give a complete equilibrium diagram from which the composition of the crystalline phases can be determined even though this cannot be done by optical means. Even in these determinations difficulties were encountered as a result of the near agreement of the refractive index of all the glasses with that of carnegieite. Thus when one takes crystalline nephelite-like material and holds it at successively higher temperatures, a temperature is finally reached at which a small trace of interstitial material of low refraction is formed but one is at a loss to decide whether it is carnegieite or glass. By raising the temperature the size of the interstitial patches can be increased until their nature is determinable. Unfortunately, however, one cannot be sure that small patches which were carnegieite have not, with the rise of temperature, been changed to patches of glass, indeed there are some mixtures in which this does take place within a narrow range of temperature.

Then again there is the difficulty of determining the temperature at which carnegieite mix-crystals begin to melt, for the first trace of glass cannot be found under the microscope on account of the correspondence of refraction in glass and carnegieite. The microscope will detect the glass only when enough has been formed to give definite isotropic patches. It was found, however, that the first appearance of glass could best be determined macroscopically in this case. Before the formation of glass the material is a white, opaque, sintered cake but on the formation of glass the interstices become filled with it, and since the index matches that of the crystals the charge becomes transparent and to all appearances entirely glassy even when under the microscope no unmistakable glass can be detected. Some difficulty is experienced, too, in determining the temperaature at which final solution of carnegieite takes place. Rare crystals of carnegieite in glass are easily overlooked, for they appear merely as indefinite birefringent patches without distinguishable outline against the glass.

These difficulties were finally solved, especially as a result of the assembling and correlation of all the results, but during the course of the investigation they were often very discouraging.

## Results of Quenching Experiments.

The results of the quenching experiments may now be given in tabular form. (Table I.)
### TABLE I.

# Beginning of inversion of nephelite to carnegieite.

Comp Ne	osition Kp*	n Initial condition	Temper- ature	Time	$\operatorname{Result}$
95	5	crystalline	1276	1 hr.	hexagonal form persists unchanged
66	"	·	1282	"	trace of carnegieite formed
90	10	66	1302	"	hexagonal form unchanged
"	"	66	1306	66	trace of carnegieite
85	15	66	1322	66	hexagonal form unchanged
66	66	66	1327	"	trace of carnegieite
80	20	66	1345	"	hexagonal form unchanged
66	"	66	1350	66	trace of carnegieite
75	25	66	1366	66	hexagonal form unchanged
"	"	66	1370	"	trace of carnegieite
70	30	66	1384	66	hexagonal form unchanged
"	"	66	1388	66	trace of carnegieite

Completion of inversion of nephelite to carnegieite.

95	5	crystalline	1335 2 hrs. a little nephelite
"	"	66	1340 1/2 hr. all carnegieite
90	10	66	1370 2 hrs. a little nephelite persists
"	"	66	1375 1/2 hr. all carnegieite
85	15	66	1392 2 hrs. a little nephelite persists
"	"	"	1397 1/2 hr. all carnegieite

# Beginning of melting of carnegieite.

95	5	crystalline	1448	1 hr.	all carnegieite
"	"	، د	1452	"	a little glass formed
90	10	66	1420	66	all carnegieite
"	"	"	1424	66	a little glass formed

### Completion of melting of carnegieite.

95	5	crystalline	1506	1/2 hr.	glass	and carnegieite
"	66	۰،	1510	·	glass	only
90	10	" "	1485	"	glass	and carnegieite
66	"	66	1489	" "	glass	only
85	15	66	1463	66	glass	and carnegieite
66	66	66	1467	"	glass	only
80	20	66	1436	66	glass	and carnegieite
"	"	66	1440	66	glass	only
75	25	66 -	1413	"	glass	and carnegieite
66	"	66	1417	66	glass	only

\* Ne = NaAlSiO<sub>4</sub>, Kp = KAlSiO<sub>4</sub>.

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Co	ompo Ne	sition Kp	n Initial condition	Temper- ature	Time	Result
	80	20	crystalline	1402	1 hr.	nephelite and carnegieite
	"	"	٠ د د	1406	"	carnegieite and glass
	75	25	66	1402	"	nephelite and carnegieite
	"	"	66	1406	"	carnegieite and glass
	72.5	5 27.8	5 "	1402	66	nephelite and carnegieite
	"	"	66	1406	"	glass only
	70	30	"	1402	"	nephelite and carnegieite
	"	"	66	1406	"	nephelite and glass
	65	35	66	1402	"	nephelite only
	66	"	66	1406	"	glass and nephelite

### Eutectic temperature and composition.

Beginning of melting of mix-crystals.

50	50	crystalline	1435	1/2 hr.	crystals and glass stringers
"	"	، د	1445	·	marked increase of glass
40	60	66	1480	"	crystals and glass stringers
"	"	66	1490	"	marked increase of glass
30	70	66	1540	66	crystals and glass stringers
"	"	"	1550	"	marked increase of glass

Completion of melting of mix-crystals.

70	30	crystalline	1420	1/2 hr.	glass and crystals
"	66	"	1424		glass only
60	40	66	1463	46	glass and crystals
"	"	66	1467	"	glass only
50	50	66	1520	"	glass and crystals
"	"	"	1524	"	glass only
40	60	66	1570	"	glass and crystals
"	"	66	1574	"	glass only
30	70	66	1629	"	glass and crystals
"	"	66	163 <b>3</b>	66	glass only

#### Discussion of Results.

The mixtures containing 50 per cent or more of KAlSiO<sub>4</sub> always show a little glass even when quenched from temperatures below the eutectic. This behavior is the result of the deviation from true composition to which reference has already been made. Concerning the method of determining the temperature of beginning of melting in such material a word of explanation is, perhaps, necessary. The glass formed at moderate temperatures occurs throughout the crystalline grains as shreds which are revealed only after close scrutiny under the microscope. These shreds do not increase very materially in amount as the temperature is raised and appear, moreover, to be of a highly viscous, presumably siliceous, glass which occasions no sintering of the powdered charge. On raising the temperature further, however, a point is finally reached at which rapid increase of glass takes place for only a few degrees rise of temperature. This glass has, moreover, quite different properties. It evidently flows comparatively freely and fills all the interstices of the powdered charge which becomes, even to the naked eye, obviously semi-vitreous. This temperature



FIG. 1.

at which rapid increase of glass is first observed is regarded as the true temperature of beginning of melting.

The method involves the personal equation to some extent. The temperature is probably somewhat lower than that which the true composition would show. Nevertheless there can be no question that the true curve would have a steep slope and approximate in position the determined curve shown in fig. 1.

The temperature of completion of melting of these somewhat impure mixtures is easily determined in the ordinary manner. On account of deviation of the mixtures from the true composition the various points are somewhat too low, no doubt. The effect of a small amount of impurity in lowering the temperature of beginning of melting may be very great if the impurity has a low melting point, whence the small amounts of glass found in these mixtures at moderate temperatures. The effect on the temperature of completion of melting, the so-called melting point, is, however, a more or less direct function of the amount of impurity. Since the deviation from true composition is small the position of the curve as far as it has been determined is believed to be substantially correct.

The equilibrium diagram is of a peculiar type, though among those deduced by Roozeboom as possible in a system involving solid solution and inversion.\* Between the potash compound and carnegieite there is a eutectic, but with nephelite a complete series of solid solutions is formed. As was noted formerly, solid solution cannot be definitely proved by optical means but such is the only possible interpretation of the thermal results. There is a continuous rise in the inversion temperature of nephelite as far as 35 per cent KAlSiO<sub>4</sub> amounting in all to more than 150°. Such a change of inversion temperature can be accomplished only through solid solution. At 35 per cent KAlSiO<sub>4</sub> the inversion curve gives place to a melting curve which shows a continuous rise in temperature of beginning of melting. If the possibility is entertained that an hiatus may exist in the series in those mixtures close to kaliophilite whose beginning of melting cannot be accurately fixed, then it may be pointed out that there should be a corresponding break in the liquidus. There is, however, no break in the liquidus at least up to about 1580°. In the neighborhood of this latter temperature there probably is a break, but this is occasioned not by the appearance of kaliophilite as a separate phase but by the appearance of the orthorhombic form of KAlSiO<sub>4</sub>. Solid solution as far as about 70 per cent KAlSiO<sub>4</sub> is established, therefore, beyond all question, while none of the evidence furnishes any reason for doubting complete solid solution.

It may seem at first thought that the evidence of the natural minerals is against complete solid solution. We have, for example, nephelite with upwards of 32 per cent KAlSiO<sub>4</sub> in solid solution but none with a greater amount. Then at the other end we have a maximum of 10 per cent of NaAlSiO<sub>4</sub> in kaliophilite. The interval is unbridged among known natural minerals, but this does not mean that no such minerals are possible. Nephelites which contain, say 20 to 30 per cent KAlSiO<sub>4</sub>, are never found in contact with kaliophilite in such a manner as to indicate approximately simultaneous formation. Only such an association would prove that the nephelite was incapable of taking up more KAlSiO<sub>4</sub>. For these reasons we

\*Zs. phys. Chem., xxx, p. 426, 1899.

must conclude that the moderate amount of KAlSiO<sub>4</sub> usually found entering into nephelite is the result of a deficiency of supply rather than of any inability on the part of nephelite to take up greater quantities in solid solution.

# Crystallization of a Typical Mixture.

The phenomena observed during the cooling of a mixture in which perfect equilibrium is attained are, perhaps, of sufficient interest to be described in detail. A mixture of 80 per cent NaAlSiO<sub>4</sub> and 20 per cent KAlSiO<sub>4</sub> begins to crystallize at  $1438^{\circ}$  with separation of crystals of carnegieite containing 6 per cent KAlSiO, (see fig. 1). As the temperature falls the liquid changes in composition towards the eutectic and the carnegieite crystals increase in amount and become richer in potash content. At the entectic temperature,  $1404^{\circ}$ , they contain about 16 per cent KAlSiO<sub>4</sub> and are then joined by hexagonal crystals (nephelite) containing 35 per cent KAlSiO<sub>4</sub>. The temperature remains constant until all the liquid has disappeared. Then as the temperature falls carnegieite immediately begins to invert to nephelite and both change in composition, becoming richer in soda, until at 1348° all the carnegieite has changed to nephelite which now has the composition NaAlSiO<sub>4</sub> S0 per cent, KAlSiO<sub>4</sub> 20 per cent.

Relation between the hexagonal and orthorhombic forms of KAlSiO, -Both forms of KAlSiO, can be obtained at low temperatures. Kaliophilite has been obtained hydrothermally by Morey and several others at temperatures in the neighborhood of 500°. The orthorhombic form was prepared in a similar manner by Lemberg.\* Both forms can likewise be obtained with the aid of various fluxes at moderate temperatures. Nevertheless a number of facts point to the stability of kaliophilite only at low temperatures and of the orthorhombic form only at high temperatures with the inversion temperature somewhere in the neighborhood of 1540°. In the present mixtures when working without fluxes the orthorhombic form was obtained only in mixtures containing 70 per cent or more of KAlSiO, and in these only at high temperatures. Moreover, ordinary uniaxial kaliophilite formed by crystallizing glass made in the iridium furnace, is converted at 1550° into excellent twinned crystals of the orthorhombic form. The change is here facilitated by the formation of a little liquid as a result of the deviation of the material from the true composition. Pure kaliophilite made by Morey suffers a change at about the same temperature or a little lower, 1540°. In this case no liquid is formed and for that reason the crystals are not as typically developed, but the quadratic section of kalio-

\* See Z. Weyberg, Centralblatt Min., p. 401, 1908.

philite with its parallel extinction is broken up into two or more areas which are in twinned relation with each other and whose extinction has no relation to the elongation. At about  $1540^{\circ}$ , therefore, or possibly somewhat lower, the hexagonal kaliophilite is converted into the orthorhombic form. The formation of the orthorhombic form at low temperatures with fluxes is not at all incompatible with its stability at high tem-



peratures only, for many such forms can be so obtained, notable examples being the forms of silica.<sup>\*</sup> The writer has not, however, been able to convert the orthorhombic form into the hexagonal form, but this does not necessarily preclude an enantiotropic relation between them, for it is not uncommon to experience great difficulty in converting the high temperature form into its low temperature equivalent.

\*C. N. Fenner, this Journal (4), xxxvi, 339, 1013.

The orthorhombic variety is encountered in the mixture with 20 per cent NaAlSiO, only at a considerably higher temperature, 1580°. The inversion point is, therefore, raised, which means that the low temperature, hexagonal form takes more NaAlSiO, into solid solution than does the high temperature form. This is precisely as one would expect it to be, since the hexagonal form is so like the corresponding form of NaAlSiO<sub>4</sub>, and, indeed, forms with it an unbroken series of mix-crystals.

On the basis of these results fig. 2 is presented as representing a partly hypothetical but very probable equilibrium diagram of the complete system. Some of the curves are shown in broken lines because they are less well supported by ascertained facts than the others, though they are believed to offer the only possible interpretation of the results obtained.

### The Composition of Natural Nephelite.

It is now established beyond question that natural nephelites are of variable composition. That the molecules NaAlSiO, and KAlSiO, are fundamental constituents of nephelite may be regarded as definitely decided by the present investigation.

Concerning the excess silica in nephelite above the orthosilicate ratio there is still some controversy. Most investigators believe that NaAlSiO, and KAlSiO, are fundamental and that the variable excess of silica is to be ascribed to the presence in variable amount of a more silicious molecule. The suggestion that this molecule is NaAlSi<sub>s</sub>O<sub>s</sub> was first made, apparently, by Clarke\* and later stated in terms of the more modern solid solution theory by Schaller+ and the writer.; Thugutt, § however, would still assign a definite formula to nephelite and assumes that it is

# $8Na_{2}Al_{2}Si_{3}O_{10}$ , $4Na_{2}Al_{2}O_{4}$ , $3K_{2}Al_{2}Si_{3}O_{10}$

and that any deviation from this formula is the result of an admixture of products of its own decomposition. He therein ignores the fact that the later students of the composition of nephelite have taken the greatest precautions in selecting only absolutely fresh material for analysis. He likewise fails to consider the fact that one can prepare nephelite showing the same variability by dry fusion, under conditions absolutely precluding the possibility of aqueous decomposition. No consideration is given,

<sup>\*</sup> F. W. Clarke, U. S. Geol. Survey Bull. 125, 18, 1895.

<sup>Jour. Wash. Acad. Sci., i, 109, 1911.
This Journal (4), xxxiii, 49, 1912.
C. R. Soc. Sci. Varsovie, VI Année. Fasc. 9, 862, 1913.
Morozewicz, Bull. Acad. Sci. Cracovie, 958, 1907.</sup> 

Wallace, Zs. anorg. Chem., lxiii, 1, 1909; and Bowen, this Journal (4), xxxiii, 50, 1912.

moreover, to the fact that  $NaAlSiO_4$  and mixtures of it with  $KAlSiO_4$  can be prepared in a form identical with nephelite and, indeed, occur so in nature in the so-called pseudonephelite, whereas the molecules chosen by Thugutt do not occur in forms at all suggesting nephelite.

Several objections have been raised to the suggestion that the albite molecule, NaAlSi<sub>3</sub>O<sub>s</sub>, is the siliceous molecule present in nephelite. Thugutt points out that albite has never been isolated from nephelite, which is perfectly true, but neither has albite been isolated from labradorite. The suggestion of Foote and Bradley that the question of the condition of the excess silica should be left open<sup>\*</sup> is safe, to be sure, but there are nevertheless good reasons for preferring the albite molecule.

It was formerly considered, if a triclinic mineral was taken into solution by an hexagonal mineral, that the triclinic mineral must be dimorphous, must have an hexagonal modification. But this idea is now known to be contrary to well-ascertained facts. We may take the case of anorthite in solid solution in nephelite, which extends as far as 35 per cent anorthite, yet anorthite has no hexagonal modification. It seems to the writer, in the light of recent studies of the actual atomic structure of crystals, to be more reasonable to assume that the anorthite atomic pattern, though of triclinic symmetry, is nevertheless sufficiently close to the hexagonal symmetry of nephelite or sufficiently amenable to modification that, under the influence of the fields of force existing within a nephelite crystal, it is capable of being so modified as to conform with the hexagonal pattern, though not in unlimited amounts. Is it surprising, then, that the albite atomic pattern should be capable of precisely the same modification by a nephelite crystal, up to a certain limit, when we consider the fact that albite and anorthite are so nearly alike in pattern that they form an unbroken series of mix-crystals?

Or if we look at the question from the point of view of phase equilibria and remember that albite and anorthite in any system form not two phases but the single phase, plagioclase, then it becomes quite inappropriate to speak of the solubility in nephelite of anorthite and of albite except as limiting values of the solubilities of the phase, plagioclase. Any nephelite forming in a magma together with plagioclase must, of necessity, dissolve the amount of both anorthite and albite (i. e. of the phase plagioclase) that is required by the conditions prevailing, sufficient opportunity for equilibrium to become established being assumed.

It may be said, then, that theoretical considerations afford

\* This Journal (4). xxxiii, 439, 1912.

the strongest additional reasons for stating the composition of nephelite in terms of the molecules  $NaAlSiO_4$ ,  $KAlSiO_4$ ,  $CaAl_2Si_2O_8$  and  $NaAlSi_3O_8$ . These appear, moreover, to be entirely adequate for the purpose, apart from the small iron content. In the following are tabulated the percentages by weight of the above four constituents in some typical nephelites. For various reasons the sums of these constituents are not 100, an important one being that  $H_2O$  seems to replace the alkaline oxides to a moderate extent in some nephelites.

	Ι	II	III	IV	V	VI	$\mathbf{VII}$	VIII	IX
Ne	65.0	63.0	56.0	70.0	68.0	64.5	73.5	70.0	9.5
Кр	13.0	12.0	32.0	19.0	19.0	18.5	13.0	12.0	89.0
An	1.5	15.0	12.0	0.0	2.5	<b>4</b> •0	2.0	4.0	1.2
Ab	9.5	2.0	0.0	10.0	9.5	5.0	6.0	11.0	0.0

I. Nephelite from Wausau, Wis. Weidman, Geology of North Central Wisconsin, Wisconsin Survey Bull., xvi, 1907, p. 317. Analysis I.

II. Same. Analysis II.

III. "Pseudonephelite" Zambonini, Zs. Kryst., lii, 606, 1913.

IV. Nephelite from Eikaholmen, Norway. Foote and Bradley, this Journal, xxxi, 27, 1911.

V. Nephelite from Mariupol. Morozewicz, Bull. Acad. Sciences Cracovie, 958, 1907.

VI. Nephelite from Coimbatore, India. Mem. Geol. Surv. Ind., xxx, pt. 3, 187, 1901.

VII. Nephelite from Kuusamo. Hackman after Ramsay, Bull. de la Commis. Geol. de Finlande No. 11, 9, 1911.

VIII. Nephelité from Monte Ferru. Washington and Merwin, Jour. Wash. Acad. Sci., v, 391, 1915. IX. Kaliophilité from Vesuvius. Zambonini, Mineralogia

IX. Kaliophilite from Vesuvius. Zambonini, Mineralogia Vesuviana Appendix, p. 23.

Dependable analyses of nephelite are apparently not very numerous and no very definite general conclusions can be drawn from them. Nephelite III shows no albite, i. e. has no excess silica above the orthosilicate ratio, and II has very little,\* showing that excess silica is not essential. When the albite is high the anorthite tends to be low (I, IV, V and VIII) and when the anorthite is high the albite tends to be low (II and III). The suggestion is that the members of the former group were formed from solutions containing sodic

<sup>\*</sup>Some of the albite of II occurs as minute inclusions. Weidman, Wis. Survey Bull. XVI, p. 318. It might be assumed, therefore, that the nephelite should be saturated with albite and that the analysis is faulty. It is possible, however, to imagine conditions under which saturation would not occur even with albite inclusions.

plagioclase and those of the latter group from solutions of calcic plagioclase, but it is impossible to be sure that this is true from the data at hand. The nephelites average upwards of 12 per cent plagioclase in solid solution.

The peculiar twinned nephelite described by Esch, from Etinde volcano, West Africa, seems to correspond definitely with the orthorhombic form of the potassium-rich nephelites.<sup>\*</sup> Esch observed slightly inclined extinction and therefore considers his mineral triclinic, but the correspondence is too great in other respects to render it likely that his form is distinct from the artificial form. It is to be noted that the nephelinites described by him, though dominantly soda-rich, are sometimes rather rich in potash as well, running to leucitites. Possibly, then, some of the nephelite is potash-rich and closely related to the artificial varieties showing the same twinning. It was suggested in a former paper that Esch's mineral might be carnegieite with its properties modified by solid solution, but this suggestion now seems quite unjustified.<sup>†</sup>

### General Considerations.

The mineral nephelite proves to be of rather complex constitution, a common feature of a number of rock-forming min-The micas, pyroxenes and amphiboles exhibit this erals. characteristic in even more marked form; indeed their constitution has not yet been satisfactorily explained. The difficulty is the result of the binding up, within one crystalline phase or mineral, of several of the components<sup>‡</sup> of the magma. While the complexity of the individual crystalline phases is greatly increased their number is correspondingly decreased and, in some respects, a simplification of the process of crystallization results. This fact is the key to the problem of the "gesteins-serie." It is the crystallization from the magma of these minerals of continuously varying composition which results in the formation from a single magma of a series of rock-types showing that consanguinity which is found to characterize the petrographic province.

Nephelite syenite is undoubtedly the most important of the alkaline rocks. Alkalic feldspar is a prominent constituent and through it nephelite syenite is related to sub-alkaline types. The suggestion has been offered in another paper that the nephelite syenites are intimately related to the mica-bearing sub-alkaline rocks, biotite granites. They are considered to

<sup>\*</sup> Sitzb. Berl. Akad., xviii, 400, 1901.

<sup>†</sup> N. L. Bowen, this Journal (4), xxxiii, 572, 1912.

<sup>‡</sup>Components in the specialized phase rule sense, not synonymous with constituents.

<sup>§</sup> The Later Stages of the Evolution of the Igneous Rocks, Jour. Geol. Supplement vol. xxiii, 55, 1915.

be probably a residuum from the granite magma, especially rich in volatile components. From the present work we obtain definite proof of a fact long suspected, viz. the existence in nephelite of the molecule KAlSiO<sub>4</sub>. This commonly occurs in amounts of 15 per cent or more and is the same molecule that plays a fundamental rôle in the formation of the micas. At the same time it is not to be expected that any definite solution of the relation between two such rocks will be accomplished experimentally except in aqueous systems. The methods of attacking such systems, combining high temperatures and high pressures, have been worked out by Morey<sup>\*</sup> and his investigations will be extended to more complex systems with a view to the solution of this and related problems.

The existence in nephelite of an average of more than 10 per cent plagioclase is of importance in connection with such rocks as iolite and nephelinite. Though free from plagioclase as a separate mineral, it is plain that one cannot consider the crystallization of the magma except as a part of a plagioclasebearing system. This system would include likewise the plagioclase rocks with which nephelinite is normally associated and consideration of the crystallization of such a system serves to emphasize the relationship of the types.

The inversion temperature of nephelite does not prove to be very useful for the determination of the temperatures of formation of minerals. The pure compound NaAlSiO<sub>4</sub> inverts at 1248° but all the materials that it takes into solid solution occasion a sharp rise in the temperature of inversion. In order to appear in the carnegieite form, separation would have to take place at least as high as  $1325^{\circ}-1350^{\circ}$ . The non-occurrence of carnegieite may, therefore, be considered as proof, if any be needed, that the separation of nephelite from magmas has always taken place at temperatures below those named.

The occurrence of the pseudo-hexagonal, twinned form of nephelite in the nephelinite described by Esch is not to be considered as evidence that separation took place at high temperatures. It is true that this form is believed to be a high temperature form of potassium-rich nephelites or kaliophilites but, unlike carnegieite, it can form at low temperatures also. Moreover it will persist at these temperatures just as the forms of silica, tridymite and cristobalite do.

#### Summary.

The present paper gives the results of an experimental investigation of the binary system  $NaAlSiO_4$ -KAlSiO<sub>4</sub>. The soda compound occurs in two enantiotropic forms, nephelite

\* Jour. Am. Chem. Soc., xxxvi, 215, 1914.

and carnegieite, with an inversion point at 1248°. The high temperature form, carnegieite, melts at 1526°. The potash compound shows two forms, kaliophilite, isomorphous with nephelite, and an orthorhombic form with twinning analogous to that in aragonite. The orthorhombic form is apparently stable at temperatures above 1540° and melts in the neighborhood of 1800°.

The potash compound has a eutectic with carnegieite at 1404°. With nephelite it forms an unbroken series of solid It is concluded, therefore, that NaAlSiO<sub>4</sub> and solutions. KAlSiO<sub>4</sub> are the fundamental molecules of natural nephelites. But, in addition to these, nephelites contain variable amounts of plagioclase in solid solution, the plagioclase varying from albite to anorthite, the latter accounting for the lime content and the former for the excess silica of the natural mineral. The composition of nephelite should, therefore, be expressed in terms of the four molecules NaAlSiO<sub>4</sub>, KAlSiO<sub>4</sub>, NaAlSi<sub>3</sub>O<sub>8</sub> and CaAl, Si, O<sub>8</sub>. Reference is made to the petrogenetic importance of the occurrence of the last two molecules, viz. plagioclase, in nephelites.

Geophysical Laboratory, Carnegie Institution of Washington,

Washington, D. C., December 4, 1916.

# ART. XIII.—Pottsville Formations and Faunas of Arkansas and Oklahoma; by KIRTLEY F. MATHER.

# Pottsville formations of the Boston Mountains.

THE Boston Mountains form an escarpment which overlooks the Ozark Plateau and extends from the vicinity of Muskogee, Oklahoma, eastward past Fayetteville, Arkansas, to Batesville, Arkansas. Their structure is monoclinal, the beds dipping gently toward the south. The strata exposed in the outlying erosion remnants and the terraced front of the mountains are in the main shales and sandstones with occasional limestones. Of these, the Morrow group embraces two units, the Hale formation and the Bloyd shale. The latter contains two limestone members, the Brentwood and the Kessler. The Morrow group rests unconformably upon the Pitkin limestone, or in places on the Fayetteville shale, and is overlain unconformably by the Winslow formation. Both unconformities are more pronounced toward the north and practically disappear toward the south where the group is lost to sight beneath the Winslow. From east to west there is a change in lithology; in Oklahoma the Morrow is largely limestone while toward Bates-ville it is dominantly clastic. Limestone lenses in the Hale formation and the Brentwood and Kessler limestone members of the Bloyd carry an abundant marine fauna which has been described elsewhere.\* A thin seam of coal in the shales between the two upper limestone members contains a fossil flora of Sewanee affinities. The early Pottsville age of the group is further demonstrated by the marine fauna, in which a large number of residual Mississippian invertebrates are associated with forms of distinctly Pennsylvanian aspect.

#### Pottsville formations south of Arkansas River.

Arkansas River and its tributaries in eastern Oklahoma and western Arkansas occupy a geosynclinal basin composed of Pennsylvanian strata. The lowest beds of the series are exposed along the southern margin of the basin, between the Arbuckle Mountains in south central Oklahoma and the Ouachita Mountains farther east. Throughout this region the Atoka formation is especially conspicuous, both because of its great thickness, 3000 to 6000 feet, and because of the recurrence of massive sandstone beds in the midst of the shales of which it is dominantly composed. Toward the north it is

\* Mather, K. F., The fauna of the Morrow group of Arkansas and Oklahoma. Denison Univ., Sci. Lab. Bull., vol. xviii, pp. 59-284, 1915. overlain by the successive formations of the "Arkansas Coal Measures."\*

Along the eastern flank of the Arbuckle uplift, the Atoka is underlain conformably by the Wapanucka limestone<sup>†</sup> which approximates 150 feet in thickness and rests with probable disconformity upon the Caney shale. Farther west, the Franks conglomerate is apparently the near-shore equivalent of the Wapanucka, Atoka, and possibly even higher strata as well. It overlaps the Caney and is found resting upon the early Paleozoic strata to the southwest.<sup>4</sup>

Traced eastward, the Wapanucka limestone at first thickens slightly and then decreases in thickness and comes to an end north of the Ouachita Mountains near the Arkansas-Oklahoma line. In the Arbuckle region, the Caney is over a thousand feet in thickness and overlies the Woodford chert, of probably Devonian age. Over a part of the area, however, the Sycamore limestone intervenes between the Woodford and the Caney and is correlated with an undifferentiated lower division of the Caney in other localities.

In the vicinity of the Ouachita Mountains, the succession is somewhat different. The Wapanucka limestone disappears in southern Oklahoma and the Atoka formation rests directly upon the Caney shale, there about 800 feet thick. The Caney overlies with apparent, and probably real, conformity the Jackfork sandstone and Stanley shale, each about 5000 feet in thickness.§ Farther east, in Arkansas, the Caney also disappears, and the Atoka rests upon the Jackfork.

### The Fauna of the Wapanucka-limestone.

Through the courtesy of Mr. C. R. Thomas, of the Oklahoma Geological Survey, I have been enabled to study a representative collection of fossils from the Wapanucka limestone. The fossils were obtained at several localities in and near the Atoka and Coalgate quadrangles midway between the Arbuckle and Ouachita Mountains.

\* Collier, A. J., The Arkansas coal field, U. S. Geol. Survey, Bull. 326, conner, A. J., The Arkansas coar heid, U. S. Geol. Survey, Bull. 520,
p. 12, 1907. Snider, L. C., Geology of East Central Oklahoma, Okla. Geol.
Survey, Bull. 17, p. 8, 1914.
† Wallis. B. F., Geology and economic value of the Wapanucka limestone of Oklahoma, Okla. Geol. Survey, Bull. 23, 1915.
‡ Taff, J. A., Geology of the Arbuckie and Wichita Mountains, U. S. Geol. Survey, Prof. Paper 31, p. 34, 1904.

STaff. J. A., Grahamite deposits of southeastern Oklahoma, U. S. Geol. Survey, Bull. 380, p. 289, 1910. #Purdue, A. H., The slates of Arkansas, Geol. Survey, Arkansas, p. 48,

1909.

The complete faunal list is as follows :----

Pentremites angustus Hambach Cromyocrinus n. sp. Archeocidaris sp. Rhombopora lepidodendroides Meek Cystodictya sp. Rhipidomella pecosi (Marcou) Productus nanus Meek and Worthen? Productus morrowensis Mather? Spirifer opimus Hall Spirifer goreii Mather Squamularia perplexa (McChesney) Spiriferina transversa (McChesney) Composita ozarkana Mather Composita gibbosa Mather Nucula parva McChesney Parallelodon sp. Myalina orthonota Mather Aviculopecten arkansanus Mather? Aviculopecten sp. Euphemus carbonarius (Cox) Griffithides morrowensis Mather?

All the genera listed above are present in the fauna of the Morrow group, and 17 of the 21 species have been found in the limestones of that group. This includes all the forms specifically identifiable with the exception of the new species of Cromyocrinus.

It is significant that none of these is known from the Kessler horizon without also being present in the Hale or Brentwood, while several of the Wapanucka forms are not known to occur in the Boston Mountains region above the Brentwood member. Moreover, none is recorded from the Hale limestone lenses, which is not also known from the Brentwood or higher strata. (Nucula parva is frequently found in the "Coal Measures" of the Mississippi Valley.) That the Wapanucka is the homotaxial equivalent of the Brentwood is further indicated by the association of *Pentremites angustus* and *Spiriferina trans*versa, residual Mississippian types, with Rhipidomella pecosi, Productus nanus?, Spirifer opimus, Squamularia perplexa, and Euphemus carbonarius, proemial Pennsylvanian forms, and Composita gibbosa, a characteristic Brentwood species. It necessarily follows that the Wapanucka is of early Pottsville age.

#### The fauna of the Atoka formation.

The Atoka formation is nearly everywhere barren of fossils; indeed it is highly probable that the formation is in part of non-marine origin. There are, however, local beds of calcareous sandstone near the base of the formation, which are crowded with the remains of marine organisms. These are known to outcrop near Clarita, Oklahoma, in the northwest corner of the Atoka quadrangle. The fossiliferous strata were discovered by Dr. L. C. Snider, formerly Assistant Director of the Oklahoma Geological Survey, and to him I am indebted for the opportunity of studying their fauna.

The fossils are preserved entirely as casts and moulds in the weathered portion of the outcropping beds from which all calcareous material has been leached. The individual specimens are indiscriminately intermingled and many were broken before fossilization took place. It is quite clear that most of the shells were transported by waves and currents until they collected in quiet water, where they were buried beneath sandy sediments.

No less than forty-two identifiable forms have come to hand from the one locality. These are listed below.

> Campophyllum torquium (Owen) Rhombopora sp. Prismopora concava Mather Chonetes choteauensis Mather Chonetes lævis Keyes Productus fayettevillensis Mather Productus gallatinensis Girty? Spirifer rockymontanus Marcou Squamularia perplexa (McChesney) Composita wasatchensis (White) Nucula parva McChesney Yoldia glabra Beede and Rogers? Parallelodon pergibbosus Mather Canevella? n. sp. Pseudomonotis precursor Mather Myalina cuneiformis Gurley ? Myalina orthonota Mather Schizodus affinis Herrick Schizodus wheeleri (Swallow)? Schizodus telliniformis Girty Deltopecten occidentalis (Shumard) Aviculopecten arkansanus Mather Plagiostoma? acosta Cox Pleurophorus subcostatus Meek and Worthen? Pleurophorus n. sp. Pleurophorus sp. Astartella n. sp. Euphemus carbonarius (Cox) Worthenia tabulata (Conrad) Orestes sp. Euconospira turbiniformis (Meek and Worthen) Strophostylus remex (White) Platyceras parvum (Swallow)

Aclisina? sp. Orthoceras sp. Metacoceras sp. Pronorites cyclolobus var. arkansasensis Smith Gastrioceras listeri (Martin) Gastrioceras hyattianum Girty Gastrioceras angulatum Girty Gastrioceras carbonarium von Buch Gastrioceras kesslerense Mather

The Atoka fauna as thus made known includes six forms not specifically identifiable and three new species, so that there remain thirty-three species known to occur elsewhere. Twenty of these have been described among the Morrow fauna of the Boston Mountains. One additional form, *Pronorites cyclolobus* var. arkansasensis, is known elsewhere only from the upper strata of the Morrow group in Carroll County, Arkansas. Another species, *Strophostylus remex*, occurs in the Lower Aubrey group of Utah, a horizon which may be closely correlated with the Morrow. The remaining forms are present in somewhat higher strata in this and adjoining regions.

Four of the Atoka species, Prismopora concava, Myalina cuneiformis?, Worthenia tabulata, and Gastrioceras kesslerense, are especially characteristic of the Kessler member of the Morrow as distinct from the lower fossiliferous beds of that group. The last named of these four is the most common species in the Atoka fauna. On the other hand, two species, Pseudomonotis precursor and Parallelodon pergibbosus, are noteworthy as representative Brentwood forms.

The evidence is quite conclusive that this fossiliferous portion of the Atoka formation cannot be much, if any, younger than the upper beds of the Morrow group. The deposition of the Atoka sediments must, therefore, have begun in early Pottsville time.

### The age of the Caney, Jackfork, and Stanley formations.

The proper correlation of the Caney shale, the Jackfork sandstone, and the Stanley shale present unusual difficulties because of the somewhat conflicting nature of the data available. G. H. Girty in his description of the Caney fauna\* has presented all phases of the problems involved. There have been found in the Stanley shale obscure plant remains which David White states are of Carboniferous age; he concludes that "it is probable that they belong either in the upper part of the Mississippian or in the lower Pottsville, but this point

\* Girty, G. H., The fauna of the Caney shale of Oklahoma, U. S. Geol. Survey, Bull. 377, 1909.

Am. Jour. Sci.—Fourth Series, Vol. XLIII, No. 254.—February, 1917. 10 requires additional paleontologic data for its determination."\* Six or seven thousand feet above the Stanley plant horizon there is found the marine invertebrate fauna of the Caney shale. This fauna is undoubtedly of Upper Mississippian age and the Caney shale may be correlated directly with the Moorfield shale, Batesville sandstone, and Fayetteville shale of the Boston Mountains.<sup>+</sup> It is further demonstrable that the Canev of the Arbuckle region and the Canev of the Ouachita Mountains are one and the same formation.

So carefully did Girty entertain all possible solutions of the really baffling problem, which would be presented if the Stanley flora should prove when better known to be of Pottsville age, that his conclusions have been misinterpreted. J. B. Woodworth states, "The fauna of the Caney shale is marine. Girty very guardedly referred the beds to the Pottsville, which reference Ulrich (in a note to the author) later proved to be correct on stratigraphic and faunal evidence.";

Ulrich considers the Caney shale to be of Pennsylvanian age, § but the evidence upon which his conclusions are based has not been published. Upon his authority, also, Purdue has referred the Jackfork and Stanley to the Pennsylvanian. In this regard he follows the lead of Branner, who long ago included all the strata above the Arkansas novaculite in the "Lower Coal Measures," and reported the total thickness of Pennsylvanian sediments in Arkansas as 23,780 feet.

With the facts now available concerning the faunas of the Wapanucka and Atoka formations, the chain of evidence would appear complete. The correlation of the Caney fauna with late Mississippian faunas in northern Arkansas is further strengthened by the determination of the early Pottsville age of the immediately overlying strata. Pennsylvanian sedimentation in the Arbuckle and Ouachita regions evidently began with the deposition of the Wapanucka and Atoka formations. The Jackfork and Stanley must be of middle or late Mississippian age, and their enormous thickness is the result of unusual conditions of sedimentation maintaining in the Ouachita region at that time.

The accurate placing in the time scale of the initiation of Stanley sedimentation must await further paleontologic discov-

\* Quoted by Girty, loc. cit., p. 8. † Girty, G. H., The fauna of the Moorfield shale of Arkansas, U. S. Geol. Survey, Bull. 439, p. 25. 1911. ‡ Woodworth, J. B., Boulder beds of the Caney shales at Talihina, Okla-homa, Bull. Geol. Soc. America, vol. xxiii, p. 457, 1912.

§ Ulrich, E. O., Revision of the Paleozoic systems, Bull. Geol. Soc. Amer-ica, vol. xxii, p. 352. foot-note ; also pl. 29, 1911.

Purdue, A. H., The slates of Arkansas, Arkansas Geol. Survey, p. 48, 1909.

¶ Branner, J. C., Thickness of Paleozoic sediments in Arkansas, this Journal (4), vol. ii, pp. 229-236, 1896.

eries, but it is now evident that that sedimentation could not have been contemporaneous with the uplifting of the Arbuckle region.\* The orogenic disturbance which resulted in the rapid accumulation of the ten or twelve thousand feet of clastic beds composing the Stanley and Jackfork cannot be included with the "Culmides" of Chamberlin. It probably was a feature of the events which mark the transition between the Waverlyan and Tennessean systems of Ulrich. Instead of one great orogenic revolution closing the Paleozoic era there would appear to be at least four such disturbances: Waverlide, Culmide, Hercynian, and Appalachian.

It is perhaps significant that the relation between the epoch of refrigeration implied by the ice-borne bowlders in the lower portion of the Caney shale and the Waverlide disturbance is analogous to that between the much more extensive "Permo-Carboniferous" glaciation and the more violent Hercynian revolution.

Finally, it should be stated that the third leg of the paleontological tripod, the evidence accorded by vertebrate fossils, supports the conclusions which have been based upon the invertebrate remains. According to Eastmant the character of the Caney fish remains indicates their Upper Mississippian age so far as the evidence goes, though it is admittedly slight.

Queen's University, Kingston, Canada. October 20, 1916.

\* Chamberlin, R. T., Periodicity of Paleozoic orogenic movements, Jour. Geol., vol. xxii, p. 333, 1914.

<sup>†</sup>Taff, J. A., Ic<sup>3</sup>-borne boulder deposits in mid-Carboniferous marine shales, Bull. Geol. Soc. America, vol. xx, pp. 201-202, 1907. <sup>‡</sup>Eastmam, C. R., Brain structures of fossil fishes from the Caney

shales, Bull. Geol. Soc. America, vol. xxiv, pp. 119-120, 1913.

# ART. XIV.—A Study of Two So-called Halloysites from Georgia and Alabama; by P. A. VANDER MEULEN.

THE term halloysite is usually applied to a massive, clay-like or earthy mineral, with a conchoidal fracture, waxy luster, and made up essentially of silica, alumina, and water. According to Le Chatelier the composition probably is  $2H_2O$ ,  $Al_2O_3$ ,  $2SiO_2 + Aq.$ , or silica, 43.5; alumina, 36.9; water, 19.6.

Analyses of this type of clay have been published from time to time, many of which show similarity to the theoretic composition, but no other tests have usually been recorded on the samples thus analyzed.

Some time ago, Prof. Ries placed at my disposal, for chemical investigation, two samples of sedimentary clay, which have gone under the name of halloysite. Both possessed the usually accepted properties of halloysite.\* They were almost pure white, had a more or less conchoidal fracture, and became somewhat translucent when placed in water.

The first of these came from Chattooga County, Georgia. On close examination, it was observed to have on the surface, and lining cracks, a number of very fine needle-like crystals, and in some of these cracks also a small amount of a black powdery substance which proved to be an oxide of manganese. The clay itself was entirely homogeneous under the microscope, appearing either amorphous or exceedingly fine-grained, and free from the small crystals mentioned above.

A number of the largest of these crystals were selected and tested by blowpipe methods. They were infusible, and became opaque on heating, had a hardness of about three, gave much water in the closed tube, contained no silica, but much alumina. These tests indicated that the crystals were hydrargillite.

Several of the best of these, about 1 mm. in length and 0.1 mm. in diameter, were selected, and the angles between faces in the prism zone measured. The angles corresponded with those of hydrargillite, described by Brögger† on crystals of Norwegian material. The end faces were so small as to render measurement impossible. The indices of refraction determined by the minimum deviation method were found to be  $\alpha = \beta = 1.554$ and  $\gamma = 1.576$ . These values are somewhat higher than those obtained by Brögger.

A sample of the clay, free from crystals, and also from the black oxide of manganese, was finely ground and analyzed. The specific gravity of the fine powder was determined by the bycnometer method, the air being removed by means of a

\* Dana, p. 688, 6th ed.

<sup>†</sup>Zeitschr. Kryst., xvi, 45.

vacuum pump in the usual manner. The results on the air dried material are given below (No. I of table).

The second clay (No. II of table), which comes from the Fort Paine Chert formation in Northern Alabama, contained no good crystals, but showed a very few small nodules of a substance resembling bauxite in appearance. The results of the analysis and the specific gravity are given herewith.

#### Analyses of Halloysite.

	I	II	III	IV
SiO	35.82%	43.30%	41.69%	43.18%
Al <sub>2</sub> Ô <sub>2</sub>	44.38	39.94	35.88	39.21
Fe <sup>°</sup> <sub>2</sub> O <sup>°</sup> <sub>2</sub>	tr.	tr.	•37	·15
CaO	none	none	•06	none
MgO	tr.	·21		tr
Na <sub>o</sub> O	1.18	•25		•08
K <sub>o</sub> Ó	none	none		none
$H_0O$ below 108° C	1.61	1.28	7.97	3.39
$H_0O$ above 108°	16.63	15.04	14.01	14.23
Total	99.62	100.02	99.98	100.24
Sp. gr. 20 C.	2.497	2.441		2.460

The results of these analyses show the clays to have a water content below that of halloysite, while the specific gravity is higher, for that of halloysite is usually given as 2.0-2.2. An analysis of halloysite (No. III) from Horse Cave, Ky., by H. C. McNeil\* is given for purposes of comparison. Analysis No. IV, made by the author, of a sample of clay which goes under the name of halloysite, from Grubb Mines, near Roanoke, Virginia, is included because it has a somewhat higher alumina-silica ratio than does halloysite of the usually accepted composition, but agrees with it in the properties ascribed to this substance by Dana.

The clays above described also contain a higher percentage of alumina than halloysite, and agree closely in chemical composition with the high alumina flint clays described by Greaves-Walker.<sup>+</sup> These clays are, therefore, not halloysite.

There is a good deal of doubt concerning the compounds present in clay mixtures such as those under discussion, especially when the material is so very fine-grained that a microscopic examination does not even give a clue as to any of the constituents. It is exceedingly unsafe to calculate the mineral composition of a clay from its chemical analysis.<sup>‡</sup> The compound assumed by many to be present in practically all clays is kaolinite, to which the formula  $H_4Al_2Si_2O_9$  is usually assigned,

\* U. S. G. S. Bull. 591, p. 345. ‡ H. Ries, Econ. Geol., ix, 402, 1914. † Tr. Am. Cer. Soc., viii, 297. and many white clays, after washing, closely approximate this formula. In the case of the Chattooga clay the high alumina content together with the presence of hydrargillite crystals on the surface points strongly toward the probability that it contains this latter compound. The Na<sub>2</sub>O might perhaps be considered as some undecomposed mineral such as albite, or it may be there in some other form. In any case it is better to leave



Fig. 1.

it out of consideration, and to assume that the clays are mixtures chiefly of kaolinite and hydrargillite, with lesser amounts of other substances. If the relative amounts of these compounds be calculated, the results given below are obtained.

	Chattooga Clay	Alabama Clay
Kaolinite	77.03%	93.12%
Hydrargillite	21.32	4.83
Water	0.00	1.61

By employing dilute sulphuric acid at a fairly low temperature it was thought possible to dissolve from such mixtures the hydrargillite, leaving the kaolinite unattacked. For this purpose, sulphuric acid of four different concentrations was employed. These were 10, 15, 20, and 25 per cent. In each case 0.2 gram of the finely powdered clay was digested with 50 grams of the acid. The temperature was held at 55°-60° C., and the digestion continued for three hours with occasional stirring. The solution so obtained was filtered. Alumina and silica were precipitated with ammonium hydroxide from the hot solution, collected on a filter. dried, ignited in a platinum crucible, and weighed. The contents of the crucible were treated with a few drops of sulphuric acid, and fumed down with a little hydrofluoric acid, ignited, and again weighed. The final residue was considered to be alumina and the loss in weight due to the hydrofluoric acid treatment, silica. The results of these experiments are given below.

	Chattoog	ga clay	Alabama clay		
Conc. of acid.	%Al2O3	%SiO2	%Al2O3	%SiO2	
10%	8.50	2.75	2.65	1.05	
15	9.40	2.27	3.10	1.45	
20	10.55	3.20	4.50	2.20	
. 25	10.20	2.00	4.55	1.45	

Even at the relatively low temperature employed, some decomposition of the hydrous aluminium silicate must have taken place. The results do not show any regularity, and no specific conclusions can be drawn from them, except perhaps, that the use of dilute sulphuric acid for the rational analysis of clavs is of doubtful value.

Brown and Montgomerv," and others, have shown that kaolin when dehydrated loses but little water at 300° C., and loses most of its chemically combined water between 450° and 500° C. It appeared interesting to study the dehydration of these clays in an analogous manner. Approximately 0.5 gram portions of the finely powdered clavs were weighed out in platinum crucibles and heated side by side. In each case the heating was continued until the loss in weight on reheating for fifteen minutes became less than 0.2 mg. This was found to be the nearest approach to equilibrium that could be reached in a reasonable time. Up to 200° C. the crucibles were heated in an air oven, but for higher temperatures a small gas-muffle furnace was employed. the temperature being measured with a thermo-electric pyrometer. The probable error in temperature readings was less than 5°C. Weighings were made at intervals of about 50°C. until all the water had been removed. Curves were plotted (fig. 1) using per cent of water lost as abscissæ, and temperature as ordinates.

\* Tr. Am. Cer. Soc., xiv, 709.

A comparison of these curves is interesting. The Chattooga clay, which contains approximately 21 per cent of hydrargillite, probably in a colloidal form, lost about six per cent of water below 300°. The bulk of the water was 'removed between  $450^{\circ}$  and  $500^{\circ}$ . This amount of water would be lost if the hydrargillite gave up most of the water combined with it, below  $300^{\circ}$ . The water remaining combined with the alumina appears to be removed at the temperature at which most of the water is removed from the kaolinite, between  $450^{\circ}$  and  $500^{\circ}$ . The Alabama clay, which contains only about five per cent of hydrargillite, also loses a small amount of water below  $300^{\circ}$ , after which the bulk is again given off between  $450^{\circ}$  and  $500^{\circ}$ . In both cases the last traces are removed only above  $900^{\circ}$ .

#### Conclusions.

The chemical analysis of the two clays shows that they contain less water and more alumina, and to have a higher specific gravity than halloysite. They may be regarded as mixtures of kaolinite and hydrargillite, with smaller amounts of other substances.

It also points to the fact already emphasized by others, that some of the high alumina clays, instead of being composed chiefly of some hydrous aluminium silicate other than kaolinite, are probably in many cases mixtures of kaolinite and some aluminium hydrate, like hydrargillite.

Under the conditions of the experiments, digestion with *dilute* sulphuric acid for the purpose of determining the constituents of a clay mixture is of doubtful value.

Dehydration of a clay mixture containing hydrargillite tends to remove most of the water of the hydrargillite below 300°; the remainder is driven off along with the chemically combined water of the kaolinite between 450° and 500.° The last traces of water are removed only above 900.°

A crystalline substance in the Chattooga clay was shown to be exceptionally well crystallized hydrargillite, and its indices of refraction were found to be slightly higher than those usually given for this substance.

Mineralogical Laboratory, Cornell University.

# ART. XV.—Methods in Reversed and Non-reversed Spectrum Interferometry (continued); by CARL BARUS.\*

11. Prism methods without grating.—A more interesting method, in some respects, in which the grating is entirely dispensed with, is shown in fig. 15. L is the beam of white light from a collimator, P a refracting prism (here with a 60° prism angle), M and N the opaque mirrors with either or both on a micrometer, P' a silvered reflecting prism (here right angled). The telescope is at T and should have high magnification. The rays L are refracted into abc and a'b'c' and the two spectra observed by the telescope at T. Each of the prisms should be on three adjustment screws, as well as the mirrors. P must be revolvable slightly around a vertical axis and capable of fore and aft motion. P' is preferably a large prism placed on a tablet. The rays b and b' are made collinear before P' is inserted and both the rays c and c' must come from near its edge.

The fringes are strong and large and lie within a relatively remarkably wide transverse strip. This may be ten or twenty times as wide as the  $D_1D_2$  doublets, which in view of the small dispersion are hardly separated. For the same reason, moreover, the range of displacement of M within which fringes are visible, rarely attains half a millimeter. Within this the fringes grow from the fine hair lines, usually oblique, to their maximum coarseness. Apart from the şmall range of displacement, these fringes are available for measurement. If both mirrors M and N are on micrometers, they may be brought forward or the reverse, alternately, and the range increased 5 or 10 times.

To change the form of the fringes, the first prism, P, may be tilted slightly on an axis parallel to LT, fig. 15. The fringes then pass through a maximum in the vertical direction (linear phenomenon). Fore and aft motion of P rotates the fringes partially toward the horizontal; but, as a rule, the component beams b and b' pass beyond the edge of P' and the fringes vanish. Just before this (the spectra separating), the strip within which the fringes lie, widens enormously. In other words, the breadth of the phenomenon depends on diffraction, not on dispersion, so that even though the prism Pscarcely separates the D lines, the striated strip has about the same width as when it is produced by highly resolving gratings.

\* Abridged from a Report to the Carnegie Institution of Washington, D. C. See this Journal, pp. 402-420, November, 1916.

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It is preferable to use sunlight directly (without a long focus condensing lens), as there is a superabundance of light. The best results are attained with a long collimator. A spectacle lens with a focal distance of one meter is excellent. The range of displacement of M is not increased, but the spectra and fringes become very sharp. If with the large collimator the spectra are just separated in the field of the telescope, by fore and aft motion of P, a magnificent display appears resembling



a thick twisted golden cord. With further separation confocal elliptic fringes often cross the gap, as in fig. 16. Here  $\alpha$  and  $\beta$  are graphs suggesting the wave-lengths of the two spectra, g being the gap or deficient overlapping. The appearance in the telescope is shown at  $\gamma$ , S and S' being the spectra. When the fringes are erect, huge vertical furrows may lie in the gap. When the gap is closed, the linear phenomenon reappears. These enlarged fringes vanish, however, within one-fourth millimeter of displacement at M.

In further experiments, screens s, s' (fig. 15) were placed in the paths of the pencils b, b', so that they were compelled to pass through vertical slits, 1 to  $3^{mm}$  wide, in the screens. In this way the interfering rays were identified. The first vertical

hair line fringes came from rays about  $5^{mm}$  behind the edge of the prism P'. Hence the pencils were here about  $1.2^{\text{cm}}$  apart when they entered the telescope. The largest and last of the fringes come from close to the edge of P'. The experiment was varied as follows: supposing both screens s and s' placed as far to the rear as the visibility of fringes permits, let the former, s, be slowly pushed forward. The fringes then contract from the very broad set, fig. 17, case 1, to the strong and narrow set, 2 (which is a mere line for a full wave-front), and then expand again to 3. If now s is left in place and s' moved forward, slowly in the same way, the identical contraction and expansion, 1, 2, 3, is reproduced. The screen s' may then be left in place and s in turn slowly moved forward with the same results, etc. (there may be six alternations), until finally the effective parts of the pencils b and b' are beyond the edge of the prism P'. In case 2, the two slits s and s' are obviously symmetrical to the interfering rays, whereas in cases 1 and 3 the diagonally opposite edges of the slits, s and s', limit the efficient pencils rigorously to a sheet.

A similar result (passage of case 2 into 3, fig. 17) may be produced by moving P forward, the case 3 appearing just before the pencils  $b \ b'$  leave the edge of P'. Again, when Mis moved rearward, when both b and b' are near the edge of P', the cases 2, 3 are obtained. In general the width of the diffraction pattern increases without changing the size of fringes, as the width of the available wave-front decreases.

12. Displacement parallel to rays.—It now becomes of importance to test the range of displacement as modified by the angle of reflection, increasing from  $\delta = 0$ . It is therefore desirable to make a few direct measurements. The angle  $\theta$  at P, fig. 15, was found to be about 49° 45', so that the total angle at M is  $\delta = 40^{\circ}$  15'. M and N are both on micrometers, with the screws normal to their faces. P' is on a micrometer with its screw parallel to bb', so that this prism is shifted right and left. The range of displacement was found at

*M*, about '04<sup>cm</sup>; 
$$x = 2 \times .04 \times .939 = .076cm$$
,  
*P*', about  $y = 07cm$ ;  $2y = .140cm$ ,

where  $x = 2e \cos (90 - \theta)/2$  and 2y are the corresponding path differences between the inception and evanescence of fringes. With a very fine slit, 2y was possibly smaller (see fig. 18).

The question at issue is thus in the first place, how the value of 2y compares with x; for in the former case the angle  $\delta$  is effectively zero. In other words, when M is displaced from M to M' over a distance e, the pencil b, fig. 18, changes to  $b_1$ , and is soon lost at the edge of P'; whereas, when P is displaced in the direction bb', over a distance y, the rays b and b'

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do not change their point of impact at the prismatic mirror P'. If pp represents the principal plane of the objective of the telescope and F its principal focus, there should be no accessory effect for the case y as compared with the case x.

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Remarks			E	e	x	2y	ż	μ	
				cm.	cm.	cm.	em.	cm.	
Mirror	right,	Plate*	right	.736	·203	•381	•405	•3901	1.526
"	left,	66	left	66	.208	.391	•408	+.0195	
66	right,	"	right	66	.203	·381	•402	$= \cdot 4096$	
"	left,	"	left	"	·207	•389	•401		
"	right,	"	right+	.736	·206	.387	•406		
"	left,	"	leit	"	•207	•389	•406		
"	right,	"	right	$\cdot 434$	·124	·234	·249	·2313	1.533
44	left,	"	left	66	$\cdot 126$	.236	.250	+.0115	
66	left,	66	right	66	.126	$\cdot 237$		$= \cdot 2428$	
			Ũ			1			

TABLE 1. REVERSED SPECTRA.

Refracting prism,  $\theta = 49^{\circ} 45'$ ;  $B = 4.6 \times 10^{-11}$  (assumed);  $z = E(\mu - 1) + 2BE/\lambda^2$ 

\* Plate slightly wedge-shaped. 
† Different part of micrometer screw.

Results bearing on this subject are given in Table I, in which the displacement, e, observed at M and at N, as well as the displacement y at P', are recorded, when a plate of glass of thickness E is inserted normally to the rays b,b'. The corresponding air path difference computed from E,  $\mu$ , B,  $\lambda$ , should be z, nearly. This is about the value (2y) observed, remembering that to set the micrometer, fringes of a particular pattern must be selected. The rotation of fringes being but 90°, or less, there are no fiducial horizontal lines.

The values of x computed from  $\theta$  and e, however, certainly fall below z, being about 6 per cent and 3 per cent short of it in the two cases, respectively: or again x is  $\cdot 019^{\rm cm}$  and  $\cdot 014$ (about 5 per cent) smaller than the mean values observed for 2y. This extra 5 per cent of path difference can not be an error of observation, or of adjustment, but must be interpreted as the path difference added, when the pencil shifts towards the edge of the prism (x) instead of being stationary as in y. In cases of inverted spectra moreover (next paper) x is usually in excess of z, and the shift is the other way. The deficiency in x, though not equally marked, is present in observations both on the right and left side of the prism P'.

13. Breadth of efficient wave-fronts and apparent uniformity of wave trains. Rotation of fringes.—It follows from

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fig. 18, that if N is displaced to M', over a distance e, the pencil b is displaced parallel to itself over

$$s = 2e \sin \delta/2$$

where  $\delta = 90^{\circ} - \theta$ . The pencil *c* is then displaced parallel to itself over a distance

$$t = s \tan \varphi' / 2 = s.$$

Since  $\theta = 49^{\circ} 45'$ ,  $\delta/2 = 20^{\circ} 7'$  and therefore  $s = 2e \times \cdot 344 = \cdot 7 e$ , nearly. If the rotation of fringes is but 90°, either s (or s/2) is also the breadth of the strips, or patches of like origin which, when sliding over each other more or less, produce the fringes. This may be treated from a graphic point of view as follows, a theory not being aimed at.

In fig. 18a, let a and b be two patches of light of like color and origin at the objective pp, fig. 18, producing interferences at the focus F, fig. 18. Hence the fringes will be arranged in the direction f, fig. 18a, at right angles to the line joining a and b. Since a and b here correspond to c and c' in fig. 18, let a be continually displaced to the right, as indicated by the arrows. In proportion as the positions ab, a'b', a''b'', are taken, the fringes must pass by rotation from f, into f'', into f'', etc.; i. e., over about 90°. In the present experiment, c, fig. 18, can never pass across c', for they are essentially separated by the edge of the right angled prism P'. Hence the rotation can not exceed 90°, for the vertical through a cannot cross the vertical through b. This is not the case when a grating replaces P', as in fig. 14; nor is it the case when, as in an earlier paper, inverted spectra are treated, and the patches a and b slide along the edge of the prism. In such cases fig. 18a may be continued symmetrically, toward the right (mirror images) and the limit of rotation is therefore 180°. All these suggestions are borne out by experiment.

Moreover if the first prism P, fig. 15, is tilted slightly on an axis parallel to LT, a (fig. 18a) will be lowered and b raised. If a and b are on the same level, the fringes are always vertical and pass through a vertical maximum, when abis a minimum. On the other hand, if a and b are not in the same level, as in the figure, fore and aft motion brings the rays c and c' (fig. 18) to or from the edge of the prism P'. Hence the case ab passes into a''b'', or the reverse; in other words the fringes pass through a horizontal maximum when ab is a minimum; etc. This is also shown by experiment.

The experiment made by moving screens with slits, forward or rearward, successively, by which the appearance and evanescence of fringes may be repeated through several cycles, is next to be explained. Here it is merely necessary to remember that the spectra c and c' are reversed, or that the colors of like origin and wave-length are successively farther apart. When the screens are alternately moved therefore, the same phenomenon is in turn produced in slightly different colors. But as abcontinually increases whereas the efficient breadth of the strips does not, the fringes soon pass beyond appreciable smallness.

When as in the earlier methods but a simple grating is used with two successive diffractions through it, the patches a and bare obviously in the same level when the longitudinal axes of spectra coincide. Hence the fringes are essentially vertical.

In the experiment with screens, s, s'. fig. 15, it is obvious that path difference remains constant. The distance from the same wave-front in the pencils b and b', fig. 18, to the principal plane pp, is always the same; but pencils different in lateral position are successively selected. On the other hand, when the prism P' is moved in the direction y, parallel to bb', path difference only is introduced, while the pencils selected remain the same. Supposing the ordinary conditions of visibility (magnification, etc.) to remain unaltered, the wavefronts are, as it were, explored in depth as to their uniformity; i. e. the distance is apparently recorded, throughout which a wave train consists of identical wave elements. Effectively, however, the rapidity with which fringes decrease in size beyond visibility is directly in question. Finally when the opaque mirror M (or N) is moved from M to M', both effects occur together. Path difference  $x = 2e \cos \delta/2$  is introduced and the pencil is displaced from b to b'.

14. Film Grating.-The method of two gratings was now again resorted to, except that the first at G, fig. 3, was a film grating. This attempt failed in my earlier work, when but a single film grating was used for the two diffractions, because of insufficient light. In the present case, two gratings (G' being reflecting) are employed, and the method succeeded The first grating constant was  $D = 10^{-6} \times 167^{\text{cm}}$ ; at once. observations were therefore necessarily made in the second order of G', so that the spectra are not as intense as with prisms. But the fringes are perfect and may be made as large as desirable, with but two in the breadth of the spectrum, for instance. The range of displacement was found to be about 6 millimeters under the best conditions (arrows). If both M and N are successively displaced in the same direction, the total displacement available between the hairlike fringes at the extremes is about 1.5<sup>cm</sup> for each mirror.

At these extremes the two patches of light on the grating G'may have been separated by several millimeters. The nature of the transformation from arrows to the oblique striations would be well reproduced, if equidistant vertical wedges were moved from right to left, or the reverse, behind a vertical slit.

The surprising success obtained with the film grating at short distances induced me to test similar methods at long distances. Figure 23 is an apparatus of this kind, in which L is the white beam incident from a collimator, G and G' are the transmitting gratings, M, N, m, n, pairs of opaque mirrors, T the telescope. The undeviated ray, d, is screened off. The component paths a+b+c, a'+b'+c' were each about 4 meters long. The method of adjustment again consists in bringing the shadow of the thin wire across the slit, into the same position of the spectra seen in the telescope when the spectra coincide. For this purpose the adjustment screws for horizontal and vertical axes on M, N, m, n, must be actuated together. To facilitate this tiresome work, with the observer at T, long levers brought from m and n, with their ends near his hands, as well as a lever from G' (fore and aft motion) were useful. Since the adjustment screws at M and N are already within reach, it is thus easy to bring any Fraunhofer line to the middle of the field and to make these fields overlap, with the guide wire central in both.

The fringes were found after some searching and seemed to be of  $D_1 D_2$  breadth, a strip of oblique lines of the usual character. They were not brilliant and hard to recover when lost. The Fraunhofer lines were still disagreeably blurred.

On exchanging the gratings (weaker ruled glass grating at G and film at G'), though the dispersion was smaller, the brilliancy of spectra was greatly improved. On cutting down the incident beam at the collimator and near G, to a breadth of not more than  $\cdot 5^{\rm cm}$ , the fringes were acceptable and capable of high magnification. They remained visible for a displacement of 5 millimeters at the micrometer at M. With fore and aft motion of G', the fringes rotated as usual from fine vertical hair lines, through the horizontal (probably arrow-shaped forms of maximum size,) back again to hair lines. Here the excursion of G' was about  $1.5^{\rm cm}$ . On tilting the grating G' in its own plane and readjusting M, the rotation is through the vertical maximum (the linear phenomenon).

The film grating may be used by reflection, on adapting the method fig. 14, for this purpose, with a ruled grating or prism at P and the film grating (with its ruled toward P) at G. If a ruled grating is put at P, the spectra and fringes are good; but naturally there is deficient illumination. Nevertheless a strong telescope may be used and a range of displacement of  $4^{\text{mm}}$ , at M, is available. This may be increased indefinitely by using a micrometer at M and N alternately. The chief difficulty was the (incidentally) unequal brightness of spectra.

Again, the method of fig. 15, apart from the drawbacks to

which that method is incident, succeeds almost perfectly, both in the first and second order spectra. The fringes are strong and clear. An Ives grating of high dispersion ( $D = 167 \times 10^{-6}$ cm.) was tested.

A prismatic method with auxiliary mirrors to accommodate the dispersion of the grating was also successfully tried. A concave reflecting grating may be replaced by a film grating used as a *reflecting* grating, with entire success. The ruled side of the film should be free (without cover glass), but the reversed side cemented on plate glass, as usual, and the latter placed towards the telescope. The prism P, in other words, admits an abundance of light, so that even the loss in reflection from the film is not serious. Sunlight should be used without a condensing lens; or if the latter is added, the light leaving the telescope is to be narrowed laterally.

15. Non-reversed spectra.—The prismatic method of cleaving the incident beam of white light is available for the superposition of non-reversed spectra, under conditions where the paths of the component rays may have any length whatever. It is thus an essential extension of the method, fig. 19, given in a preceding paper (PP' prisms, M,N mirrors, Gp, Ives prism grating, T telescope), where the path differences were essentially small and the spectra reversed.

In fig. 20, P is the first prism cleaving the white beam, L, diffracted by the slit of the collimator. M and N are the opaque mirrors, the former on a micrometer. For greater ease in adjustment, the second prism P' is here right angled, though this is otherwise inconvenient, since the angle  $\delta = 90^{\circ} - \phi$ , is too large. The rays reflected from P' impinge normally on the reflecting grating  $G(D = 200 \times 10^{-6})$  and are observed by a telescope at T. P, P', M and N are all provided with the usual three adjustment screws. P' must be capable of being raised and lowered and moved fore and aft. The field is brilliantly illuminated. When the path difference is sufficiently small, the fringes appear and cover the whole length of superposed spectra, strongly. They are displaced, with rotation, if M is moved normally to itself.

As first obtained the fringes were too close packed for accurate measurement. But experiments on the displacement of the mirror M, for successions of 40 fringes replacing each other at the sodium lines, showed a mean displacement of  $39 \times 10^{-6}$  cm. per fringe. The computed value would be

$$\frac{\lambda}{2\cos\delta/2} = 36.4 \times 10^{-6} \,\mathrm{cm.},$$

assuming  $\delta = 90^{\circ} - \phi$ . The difference is due both to the small fringes which are difficult to count and to the rough

value of  $\delta$ . The range of measurement is small (if M only moves) not exceeding 1.5 millimeters for a moderately strong telescope. Usually but one-half of this displacement is available, as the fringes increase in size (with rotation) from fine vertical hair lines to a nearly horizontal maximum, and then abruptly vanish. This is only one-half of the complete cycle.

If we regard the component beams,  $a \ b \ c$  and  $a' \ b' \ c'$ , as being of the width of the pencil diffracted by the slit of the collima-



tor, it is clear that the maximum size of fringes will occur, when c and c' are as near together as possible; furthermore, that as M moves toward P', c continually approaches c', until b drops off (as it were) from the right angled edge of the prism P'. To get the best conditions, i. e., the largest fringes, c must therefore also be moved up to the edge of P and very sharp angled prisms be used at both P and P'. The largest fringes (lines about 10 times the  $D_1D_2$  distance) obtained with the right angled prism were often not very strong, though otherwise satisfactory. Much of the light of both spectra does not therefore interfere, being different in origin.

Results very similar to the present were described long ago\* and found with two identical half gratings, coplanar and

\* Phil. Mag., xxii, pp. 118-129, 1911; Carnegie Publ. No. 149, chap. vi.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 254.—FEBRUARY, 1917. 11 parallel as to rulings, etc., when one grating was displaced normally to its plane relative to the other. The edges of the two gratings must be close together; but even then the fringes remain small and the available paths also. Strong large fringes, but with small paths, were obtained by the later method\* of two identical transmitting gratings, superposed.

If the prism P' is right angled (a special case of fig. 19), it may be rotated as in fig. 21, so that the rays c and c' pass off towards the observer. They are then to be regarded through an Ives prism grating G and a telescope at T. This method admits of much easier adjustment. With the component beams a b, a' b', coplaner, horizontal and of about equal length in the absence of the prism P', the latter is now inserted with its edge vertical (rotation) and the white slit images in T(without G) superposed, horizontally and vertically. G is then added and the micrometer at M or N manipulated till the fringes appear. As above, they are largest when c and c' are as nearly as possible coincident and vanish as horizontal fringes at the maximum.

The case of fig. 20 was subsequently again tried on the large interferometer, the distance P to M-N being about 2 meters. G, in these experiments, was a concave grating and T a strong lens near the principal focus of G. The adjustment for long distances is not easy. The equilateral triangle of rays, a, a', b', b, should be first carefully levelled, the edges of P and P'being on the median line. With G placed at the proper distance, the two spectra seen at T will usually be quite distinct in the field. They should show the shadow of the black line across the slit, at the same level in the spectra. The longitudinal axis of the spectra may then be made collinear by slightly tilting the edge of P' to the vertical, on a horizontal axis, with the adjusting screws. M and N are then rotated on a vertical axis till the D lines coincide. Small changes may be completed at M and N. The fringes when found are usually strongly, but very fine, less than the  $D_1D_2$  distance in width. I have been able to increase them to a width of  $2D_1D_2$ , but they are then faint. The two illuminated strips on the grating may even be an inch apart; but the fringes are as usual larger, when this distance is the smallest attainable (virtual coincidence). The grating may be moved fore and aft without As N is displaced on its micrometer, the interferences effect. are first seen as vertical hairlike striations, which gradually enlarge, rotate and vanish just before reaching the horizontal and at maximum size. The range of displacement did not exceed  $\cdot 15^{\text{cm}}$  for this rotation of 90°. Since N and T are close together, the manipulation is convenient here, but with another

\* Physical Review, vii, 1916, p. 587, 1916; Science, xlii, p. 841, 1915.

lens at T' the phenomenon could be traced further on the M side.

To secure a smaller angle of incidence and reflection,  $\delta/2$ , at M, fig. 22, the combination of a silvered 20° prism, P, and a 30° prism, P', was tested. M and N are the opaque mirrors, G the concave grating with its focus at T for inspection by a strong lens. L is the incident beam of white sunlight from the collimator, which is split into the component pencils *abcd* and a'b'c'd' and interfere at T. The results, however, were about the same as above, the range of displacement at Mfor 90° of rotation of fringes being about  $\cdot 15^{\text{cm}}$ . As a and bmake angles,  $\phi$  and  $\phi'$ , with the line of symmetry LL', was about 10°,

$$\delta = \phi' - \phi.$$

At a subsequent opportunity I made further trials with the paired prisms of 20° and 30°, but failed to increase the fringes above about  $D_1D_2/2$  width. Two micrometers, one at M and the other at N, were installed, and moved forward in alternate steps, within a range of over  $2^{\rm cm}$ , naturally without modifying the fringes. These are now observed on both sides (N and M), each with the micrometer which is manipulated. One may note in passing that the two screws are being incidentally compared.

It is noteworthy that the 30° prism at P' is no marked improvement as to range of displacement over the 90° prism at P', previously used. In other words, the effect of decreasing the angle of reflection,  $\delta$ , at M is, unexpectedly, of small importance in relation to the range of displacement at M. This result has already been accentuated in other ways, above, §13.

16. Non-reversed spectra. Restricted coincidence.—In fig. 24, the white ray L from the collimator is diffracted by the grating G and the two spectra a and a', thereafter reflected by the parallel opaque mirrors M and N, to be again diffracted by the grating G'. The rays are observed by a telescope at T. If the gratings G, G' have nearly the same constant, it is obvious that the field of the telescope will show a sharp white image of the slit, for each mirror. If M N G G' are adjusted for symmetry by aid of the adjustment screws on each and the rulings are parallel, the two white slit images will coincide horizontally and vertically. If now a direct vision spectroscopic prism, or a direct vision prism-grating G'', is placed in front of the telescope, the superposed white slit images will be drawn out into overlapping non-reversed spectra, which will usually show a broad strip of interference fringes. The equation is  $n\lambda = 2e \cos \delta/2 = \bar{2}e \sin \theta$ .

This equation is not obvious, as for constant  $\lambda$ , the distance being G and G' measured along a given ray (prolonged) for any position of M or N is also constant. The equation may be corroborated by drawing the diffracted wave-front at G' for M and M', which cuts off a length  $2e \sin \theta$  from d''.

Since sin  $\theta = \lambda/D$ , if D is the grating space, the last equation becomes n = 2e/D or per fringe

 $\delta e = D/2$ 

a remarkable result, showing that the displacement of the mirror M per fringe is independent of wave length and equal to



half the grating space. An interferometer independent of  $\lambda$  and available throughout relatively enormous ranges of displacement is thus at hand. It may be shown that it is also independent of the angle of incidence at G.

To change the size of fringes it is necessary to rotate the grating G' (relatively to G) on a horizontal axis normal to itself. They then both rotate and grow larger, attaining the maximum of size when the fringes are vertical. Fringes quite large and black may be obtained in this way.

To show the close relation of the present experiments with one reflection, to the earlier work with crossed rays and two reflections, experiments may be made with homogeneous light. Accordingly the sodium arc with a wide slit was installed. Strands of fringes with nodules were obtained as before. These rotated in marked degree (180°) from vertical hair lines, through coarse vertical strands with horizontal nodules, back to vertical hair lines again, as either M, or G, were suitably displaced normally to their planes. To shift the fringes of any

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form into the middle of the wide slit image, a glass compensator in either b or b' may be resorted to, or both M and G'may be displaced together. Again, whereas the micrometric displacement of M produces a marked displacement of fringes within the strip in accordance with the equation, the micrometric displacement of G' leaves the fringes stationary within the strip.

Very remarkable results were obtained with compensators of glass plate. Placed in one or both beams and rotated around a vertical axis, they rotate the fringes. If however they are placed nearly normally in one beam, they produce no effect either of rotation or on the size of the fringes; but the grid is displaced bodily across the wide yellow slit image. Glass plates '2, '5<sup>cm</sup> were used. It is not until the thickness of plate reaches 2<sup>cm</sup> that appreciable thinning of the interference fringes occurs when the plate is placed in one beam.

In case of homogeneous light the Ives prism grating G'' is not needed and much more light is available if the telescope is used directly. The strands of interferences being on a yellow ground are not very strong, Nevertheless a few measurements of ranges of displacement were made by moving both M (displacement e) and G' (displacement h), alternately. The following values of e, h, and  $h \tan \theta'$  were found, the film gratings having nearly the same constants :

$$e = \cdot 5^{cm}$$

$$h = 1 \cdot 30^{cm}$$

$$h \tan \theta = \cdot 49^{cm}$$

 $\theta = 19^{\circ} 37'$  $\theta' = 20^{\circ} 40'$ 

e and h tan  $\theta'$  coincide as closely as may be expected, seeing that the fringes in neither case can be quite brought to vanish.

17. The same, continued. Duplicate fringes. Achromatic fringes.—The occurrence of strands and apparently duplicated fringes has already been suggested in the preceding paragraph. In further experiments definite results were eventually obtained, with sunlight. These occur in very great variety, but typical phases may be accentuated. In intermediate cases fine large strands occur. These pass into each other continuously; the manner does not admit of description. They are seen best in the principal focal plane and both sets are about equally strong.

To obtain these fringes the adjustment was first carefully made with the sodium arc. Thereupon the arc was replaced by concentrated sunlight and fine fringes were recognized in the superposed spectra (longitudinal and transverse axes coinciding). These fine fringes were then enlarged both by rotating the grating G' (fig. 24) on its normal axis and readjusting M in each case, and by adding trial compensators in the M or N pencils. A glass plate 3 millimeters thick gave the best results. Rotation of the compensator in the first place moves the fringes as in interferometry, as does also the normal micrometric displacement of M. If this motion requires readjustment of M the range of displacement is curtailed and the corresponding change of phase appears. In the second place the compensator on rotation traces the contours of the curves by successively accentuating vaguer parts, as will presently be explained.

The most remarkable results occurred on widening the slit. Supposing that large strands were visible in case of the fine slit, and that this was gradually widened until the slit width was half a millimeter or more; the strands were found to have coalesced in a way which defies description. In their place appeared a wide vertical strip of equidistant parallel crescents. The Fraunhofer lines had long vanished and the appearance of the spectrum was whitish and intense. The fringes in question may thus be termed achromatic. The strips appear quite regular through the breadth of the spectrum and its width may be one-third of the length of the spectrum. The fringes move with the normal displacement of M (interferometry) and the range is large ( $\cdot 5^{cm}$  without adjustment) provided  $\dot{M}$  does not require readjustment by rotation. Simultaneously the strip is displaced longitudinally in the spectrum in the usual way.

On closing the slit the ellipses break up into sharp strands again without offering a systematic clue as to the manner in which this is done. The strands usually trend more or less vertically with two sharp strong groups, flanked by one or more weak groups on each side.

On removing the condenser, these crescents became more slender but much sharper, so that in spite of the diminished light they could be well seen. They were then found to be like the approximately confocal ellipses of displacement interferometry, though not subject to the same laws. They embraced over one-third of the visibly overlapping (green yellow through red) spectra, terminating in very fine hair-lines on one side but coarse lines on the other. On opening the slit from a breadth of 0<sup>cm</sup> to about  $\cdot 1^{mm}$  the evolution was curious. With a very fine slit a relatively narrow strip of strong slanting lines was seen in the yellow. As the slit widened they developed curvature, adding the more slender complements of the ellipses on the red side, until this part of the spectrum was filled with confocal half ellipses having a transverse major axis. The range of displacement of M is practically indefinite, depending simply on the degree to which the spectra overlap. Three or four centimeters were tried. Both sides of the ellipses may be traversed by rotating the plate compensator, which successively accentuates (in a transverse strip) a definite part of

their contours. In this way the thick apices or either of the hairlike lateral ends may be clearly brought out.

To further study this result the grating  $G'^*$  was successively rotated in small amounts on a normal axis with adjustment at M. It was thus possible to find both the upper ends of the ellipses and their lower ends, as well as the central part. The confocal ellipses are extremely eccentric with very turgid apices so that the central part (if in the spectrum) consists of trans-



verse straight lines. Motion of M moves the fringes to and from the center where they originate or evanesce. The ellipses shift as a whole with M without changing form appreciably throughout the spectrum, but they move very slowly, quite differently in this respect from the round ellipses in displacement interferometry which are extremely sensitive to displacement of M. In the present work it may take 5 or  $10^{\text{cm}}$  at Mto pass the ellipses quite through the spectrum. They are strong and fine in spite of the film gratings used.

18. The same continued. Prismatic Adjustment.—The 60° prism has certain advantages in experiments like the present, particularly when non-reversed spectra are to be obtained. Fig. 25 is a device of this kind, in which P is the separating prism and P' the collecting prism, the beam of white light L from a collimator entering the flat face normally on the front side and issuing normally on the rear side at c and c'. M and N are opaque mirrors parallel to each other, G a direct vision prism-grating. The telescope is at T. The reflection may be either internal, as in the strong lines of fig. 25; or it may be external on silvered faces of the prisms

\* When nearly centered rotation of M about a horizontal axis is also sufficient to complete the centering of the ellipses.

p and p', the appurtenances being shown in dotted lines. In this case the separated rays, a, a', b, b', are collected at c'', c''', to be joined in the telescope at T. The internal reflection being total, I made use of it for the following experiments. M and N and P' are on micrometers with the screw in the directions normal to their faces. P, M, N, P' must all be adjustable. After preliminary measurement for equal distances, the fringes were found. They were strong but fine, beginning with vertical hair lines and gradually rotating as they grew coarser till they rather abruptly vanished. The displacement of the M mirror did not exceed  $\cdot 06^{\text{cm}}$ , nor the rotation  $30^{\circ}$ . The spectra being non-reversed, the fringes covered the whole field.

One would naturally suppose that the abrupt evanescence of fringes was due to the escape of the beam of the edge of the prism P', but this is not possible as the mirror M was traveling toward the rear. Furthermore the fore-and-aft motion of the prism P' over several millimeters had scarcely any effect on the fringes. This is unexpected; for the rays, c, c', are compelled to approach or recede from each other by this motion. Finally the sodium doublets may be moved at some distance (many times their breadth) apart, without destroying the fringes. They are often most distinct when the D lines are not superposed. The same is also true for the longitudinal axes, though to a less degree.

To enlarge the fringes, the prism P' may be rotated around a horizontal axis parallel to LT. The fringes then also rotate, but the increase of size so obtained is usually not striking. Moreover no observable effect either on the size of fringes or on the range of displacement is produced by inserting compensators in one beam or both. A great variety of different adjustments showed a range of displacement at M, about the same (.06<sup>cm</sup>), whether the patch of light on the prism was wide or narrow. The range of fore and aft motion of P' within which fringes are visible was  $\cdot 52^{\text{cm}}$ . They vanish quite abruptly when the light is near the edge of the prism, although both spectra are still strongly visible. When the light is nearer the base of the prism, they vanish more gradually. Definite strips of white light on both sides of the prism therefore coöperate to produce the fringes. The attempt to find a systematic method for enlarging the fringes failed, possibly because the prism angles were not quite identical. The striking contrast in the results obtained here in comparison with those of the preceding paragraph, although both methods are essentially the same, is noteworthy.

It is for this reason that I thought it desirable to test the method in fig. 26 which accomplishes with a prism, what was done in my original experiments<sup>\*</sup> with reversed spectra, by the aid of a grating. In the figure the incident beam of white light L from a collimator strikes the 60° prism at its edge, and is then refracted into the paired pencils a, a'. Those are reflected normally by the opaque mirrors M and N, again refracted by P as each pencil nearly retraces its path. The return beams however are given a slightly upward trend, so as to impinge on the opaque mirror m (curved or plane). The rays reflected from m, in such a way as to avoid the prism P, may be reunited in the focus F observed by the lens T, or (if parallel) collected by a telescope at T. In view of the prism, the spectra are small and reversed, but may be brought to overlap at the red ends which are towards each other.

The small dispersion makes it necessary to use a strong telescope if the Fraunhofer lines are to be visible and the D lines separated. When the adjustment has been made symmetrically, a strong linear phenomena may be found not differing in appearance from the results obtained when a grating was used at P, fig. 26. When the mirror M is displaced, however, the fringes first appear in the form of multiple vertical hair lines, which grow coarser until but a single dark line flanked by a bright line is visible. With further displacement the phenomenon again vanishes in passing through multiple hair lines. An important result is the small range of displacement. This was found to be, between appearance and evanescence of fringes, about

$$\delta e = :12 \text{ cm.},$$

thus scarcely larger than a millimeter, whereas in the case where a grating  $(D = 352 \times 10^{-6} \text{ cm.})$  was used in place of P, the range of displacement was of the order of 5 millimeters.

Suppose that for low dispersion, the fringes may be regarded as extremely eccentric virtually linear ellipses, the lateral distance between which very rapidly diminishes, so that ( $\delta e = \cdot 12$ ) but

$$\frac{1}{2} \frac{\cdot 12}{3 \times 10^{-3}} = 2000$$

can be seen by the given telescope. These lines would move behind the strip carrying interference fringes, as M is displaced. If now the dispersion is much increased, say from  $d\theta/d\lambda = 2 \times 760$  for the prisms to  $2 \times 2880$  for the grating, the ellipses will be much less eccentric as a whole and their lines would have grown coarser, so that many more would be visible by the given optical system. As the dispersion is increased 2880/760 = 3.8 times, the range of displacement

\* This Journal, xl, p. 486, 1915.

should increase similarly to  $12 \times 3.8 = 4.6^{\text{cm}}$ . The plane ruled grating  $(D = 352 \times 10^{-6} \text{ cm.})$  was now again mounted in place of P and under good illumination the range  $48^{\text{cm}}$  was found experimentally. This agrees very well with the estimated value. Moreover on close inspection it is discernible that the linear phenomenon really consists of extremely eccentric ellipses which in case of the best adjustment manifest the very sharp arrowlike forms. It also enters and vanishes in multilinear form, though the lines are not hair lines. Thus the assertion that increased uniformity of wave train accounts for the long range of displacement and visibility in case of the grating is not warranted.

[TO BE CONTINUED.]

Brown University, Providence, R. I.

#### ART. XVI.—On the Identity of Hamlinite with Goyazite; by Waldemar T. Schaller.

FARRINGTON\* has recently stated that the present evidence hardly seems sufficient for regarding the two minerals, goyazite and hamlinite, as identical. Damour's original formula for goyazite would then have to be accepted even though it "evidently needs confirmation" as Farrington states.

The resemblance of goyazite and hamlinite in their physical and optical properties is great enough to warrant the suggestion that their chemical composition is of the same type of formula, and since Damour's calcium has been shown to be essentially strontium, the two minerals have the same qualitative composition, both being hydrous phosphates of aluminium and strontium. If their formulas are of the same type, it is most reasonable to consider them identical—until they are proven to be different.

The table published<sup>†</sup> earlier by the writer showed the probable identity of the two minerals goyazite and hamlinite. In order to emphasize the possible distinction between these two minerals, Farrington has published a table of differences between them; there are, however, three errors in the six items listed in this table.

The percentage of  $P_2O_5$  for hamlinite is wrongly given as 20.92 per cent. It should be 28.92 per cent. The suggestion was earlier made that the separation of  $P_2O_5$  from  $AI_2O_3$  was probably not accurate in Damour's analysis of goyazite, so that the comparison between the sums of  $P_2O_5$  and  $Al_2O_3$  for the two minerals (65.53 and 62.87), is probably the most valid comparison of the analytical figures.

Goyazite is stated by Farrington in his table to be "Infusible." The original description states : "A la flamme du chalumeau, il fond difficilement sur les bords des plus minces fragments." Damour's statement regarding goyazite, "il fond difficilement," and Penfield's statement for hamlinite, "fuses about 4," show a resemblance, not a difference.

The table of Farrington states further that hamlinite is "slowly soluble in acids." This statement, quoted in Dana's System of Mineralogy, on page 762, must be somewhat modi-

+ Schaller, W. T., The alunite-beudantite group, this Journal (4), xxxii,
359, 1911. Also, U. S. Geol. Survey Bull. 509, p. 70, 1912.
+ Damour, A., Note sur un nouveau phosphate d'alumine et de chaux, des

terrains diamantifères, Bull. Soc. Min., France, vol. xvii, 204, 1885.

<sup>\*</sup> Farrington, O. C., Studies of Brazilian favas, this Journal (4), xli, p. 358, 1916.

fied by Penfield's later statement\* that "hamlinite is almost insoluble in boiling dilute hydrochloric acid," and by Bowman's statement+ that the "mineral is insoluble in hydrochloric acid."

By correcting these errors in Farrington's table, the main supposed differences disappear and the list of similarities of the two minerals, as shown below, is sufficient to justify the conclusion that hamlinite is identical with goyazite—at least until their difference is proven.

Similarities in properties of goyazite and hamlinite, supporting the conclusion that the two minerals are identical.

Goyazite	Hamlinite.
Yellowish white.	Colorless, yellowish, honey-yel-
	low, reddish brown.
More or less-transparent.	Transparent.
Uniaxial, positive.	Uniaxial, positive.
Cleavage, good, basal.	Cleavage, good, basal.
$\mathbf{H}=5.$	H = 4.5, 4+.
S.G. = 3.26	S.G. = 3.228, 3.2, 3.159 - 3.283,
	3.219 - 3.266.
Fuses with difficulty.	Fuses about 4.
Not attacked by acids.	Insoluble in HCl.
Per cent Al <sub>2</sub> O <sub>5</sub> + P <sub>2</sub> O <sub>5</sub> = $65.53$ .	Per cent $Ai_{a}O_{a} + P_{a}O_{b} = 62.87$ .
Per cent H <sub>o</sub> O (det. by loss on	Loss on ignition (hamlinite from
ignition?) = 16.67.	Switzerland) = $15.6$ to $16.0$
Ç .	per cent.
Hydrous phosphate of alumin-	Hydrous phosphate of alumin-
ium and strontium.	ium and strontium.

\* Penfield, S. L., On the chemical composition of hamlinite and its occurrence with bertrandite at Oxford County, Maine, this Journal (4), iv, 313, 1897.

† Bowman, H. L., On hamlinite from Biennenthal, Switzerland, Mineralog. Mag., xiv, 391, 1907.

#### SCIENTIFIC INTELLIGENCE.

#### I. CHEMISTRY AND PHYSICS.

1. The Occurrence of Free Carbon Monoxide in the "Floaters" of Kelp.—SETH C. LANGDON has made the interesting observation that the gas in the bulb and hollow stem of the large Pacific coast kelp, Nereocystis luetkeana, contains carbon monoxide in quantities varying from 1 to 12 per cent by volume. This gas has never before been found in the free state in a living plant. This kelp is a very large brown one. The author worked with specimens 85 feet long, and much longer ones have been reported. This enormous growth takes place in the short period of 10 or 15 Another interesting feature of this plant is the fact that weeks. while it contains about 92 per cent of water, more than one-fourth of the remaining 8 per cent consists of potassium chloride, and the commercial extraction of this valuable salt from the kelp has been extensively discussed. The hollow space in the large specimens has a capacity of from 3 to 4 liters, and it has been found that the gas contained in this cavity is almost always under less than atmospheric pressure. Many of these pressures were determined, most of them ranging between 520 and 600<sup>mm</sup>, while the normal atmospheric pressure is 760<sup>mm</sup>.

The gas from nearly 1000 specimens was examined, and almost invariably carbon monoxide was present, the average amount being about 4 per cent. Carbon dioxide was either practically absent, or present in very small quantity, while oxygen varied from about 22 per cent, or about the same as in the atmosphere, down to about 15 or 16 per cent. It would seem that a mixture shown by one of the analyses to contain 12.2 per cent of carbon monoxide and 17.4 per cent of oxygen would be explosive when exposed to a flame, but the author makes no mention of such a circumstance. The samples of gas for analysis were carefully taken from the plants in their natural situation, sometimes over mercury, and sometimes by displacement of sea-water which had been saturated with the gas from other specimens.

The qualitative tests for carbon monoxide in the gas were elaborate and convincing. Palladium chloride paper was blackened, very dilute blood gave the characteristic change of color, the spectrum of blood treated with the kelp gas and ammonium sulphide showed the characteristic behavior of carbon monoxide, a guinea pig placed in a vessel through which the kelp gas was passing died in less than 10 minutes, while a canary bird died in about 15 seconds and a young chicken in about a minute. All these animals showed clear evidence from blood color or blood tests of carbon monoxide poisoning.

The author suggests that the presence of carbon monoxide in the kelp may indicate an intermediate step in the reduction of carbon dioxide in connection with photosynthesis, a theory ad-

vanced by Baever. He mentions a possibility also that the carbon monoxide may be an accumulated waste product, or that it may be formed by processes of decay. He does not mention, however, an explanation that appears to be more plausible and interesting than the others, namely, that the carbon monoxide is produced by the plant as a poison to protect itself from such animals as might bore into it, make a habitation in its cavity or feed upon its substance. Since carbon monoxide is the simplest of organic poisons, it is perhaps reasonable to suppose that it might be utilized in this way by a simple organism like kelp, while higher plants produce alkaloids and other more complex poisons. It will be interesting to examine other plants of low orders for the presence of carbon monoxide. It appears that seaweeds are generally very free from the attacks of marine animals, and it seems possible that we now have an explanation of this immunity. The further suggestion may be made that possibly the curiously large amount of potassium chloride in this kelp and also the iodine that occurs generally in these plants may be protective poisons.-Jour. Amer. Chem. Soc., xxxix, 149.

H. L. W.

2. The Atomic Weight of Lead of Radioactive Origin.—The results of recent work by several independent investigators have shown with very little room for doubt that the metal derived from this source has a much lower atomic weight than ordinary lead. This conclusion is of such theoretical importance that THEODORE W. RICHARDS and CHARLES WADSWORTH, 3d, have extended the investigations previously made by Richards and Lembert upon the same subject. Their results entirely support the earlier conclusion. Atomic weight determinations were made with ordinary lead and four samples of radioactive lead with the following results:

Ore.	Origin.	Atomic wt.
Galena (?)	American ordinary lead	207.18
Carnotite	Colorado, U. S. A. (?)	207.00
Carnotite	Radium Hill, N. S. W.	206.34
Bröggerite	Moss, Norway	206.12
Cleveite	Langesund, Norway	206.08

The last sample is the most carefully selected one, and is probably most nearly free from ordinary lead. While it is possible that there may be two kinds of radioactive lead with different atomic weights, it seems more probable that the higher results from the carnotite ores are due entirely to the accidental admixture of ordinary lead. Careful spectroscopic examination showed no lines peculiar to the radioactive material. It was found that the magnitude of the radioactivity of the samples of lead seemed to bear no relation to the lowering of the atomic weight.—Jour. Amer. Chem. Soc., xxviii, 2613. H. L. W.

3. Engineering Chemistry; by THOMAS B. STILLMAN. 8vo, pp. 743. Easton, Pa., 1916 (The Chemical Publishing Co.).—The

appearance of five editions of this book since the first issue in 1895 shows that it has been extensively used. The sub-title of the work describes it as "A manual of chemical analysis for the use of students, chemists and engineers," but it is to be observed that descriptions of many physical tests, copies of specifications and other topics not dealing strictly with chemical analysis are included. On the other hand, the book deals with only a restricted field of analytical chemistry, confining itself practically to such materials as are used in civil or municipal engineering. However, the book presents much that is useful in this field, and it is to be highly recommended to those who are interested in this kind of work.

Among the subjects most extensively treated are the proximate analysis of fuels, their colorimetry and their physical examination, the analysis of iron, steel, and a number of non-ferrous alloys, the analysis and physical tests of cements, concrete, clay, sand and building stones, the examination of asphalt and other bituminous road materials, of coal-tar lubricating oils, illuminating oils and fuel oils, soap analysis, varnish analysis, paint analysis, the chemical and physical examination of paper, the analysis and treatment of boiler waters and potable waters, the analysis of flue gases, illuminating gases, etc., the manufacture of producer gas, water gas and acetylene, photometry and pyrometry. Many official methods are quoted and many interesting details of manufacturing operations are given. H. L. W.

4. Qualitative Analysis; by E. H. S. BAILEY and HAMILTON P. CADY. 8vo, pp. 294. Philadelphia, 1914 (P. Blakiston's Son & Co. Price \$1.50 net).-This is the eighth edition of a wellknown laboratory guide, which gives an excellent course of instruction in chemical analysis. The methods of qualitative separation and detection are well chosen and clearly presented. The title page states that the book is based upon the application of the theory of electrolytic dissociation and the law of mass action. There is a rather elaborate introduction dealing with the topics just mentioned, and the ionic nomenclature is used to an extreme extent throughout the practical part. There are some teachers who would prefer to lead up to the ionic theory by means of the facts encountered in qualitative analysis, rather than to attempt to explain the facts by means of a theory, but at present the latter method appears to be popular. There is a generalization on page 32 which needs modification to correspond with all the facts : "The solubility of difficultly soluble salts of strong acids, however, is not increased by the addition of an acid." H. L. W.

5. X-Ray Wave-Lengths.—A valuable paper on the new branch of spectroscopy—the study of the wave-lengths of characteristic or fluorescent X-rays—has been recently written by MANNE SIEGBAHN. The article begins with a list of 66 bibliographical references which indicates how rapidly the subject has grown in the course of a very few years. The author then describes the various types of bulbs and spectrometers which have proved most efficient in producing and analyzing the radiations in question. The vacuum spectrometers perfected by Siegbahn and others are illustrated and explained in detail. This is followed by a discussion of the relations between the speeds of the exciting cathode rays and the excited characteristic X-rays. The rest of the article is devoted mainly to the relatively accurate wave-lengths determined experimentally by Siegbahn and his co-workers, full credit being also given to the more exploratory and less accurate work of their predecessors.

In the case of the K-group the wave-lengths cover the interval from  $\lambda 0.292$ , for neodymium, to  $\lambda 11.951$  for sodium. Eight series of lines have been traced for the K-group. The wavelengths belonging to the L-group fall into 14 series extending from  $\lambda 0.596$  for uranium to  $\lambda 12.346$  for zinc. For the elements of high atomic numbers,—gold to uranium,—the author has discovered a third group of lines which he calls the M-series. The paper closes with a very useful table containing all the accurately known wave-lengths, the number of which is 1729.-Jahrbuch d. Radioaktivität u. Elektronik, vol. xiii, pp. 296-341, Sept., 1916.

H. S. U.

6. General Physics; by WILLIAM S. FRANKLIN and BARRY MACNUTT. Pp. viii, 604; 479 figures. New York, 1916 (McGraw-Hill Book Co.).—This book has the sub-title "An Elementary Treatise on Natural Philosophy" and it is designed as a text-book for colleges and technical schools. The field covered is divided into five parts: I Mechanics (pages 5-104), II Theory of Heat (107-177), III Electricity and Magnetism (181-343), IV Theory of Light (347-484), and V Theory of Sound (487-528). Each part is preceded by a list of titles of selected reference books together with comments on their nature and scope. But little space is devoted to statics and elasticity since these subjects have been presented at some length in two earlier volumes by the same authors. A list of 409 problems, for solution by the student, constitutes Appendix A.

The spirit and method of the calculus pervade the entire text. In this connection the authors say: "The method of differential calculus is used quite freely in this elementary treatise on physics, but the authors believe that the use of this text does not depend upon the previous study of calculus by the student. Indeed the authors are convinced that the use of this book or its equivalent is a necessary preparation for the study of calculus; and the authors suggest that the student be required to turn again and again to the brief discussion of the methods of differential and integral calculus in Appendix B". As a matter of fact, formal proofs depending upon theorems of the calculus are presented in small type and in such places as not to interfere, in the least, with the continuity of the main body of the text.

The authors' style is lucid and straightforward. Clearness of conception is facilitated in other branches of the subject by numerous mechanical analogies, presented both graphically and by the use of corresponding sentences in parallel columns. The definitions of units and the statements of fundamental laws are

characterized by accuracy and succinctness, and the entire text is as rigorous as possible for an elementary book. The diagrams are clear and to the point, italic and clarendon type are frequently used for emphasis, and the number of misprints is negligible. On the other hand, the innovations in terminology frequently introduced by the authors may not be pleasing to all readers. For example, the terms "spin-inertia," "spin-velocity," and "spin acceleration" are substituted for moment of inertia, angular velocity, and angular acceleration, respectively. The opinion is advanced (on page 285) that it is unsuggestive to speak of charging an electric condenser but that it is extremely suggestive to speak of "squeezing" a condenser. The statement (p. 33) that "The limiting value of  $\frac{\Delta y}{\Delta t}$  is always represented by  $\frac{dy}{dt}$ ...." must refer to the succeeding pages of the book since the symbol y does not seem to have become obsolete, especially with English writers. Nevertheless, as implied by most of the foregoing comments, the book, as a whole, seems to be a valuable contribution

to the pedagogy of the subject. H. S. U. 7. Cosmical Evolution, Critical and Constructive. Second Edition; by Evan McLennan. Pp. xxi, 490. Corvallis, 1916 (The Author).—The copy of this book submitted for review was accompanied by a circular from which a few quotations will be made for the purpose of presenting the author's point of view. "This book comprises the principal part of the author's life-work, continued over a period of about forty years." "It contains undoubtedly the most complete and destructive criticism of the accepted fundamental views of physical science that has ever been published; and it also contains an equally complete constructive theory." "To all those who receive this book for review . . . . the author earnestly and finally appeals for an impartial and adequate treatment of it."

In the winter of 1914–15 the final manuscript was given a critical examination by the heads of the physical departments of four of the principal colleges of the western United States. "All of the results of this examination, for which permission to publish has been obtained, are given in Appendix A, together with the author's replies thereto." The opinion of one of the physicists is summed up, on page 408, in the following words: "In reading over your first part I have not found one single argument that is valid. In some cases you have misunderstood the facts, in others you have drawn conclusions that are not warranted by the facts and in many cases you have quibbled over or misunderstood definitions of terms which are the most elementary foundation of physical science and which are verified experimentally thousands of times every year in laboratories." The writer of the present notice has fully verified this adverse criticism, but has found it to be altogether too mild and considerate. In our opinion the only use to which the text can be put is to furnish teachers of elementary logic with numerous simple illustrations of logical fallacies. H. S. U.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIV, NO. 254.—FEBRUARY, 1917.

8. An Introduction to Astronomy. New and Revised Edition; by Forest RAY MOULTON. Pp. xxii, 577. New York, 1916 (The Macmillan Co.).-The present volume has been entirely rewritten. "As in the first edition, the aim has been to present the great subject of astronomy so that it can be easily comprehended even by a person who has not had extensive scientific training." Since it is impossible to even begin to do justice to this elegant book in a brief notice it seems desirable to suggest its scope by quoting the titles or sub-titles of the chapters, which are : I Preliminary Considerations. II The Shape of the Earth. The Mass of the Earth and the Condition of Its Interior. The Earth's Atmosphere. III The Rotation of the Earth. The Revolution of the Earth. IV Reference Points and Lines. V The Constellations. VI Time. VII The Moon. VIII The Law of Gravitation. Orbits, Dimensions, and Masses of the Planets. IX Mercury and Venus. Mars. Jupiter. Saturn. Uranus and Neptune. X Comets. Meteors. XI The Sun's Heat. Spectrum Analysis. The Constitution of the Sun. XII General Considerations on Evolution. Data of Problem of Evolution of Solar System. The Planetesimal Theory. Historical Cosmogonies, and XIII The Apparent Distribution of the Stars. Distances and Motions of the Stars. The Stars. The Nebulæ.

With regard to details no pains seem to have been spared, either by the author or by the publishers, to make the volume as attractive and useful as possible. Of the 194 figures no less than 68 are photographic illustrations, those pertaining to the moon, the Pleiades, comets and nebulæ being especially beautiful. Five star maps have been incorporated to enable the reader to quickly recognize the constellations. Lists of problems (243) have been given at the ends of the principal divisions of the chapters. "They cannot be correctly answered without a real comprehension of the principles which they involve, and in very many cases, especially in the later chapters, they lead to important supplementary results." The volume closes with both author and subject indexes. Unquestionably this book is the most up to date and inspiring presentation of the subject that the writer of this notice has ever seen. H. S. U.

#### II. GEOLOGY AND MINERALOGY.

1. Some Geophysical Observations at Burrinjuck; by LEO A. COTTON. Proc. Roy. Soc. N. S. Wales, vol. xlix, pp. 448-462, 1915.—Studies of the strength of the earth's crust resulting in the contrasted doctrines of high rigidity and of isostasy have dealt largely with the validity of assumptions and the discussion of theoretical conclusions. Experimental observations have been concerned chiefly with the crushing strength of rocks under actual and hypothetical conditions. The results of geophysical research have so far been unable to answer the question raised by geologists, viz., do the adjustments of level initiate cycles of erosion and determine the locations of areas of denudation and of deposition, or do adjustments of level result from shifting of load by streams and other transporting agents?

In a problem involving a large number of unknown factors any new line of investigation is welcome, and for this reason the experiments being conducted in New South Wales assume high value. It was my good fortune to see the geologic features along a 40-mile stretch of the Murrumbidgee and to note the methods adopted for this line of investigations.

The Burrinjuck dam on the Murrumbidgee River, now nearing completion, is a rival of the Roosevelt dam of Arizona, which it resembles in form and geological setting. The dam, 240 feet high, will form a lake 41 miles long, holding 33,000,000,000 cubic feet, 1,031,250,000 tons of water, equal in weight to a mass of sand and gravel 2 miles long, 1 mile wide, 322 feet deep. If the earth's crust is sufficiently elastic or plastic to yield in response to a load of such weight and dimensions, it should be possible to record the fact with suitable instruments. Acting on the suggestion of Dr. W. G. Woolnough, three seismographs were obtained, two of the Rebeur-Ehlert type, previously used by Hecker and Schweydar in the investigation of earth tides, and one of the Zöllner suspension type designed by Hecker. Careful considera-tion was given to the selection of sites by David and Cotton, geologists; Father Pigot, seismologist; and D. F. Campbell, resident engineer. The geologic conditions were kept in mind and elaborate precautions were taken in the installation of instruments. Tunnels 60 to 80 feet long were excavated in rock and the pendulums placed in the innermost of three compartments, the second of which contains the recording apparatus. The instruments were first used to supplement geologic investigations on the normal stability of the earth's crust at Burrinjuck. The pendulums are recording four types of movements : earthtides, which will be compared with those recorded on the instrument of the International Geodetic Association at Cobar, 360 miles from the coast (Burrinjuck is 125 miles from the sea); earthquakes; fault movements; slow deflections from the vertical. This last type of movements "may be related chiefly to the water loads or may be due to other causes, but it seems almost certain that the former cause is in operation." The results of the experiments so far carried out look toward a conclusion that either elastic yielding or isostatic adjustment affects areas as small as a few square miles. Cotton raises the pertinent question as to whether the extremely contrasted views of Barrell and Hobbs on the one hand and of Hayford and Bowie on the other hand may not be reconciled on the basis of the stability of a given area prior to the removal or deposition of a load.

Further reports on the Burrinjuck experiments will be awaited with interest, and it is highly desirable that similar investigations be undertaken within the United States. H. E. G.

2. Geology of Cincinnati and Vicinity; by NEVIN M. FENNE-Geological Survey of Ohio, Fourth Series, Bulletin No. 19, MAN. 1916, 207 pp., 59 figs., 12 pls.- Educators have frequently called attention to the dearth of books and articles on geology suitable for the elementary student and general reader. In the fields of botany, zoology, and even physics are many descriptive and explanatory treatises, and even periodicals which are widely read by the non-professional public, but most publications dealing with geology need the interpretative assistance of a teacher. One reason for the scarcity of suitable books on the earth sciences is the unusual difficulty of preparing a manuscript which combines authoritative statements with simplicity of writing. In this connection the "Geology of Cincinnati and Vicinity," by N. M. Fenneman, deserves high praise. It is prepared to meet an educational demand. It is well planned and clearly written, discards controversial matter and supplements the statement of hypothesis and fact by description and illustration of local features. The book may be studied with profit as a type of a local geologic report.

H. E. G.

3. Field Geology; by F. H. LAHEE. 12mo. Pp. 508; figs. 409 in text. New York, 1916 (McGraw-Hill Book Co.).-There has long been need of a work of this nature, which could be placed in the hands of students who are taking their first practical field work in geology. The excellent little hand-book of the late Dr. C. W. Hayes is well known to professional geologists, but is of a rather technical character, written more especially to meet the demands of the U. S. Geological Survey, and less adapted to the use of beginners. The present volume gives the student those criteria which, on the one hand, will enable him to understand what he sees in the field and on the other will suggest to him the data that should be searched for to gain a solution of his problem. The scope of the work may be indicated by a mention of some of the topics treated : identification of rock features, characters of rock particles and pebbles, surface features of sediments, structures of sedimentary rocks, field interpretation of sedimentary materials, features of igneous rocks, folds, faults, metamorphic rocks, mineral deposits, topographic forms and expression, topographic maps and profiles, geologic surveying, geologic maps, diagrams and sections, geologic computations, preparation of reports, etc. The work is clearly and simply written with avoidance of details and discussions, the writer having evidently his student audience in mind.

It is published in a form and size convenient for transporting; it is well printed and very fully illustrated by half-tones, sections and diagrams. The only criticism which could be passed on its make-up, is that if a greater reduction in the reproduction of the drawings had been made, the illustrations would have been as serviceable and had a neater effect; compare figs. 49 and 281 for example.

The book is commended for examination to all teachers who have courses in field geology. L. V. P.

4. The Fundamental Principles of Petrology, translated from the German of E. WEINSCHENK by A. JOHANNSEN. 8vo. Pp. 214; 137 figs. in text, VI pls. New York, 1916 (McGraw-Hill Book Co.).—This translation of Grundzüge der Gesteinskunde has been well carried out by Professor Johannsen, and in several ways the book is an improvement on the original work. As its name implies, it is not in its nature descriptive of the different kinds of rocks, but treats of such subjects as volcanism and the origin of igneous rocks, differentiation, rock-weathering, the nature of sediments, contact metamorphism, post-volcanic processes, regional metamorphism and jointing and rock-textures. These subjects are treated in a simple and yet condensed way so that the work, as intended, is suitable for students commencing work in petrology. Regarding matters concerning which there is yet no agreement it naturally, for the most part, presents the views of the German school of geologists. Professor Weinschenk himself has worked largely in areas of regionally metamorphosed rocks, and thus in the subject of metamorphism he speaks with a certain authority and presents views of his own. The book may be usefully read by teachers and students who are not acquainted with it in the original text and in giving them this opportunity the translator has performed a commendable task. The volume is well printed and handsomely illustrated. L. V. P.

5. L'Oural du Nord ; Le Bassin des Rivières Wagran et Kakwa, par Louis DUPARC et MARGUERITE TIKANOWITCH, (Mem. Soc. de Phys. et d'Hist. Nat. de Genève, vol. xxxviii, fasc. 2, pp. 69-166. Pls. 6-7, 1914).—In continuation of the geologica land petrographical researches being carried out on the northern part of the chain of the Ural Mts., by Professor Duparc and his student assistants, the present work is an interesting addition. There is no topographic map of this region and the field work is mostly of the nature of a reconnaissance, but the exploration of the area derives importance in connection with the occurrence of platinum. Here again, as elsewhere in the Urals, occur great masses of gabbros associated with olivine and pyroxene rocks, similar types to those described in former publications by the senior author. The main part of the work is devoted to a detailed petrographic and chemical study of the rock types collected.

L. V. P. 6. Étude comparée des Gites Platinifères de la Sierra de Ronda et de l'Oural; by LOUIS DUPARC and AUGUSTIN GROSSET. Mem. Soc. Phys. et Hist. Nat. de Genève, xxxviii, 253, 1916.— Platinum has recently been found in connection with peridotite rocks that occur in the Sierra de Ronda, Province of Malaga, Spain. A petrographic study of the rocks of this locality shows, however, that the character of this occurrence is quite distinct from that of the classic locality in the Ural Mts. The conclusion is reached that the primary occurrences of platinum may be of the following three types: (1) In dunite rocks. Occurrences of this kind are the most common and richest; this type is found in the Urals Mts. (2) In pyroxenites which are composed of a monoclinic pyroxene, olivine and magnetite; this is a less common type and poorer in content of platinum. (3) In peridotites which contain both orthorhombic and monoclinic pyroxenes and commonly a brown spinel and chromite. They may be completely changed to serpentine. The occurrence in the Sierra Ronda is of this type. So few examples of this sort are known that it is impossible to make any generalizations concerning their probable richness. W. E. F.

7. Ètude Cristallographique et Optique d'un certain nombre de Minéraux des Pegmatites de Madagascar et de Mineraux de l'Oural; by RENÉ-CHARLES SABOT. A doctor's thesis presented to the University of Geneva, 1914.—This paper gives the results of the study of a number of minerals from Madagascar and the Ural Mts. Their crystals are figured and described, their optical constants and in a number of cases chemical analyses The list of Madagascar minerals is as follows: are given. from Ambatafotsikely, quartz, muscovite, monazite, columbite, euxenite, ampangabeite, strüverite, hematite, spessartite; from Ambositra, zircon; from Amampatsakana, mica; from Antsongombato, tourmaline and apatite. The following minerals from the Urals Mts. were described: from Tokowaia, brookite, topaz, spessartite, hematite, rutile, quartz; from Syssert, muscovite, tourmaline. A detailed study is also given of the amphiboles in the diorite pegmatites of the platinum districts. W. E. F.

8. The Geological History of Australian Flowering Plants; by E. C. ANDREWS, pp. 171-232, September, 1916.—ERRATA.

Page 186, line 14, for were contemplated, read are considered.

"	186,	66	21,	66	Coprisma,	read	Coprosma.
"	207,	"	12,	"	Holartic	" "	Holarctic.
"	207,	66	20,	"	Malaleuca,	"	Melaleuca.
66	207,	"	35,	"	Resticece,	"	Restiaceæ.
"	211.	66	8.	66	Leuconden	dron	read Leucodendron.

#### OBITUARY.

WILLIAM ELLIS, formerly superintendent of the magnetic and meteorological department at the Royal Observatory, Greenwich, died on December 11 in his eighty-ninth year.

CLEMENT REID, of the Geological Survey of Great Britain, well known for his work in paleobotany, died on December 10 at the age of sixty-three years.

DANIEL OLIVER, professor of botany at University College, London, from 1861 to 1888, died on December 21 in his eightyseventh year.

A. M. WORTHINGTON, professor of physics at the Naval Engineering College at Keyham from 1887 to 1909 and at the Royal Naval College at Greenwich from 1909 to 1911, died on December 5 at the age of sixty-four years.

December 5 at the age of sixty-four years. JOHN WRIGHTSON, professor of agriculture at the Royal Agricultural College, Cirencester, died on November 30 at the age of seventy-six years.

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#### [FOURTH SERIES.]

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ART. XVII.—A Method for the Determination of Dissociation Pressures of Sulphides,\* and its Application to Covellite (CuS) and Pyrite (FeS<sub>2</sub>); by E. T. Allen and ROBERT H. LOMBARD.

#### I. INTRODUCTION.

Among the sulphides there are a considerable number, if we include those of complex composition, which dissociate (lose sulphur) at accessible temperatures. In all such instances the dissociation pressure is of course an essential condition of formation of the sulphide. This fact was impressed upon us in a preliminary study<sup>+</sup> of the sulphides of iron and copper. Very little work has been done on the subject; in fact only the dissociation pressure of covellite (cupric sulphide) seems to have been studied with any approach to accuracy, though some preliminary work has been attempted with pyrite.<sup>‡</sup> In measuring the pressures of sulphur vapor, it is obvious that a mercury gauge would be out of the question. Three§ methods have been employed heretofore; a dynamic method in which is determined the quantity of sulphur volatilized in a measured

\* This work is a portion of an investigation of the copper sulphide-ores undertaken by this laboratory in co-operation with Prof. L. C. Graton and colleagues of the Harvard Mining School.

†Annual Report of the Director of the Geophysical Laboratory, 1914, p. 156.

<sup>‡</sup>Karl Schubert, Dissociation der einiger Oxyde, Karbonate, und Sulphide. Dissertation, Berlin, 1909. Schubert made use of the Victor Meyer principle. See also Hempel and Schubert, Z. für Elektrochemie, xviii, 729, 1912.

§ A method for the determination of vapor densities at high temperatures published by G. E. Gibson might be used for the solution of this problem. The method depends on the elasticity of a quartz membrane. Unfortunately the apparatus appears to be unusually difficult to construct. See G. E. Gibson, Dissertation, Breslau, 1911; also Proc. Roy. Soc. Edinburgh, xxxiii, 1, 1912.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 255.—MARCH, 1917. 13 volume of nitrogen, the gas being passed over the sulphide while the latter is held at constant temperature; a static method in which the sulphide is maintained at constant temperature while sulphur vapor at a known partial pressure in a mixture with nitrogen is passed over it, the sulphide losing or gaining in weight according as its dissociation pressure is greater or less than the sulphur vapor pressure; and finally a static method in which the sulphur vapor pressure is directly measured by the very ingenious spiral quartz-glass gauge devised by F. M. G. Johnson.\* The first two methods were used by Wasjuchnowa, + the last + by Preunner and Brockmöller.

We had prepared to use the spiral gauge in the investigation of the stability relations of the copper-iron sulphides, but the outbreak of the European war about that time prevented the importation of quartz-glass gauges, and the construction of sufficiently sensitive instruments in this country proved impossible.

#### II. New Method for Dissociation Pressures.

In this dilemma the present method was devised. It consists in balancing the dissociation pressure to be determined by a known vapor pressure of liquid sulphur. For this purpose an evacuated glass tube is required, having at each end a small bulb (fig. 1). One of these bulbs contains the sulphide, the other the liquid sulphur. Now while the sulphide is held at any desired temperature, the experimenter ascertains the temperature at which the sulphur must be heated in order that its vapor pressure may equal the dissociation pressure of the sulphide. It is obvious that the sulphur bulb must be the coolest part of the system, and that the method applies only to cases where sulphur is the only volatile product. In practice it is necessary to find by trial two temperatures for the sulphur, thus fixing two pressures, at one of which the sulphide loses sulphur, at the other remains unchanged; or gains, if the dissociation product was originally chosen for experiment. the first temperature it is evident that the vapor pressure of the sulphur is lower, at the second higher than the dissociation pressure of the sulphide. Between these two pressures lies the dissociation pressure. In an actual determination, the interval between the two sulphur temperatures is narrowed down as far as practicable, the size of the interval at any point depending naturally on the steepness of the dissociation pressure curve.

\* Z. phys. Chem. lxi, 457, 1908.
† Das Gleichgewicht Cupro-cuprisulfid. Dissertation, Berlin, 1909.
‡ Z. phys. Chem., lxxxi, 149, 1912. Preunner and Brockmöller used the spiral gauge as a zero instrument.

This method suggested itself to us during a study of the copper-iron sulphides. At that time we were unaware of the fact that Wasjuchnowa had made use of the same principle, though less conveniently applied, in a control method, the second mentioned above. She even conceived the idea of using an evacuated tube, though she never actually tried it. The method was used by her as a control only, most of her work having been done by the dynamic method.

Apparatus.—The tube used in our measurements (see fig. 1) is made of Jena combustion glass where temperatures below about 675° are to be reached; for higher temperatures quartz-



FIG. 1. Tube of glass (or quartz glass) for the determination of dissociation pressure. 1. Side view. 2. Top view.

glass is employed. The apparatus is constructed as follows: Two glass tubes, about  $1^{cm}$  in inside diameter, are first sealed to either end of a stem of proper length and about  $5^{mm}$  in inside diameter. One of the tubes is then closed and blown into a small cylindrical bulb about  $2^{cm}$  in length to hold the sulphur. To prevent the liquid sulphur from flowing out into the stem, the bend at B is made. Two glass hooks to hold the thermocouples in place are now attached at  $E_1$  and  $E_2$ . A constriction D is then made at a convenient distance from the open end of the tube after which about 0.5 g.\* of pure sulphur† is dropped into the bulb A, melted and solidified. A small glass tube which contains 0.2 g. or more of powdered sulphide is now slipped into the bulb C. In some cases small lumps about  $2^{mm}$  in diameter were substituted for the powder. D is

\* This quantity always insures a liquid phase under our working conditions.

<sup>†</sup>The sulphur we used was three times distilled *in vacuo*. Since investigations of the boiling point of sulphur have disclosed no material difference in the boiling points of different samples, and since our results make no pretension to high accuracy, the sulphur used in these experiments was not further investigated. 178



\*The pipe-covering construction used in furnace 1 was tried by us at first; but the fire clay construction of furnace 2 is preferable on account of its greater durability.

then further constricted<sup>\*</sup> to a thick-walled capillary. The open end of the tube, after being drawn down to proper size, cut off and smoothed in the flame, is attached to the vacuum pump by a piece of heavy-walled rubber tubing, and the pump is started. A little caution is required at first to prevent any sulphide powder from being sucked into the capillary. When the pressure is sufficiently reduced (to  $1^{mm}$  or less), the sulphur is again melted by the free flame and the apparatus is carefully heated throughout its whole length to remove water vapor as completely as possible. While the pump is still in action, the tube is slowly sealed off at D.

The furnaces.—The above apparatus is heated by a pair of coaxial cylindrical furnaces which are attached to carriages in a horizontal position in such a way as to slide easily on a track (figs. 2 and 3). By this means the two furnaces may be easily slipped over the glass tube and brought tightly end to end when an experiment is to be made; or quickly drawn apart when the system requires to be chilled after sufficient reaction has taken place. The most important consideration in the construction of the furnaces is the maintenance in both of them of constant temperature ranges of sufficient length so that each bulb of the glass tube (fig. 1) shall be kept at a uniform temperature throughout, and so that a slight displacement of the tube from its proper position in the furnace can not disturb this uniformity. To fulfil this important condition it was found necessary to make the furnaces of considerable length and to use three separately controlled heating coils for each furnace. In our most satisfactory installation the furnace which serves to heat the sulphide is 46<sup>cm</sup> long, while the other, used for heating the sulphur, is 68em long.

The two main heating coils are made of nichrome wire 1.3<sup>mm</sup> in diameter and having a resistance of 0.75 ohms to the meter. The coils are wound on alundum tubes about 5<sup>cm</sup> external (4<sup>cm</sup> internal) diameter, 8 turns to the inch. The longer one has a total resistance cold of about 23 ohms, the shorter about 11.5 ohms. The auxiliary coils at each end of the furnaces are made either of nichrome tape, wound spirally into a flat disk with heavy asbestos paper as the insulator, or, for higher temperatures, they are constructed of flat circular disks of alundum with a spiral groove in one side; the wire is laid in the groove and cemented in by a paste of ground alundum and water, which is then dried and baked. This device was contrived by Mr. J. B. Ferguson of this laboratory. For these auxiliary coils, wires or tapes about 7 meters in length and having a total resistance of 5 ohms were found adequate.

\* If the tube is not partially constricted before the sulphide is dropped in, oxidation is to be feared because of the hotter flame and longer time required to draw down the wider tube.

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The current in each of the six furnace coils is separately controlled by a sliding resistance. Ours possessed a resistance of about 30 ohms and a carrying capacity of 5 amperes. With this arrangement the currents could be regulated to about  $\cdot 01$ ampere. The coils were used either in 55 volt or 110 volt circuit according to the desired temperature. An important



FIG. 3. Apparatus used in the determination of the dissociation pressures of sulphides.

detail of the furnace construction, which should be mentioned, is a pair of asbestos plugs, A, B, fig. 2, which afford the necessary thermal insulation between the two furnaces. These plugs fit the alundum tubes which form the working spaces of the furnaces. They are about 2.5<sup>cm</sup> thick. Each plug is pierced in the center with a hole which admits the stem of the glass apparatus (fig. 1) easily, and each is split into halves so that it

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may be readily set in position when the tube is put into the furnace (fig. 2). Thus the constant temperature portions of the two furnaces may be kept several hundred degrees apart.

In these furnaces it is possible to maintain temperature regions of from 4<sup>cm</sup> to 12<sup>cm</sup> in length, over which the variation is not more than 0.5°. This requires frequent temperature readings throughout the entire length of the apparatus at inter-







vals of about 3<sup>cm</sup> and frequent adjustment of the currents as the temperature readings may indicate—a process frequently consuming four or five days. A curve plotted from data of this kind is given in fig. 4. Such curves were worked out at temperature intervals of about 25°. It is obviously essential that no point on these curves between the positions of bulbs A and C (see fig. 1) shall be lower than the temperature of bulb A containing the sulphur. The furnace ends must of course fit well together or a cold region will be found at the joint.

Calibration of thermocouples.—All the thermocouples used in these experiments were of platinum-rhodium, and their readings were carefully taken at the following melting points:\* tin 231.9°, cadmium 320.9°, zinc 419.4,° sodium sulphate 885°, silver 960.2°, copper 1082.8°. In some instances the reading was also taken at the melting point of antimony 630.0°.

Manipulation.—When the furnaces are ready for an experiment they are drawn apart on their carriages, the split plugs are removed and the thermocouples pushed through their porcelain jackets till the junction of each projects a few inches beyond the inner ends of the furnaces. The thermocouple in furnace 1 is then slipped over the hook E, of the glass tube and so adjusted that the thermojunction is brought close alongside of the sulphide powder. The glass tube is now supported and guided by one operator while the other draws it carefully into the furnace by means of the thermocouple, until the glass chamber enclosing the sulphide is within the region of constant temperature. The split plug B (fig. 2) is now placed in position. Furnace 2 is pushed up close to the bulb A (fig. 1) so that the second thermocouple may be attached to the hook  $E_{a}$ ; the plug A is set in place, and while the two thermocouples are held taut the two furnaces are brought carefully together so that the tube is not displaced. Although the whole operation requires but a few minutes, the temperature in the middle of each furnace naturally falls 10° or 15°, but it rises rapidly again and soon returns to its former value. After a period of several hours, during which the temperature is carefully maintained constant, the furnaces are quickly drawn apart, the plugs removed by forceps, the thermocouples detached and the tube withdrawn. This operation generally requires less than a minute, and, since the tube is very light and its heat capacity small, its cooling is very rapid.

Vapor pressures of sulphur. — We used in our experiments values for the vapor pressure of sulphur obtained by other investigators, namely, Ruff and Graf, Matthies, and Bodenstein. The determinations of Ruff and Graft which extend from 0° to 211.3° were made by the dynamic method; the sulphur was volatilized in a stream of hydrogen. Bodensteint made five determinations by observing directly the boiling point of sul-

\* The nitrogen thermometer from zinc to palladium, Arthur L. Day and Robert B. Sosman, this Journal (4), xxix, 93, 1910. † Z. anorg. Chem., lviii, 209, 1908. ‡ Z. phys. Chem., xxx, 118, 1899.

phur under measured pressures. His determinations extend from 374° to 444.8°. Some years later Matthies\* supplemented these by measurements extending from 210.2° to 379.4°, using the same method as Bodenstein. Earlier determinations by Regnault + extended to higher temperatures ( $450^{\circ}$  to  $570^{\circ}$ ), but as they are beyond the range of our experiments they are not quoted.

For the convenience of the reader the data of Ruff and Graf, Matthies, and Bodenstein are tabulated below.

			Obse	rver		
Ruff	and Gra	af	W. Ma	tthies	Ma	x Bodenstein
	t in C°	p in mm. of mercury	$t  ext{ in }  ext{C}^{\circ}$	p in mm. of mercury	$t  ext{ in } \mathrm{C}^{\circ}$	$p \text{ in mm. of } \\ mercury$
	49.7	0.00034	210.2	1.35	374.	240.
	78.3	.0023	216.7	$2.10^{+}$	393.	336.
	89.0	.0057	222.4	$3.20^{+}$	410°	443.
	99.3	.0089	230.6	4.48	427.0	580.
	104.0	·0115	234.4	5.54	444.8	764.5
, 	110.8	·0200	237.3	6.5		
	114.5	.0285	241.8	8.45		
	123.8	$\cdot 0535$	265.0	20.5		
	131.9	.081	306.5	53.5		
	132.2	.079	341.7	105.5		
	$133 \cdot 1$	.088	352.5	133.0		
	141.0	·131	363.0	176.0		¢
	147.0	$\cdot 192$	379.4	250.1		
	157.0	$\cdot 332$				
	162.0	$\cdot 403$				
	172.0	$\cdot 629$				
	189.5	1.38				
	211.3	3.14				

TABLE I.

The vapor pressures of sulphur as determined by other observers.

#### III. The Dissociation Pressure of Sulphides.

Just how widely applicable the above method is to the determination of dissociation pressures can not yet be predicted, as too little is known about the stability of the various sulphides, but we can see no impediment to its use at any temperatures where quartz glass will hold gas tight (1100° to 1200°).

<sup>\*</sup> Physik. Zeit., vii, 395, 1906.

<sup>&</sup>lt;sup>1</sup> Mem. de l'Academie, xxvi, 339, 1862.
<sup>1</sup> Matthies states that his results below 4 mm. pressure are unreliable.

We have used quartz glass in a number of measurements, and have found no special difficulty with it. Doubtless some sulphides like cuprous sulphide do not decompose appreciably within this temperature range, and some volatilize unchanged. Others like FeS<sub>2</sub>, CuS, CuFeS<sub>2</sub>, Cu<sub>5</sub>FeS<sub>4</sub>, PtS<sub>2</sub> and presumably those of many other heavy metals dissociate at considerably lower temperatures and are within the range of the method.





FIG. 5. Dissociation pressure curve of covellite (CuS).

+ + Authors' results.

 $\odot \odot$  Wasjuchnowa's results.

🕲 🧿 Preunner and Brockmoller's results.

#### 1. Dissociation of covellite (CuS).

In each particular case where the method is applied, there must of course be some means of ascertaining whether the sul-

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phide has gained or lost sulphur or has remained unchanged. This may always be determined by an analysis of the product and perhaps, with sufficient care in handling, it might be determined by weighing the sulphide before and after the experiment, though this latter method so far has not been tried. special cases the question may be settled by the change in some physical property. Thus the dissociation of covellite is most readily detected by an inspection of the color. Covellite is deep blue, while chalcocite, its dissociation product, is dark grey. Small lumps of the mineral about 2<sup>mm</sup> in diameter were found very convenient to handle and on such surfaces as they presented the colors could be easily distinguished. Such lumps of covellite are readily penetrated by sulphur vapor under these conditions, for in a number of cases the lumps were removed from the apparatus after experiment, broken open and examined with a lens, and the change was nearly always complete. A pure synthetic covellite was used in some of the experiments; in others chalcocite either natural or synthetic. The natural chalcocite, from Butte, Montana,\* showed the following composition :

	Cal. for $Cu_2S$
79.67	79.85
20.16	20.15
•14	
.08	
100.06	100.00
	79.67 20.16 .14 .09 100.06

Frequently lumps of both chalcocite and covellite were used in the same experiment but the resulting products could never be distinguished from one another except by the shape of the lumps. The results follow:

TABLE II.

Dissociation pressures of covern	ite from 4	400° to	$490^{\circ}$
----------------------------------	------------	---------	---------------

Temperature of sulphide in C°	Temperature limits of sul- phur in C°	Corresponding pres- sure limits of the sulphur in mm. of mercury	Mean dissoci- ation pressure in mm. of mercury	Estimated error in mm.
400.	183 -198	1-2	1.5	± 1.
410.	198 - 210	2 - 3.4	2.7	$\pm 0.7$
433.7	246 - 251	10-12:5	11.2	$\pm 1^{.}$
450·	280 - 284	30 - 32	31.0	± 1.
<b>46</b> 0·	306 -315	50-60	55.0	$\pm 5$ .
468.	334 - 337	90-96	93.	$\pm 3.$
$475 \cdot$	363 -365	166 - 174	170.	$\pm 4$
482	389 - 391	314 - 326	320.	$\pm 6.$
485	401 -403	386 - 399	393.	± 7.
490.	417.5-420	501-520	510.	$\pm 10^{\circ}$

\* Analyzed by Eugen Posnjak.

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These results are plotted in fig. 5. They are expressed tolerably well by the well-known equation :  $\log p = -\frac{A}{T} + B \log T + C$ . By substituting the observed values of p at 410°, 460° and 485° respectively, the following values of the constants were found : A = -96397.514, B = +356.43227, C = -1150.98605. From these values, p at the other temperatures was calculated. The calculated and observed values of p are compared in the following table :

c 1 3			TT	100
· • •	AD	TT		
л.	AD		- 1 1	

Comparison of observed and calculated values of p, the dissociation pressure of covellite

Abs. temp.	Temp. C°	p observed	p cal.	diff.
763	490.	510.	600.	-90.
758	$485 \cdot$	393.	393.	0.
755	482.	320.	306.	+14.
748	475	170.	$173 \cdot$	<u> </u>
741	468.	93.	100.	<u> </u>
733	<b>46</b> 0·	55.	55.	0.
723	<b>450</b> .	31·	27.	$+ 4 \cdot$
707	433.7	9.7	11.2	+ 1.5
683	410.	2.7	2.7	0.
673	400·	1.5	1.8	- 0.3

Though the formula serves fairly well for the purposes of interpolation it is our belief that a graphic interpolation gives more accurate results.

Results of other observers. In Table IV our results are compared with those of other observers. Wasjuchnowa's original results were not stated in terms of pressure; only the mass of sulphur, volatilized at a measured temperature in 1 liter of nitrogen under standard conditions, is given. As the results are probably not accessible to every reader we quote them below in their original form.

The partial pressure of the sulphur vapor is given by the formula



where m is the mass of sulphur volatilized in 1 liter of nitrogen at the given temperature and the pressure p, and  $\nu$  is the average number of atoms in the molecule of sulphur under the

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TABLE IV

Comparison of the results of all observers on the dissociation pressure of covellite (CuS)

	Dissociation pressures in mm. of mercury				
Temperature in C°	Results of Preunner and Brockmöller determined by the spiral quartz gauge	Results of Wasjuch- nowa determined by the dynamic method	Results by the authors' method		
393.4		0.6			
400.			1.5		
405.8		- 1.6			
410.			2.7		
421.5		5.3			
425.2		7.0			
433.7		, 0	11.2		
126.0		14.0			
400 2		91.8			
444.0		210			
4474	• • •	290	 0 1		
450.	80.	(34)	01 ~~		
460.			99		
467.3		110			
468.		,·	93		
470.	200	(145)			
$475 \cdot$	.250	(195)	170		
480.	313.	(255)			
482			320		
483.8		295			
485.			393		
490.			510		
500.	980.	(560)			
502.3		595			
0020		000			

TABLE V.

Wasjuchnowa's original results on the dissociation pressure of covellite (CuS).

	1	2	3
Temperat C°	tur des CuS T1 abs	Schwefel menge pro l l. Stickstoff g.	Dampfdruck des Schwefels über dem CuS berechnet f. S <sub>5.3</sub> , bei 444 <sup>.5</sup> °C.
393.4	666.4	0.0054	Schwefel in g pro 1 l.
405.8	678.8	0.0131	= 0.2239
421.5	694.5	0.0402	$p_{S} = 21.8^{mm}$
436.2	709.2	0.1220	^ D <sub>5'3</sub>
447.4	720.4	0.2884	
467.3	740.3	1.290	
483.8	756.8	5.274	
502.3	775.3	30.380	

\* Results in ( ) are interpolated by Preunner and Brockmöller.

same conditions. Wasjuchnowa had at her disposal only one value of  $\nu$  (at the boiling point of sulphur) and was, therefore, able to calculate only one of her results in terms of pressure. Preunner and Brockmöller\* by the aid of their data on the vapor density of sulphur calculated a part of her results (447°-502°) in terms of p by a method which they describe. In a similar way we completed the series. The results are given in Table V. Wasjuchnowa also gives one other result by a different method, † viz.

${\mathop{\rm Temperatur}\limits_{{\mathop{\rm C}}^\circ}}$	des Schwefels T. abs.	$\operatorname{Temperate}_{\mathrm{C}^{\circ}}$	ur des CuS T₁ abs.	Schwefel in g überfuhrt von 1 l. N bei 0° C und 760 <sup>mm</sup>
216.5	489.5	425.2	698.2	0.0559

If the mass of the sulphur is calculated as above in terms of p, the value  $7^{\text{mm}}$  is obtained which we give in the table. If, however, we take the vapor pressure of sulphur from Ruff & Graf's results we get, at 216.5° by a short extrapolation, 4<sup>mm</sup>. The discrepancy is unaccounted for. In the lower part of the curve our results agree surprisingly well with those of Wasjuchnowa,<sup>‡</sup> while both are much lower than those of Preunner and Brockmöller. The suspicion naturally arises that their higher results have been due to water vapor in their apparatus or in the sulphide or possibly free sulphur in the latter, but an examination of their procedure seems to set the suspicion at rest.§ It is certain that their temperatures were not very uniform; variations of 5° occurred along the dissociation chamber of their apparatus, but even this would not account for the great differences between their results and ours. Thev admit that their pressure measurements varied considerably (Die Messungen wichen erheblich voneinander ab), but they do not account for the variation. The small temperature interval within which the dissociation of cupric sulphide reverses itself in the lower part of our curve, and the care with which the temperature measurements were performed give us special confidence in that portion of it.

#### 2. Dissociation pressure of pyrite.

The mineral used in these experiments was a very pure variety of pyrite of the kind used in wireless telegraphy, which is said to come from Colorado. No impurities could be certainly detected in 1 g. though doubtful traces of silica and

\* Z. phys. Chem., lxxxi, 150, 1912. † Das Gleichgewicht Cupro-cuprisulfid, Dissertation, Berlin, 1909, p. 25. ‡ W. used for the two points obtained at 484° and 502° a different method for condensing the sulphur. § Z. phys. Chem., lxxxi, 152, 1912.
heavy metals were found. Both sulphur and iron were determined.

		Found	Cal.
	Fe =	46.71	46.56
	S =	53.29	53.44
	$SiO_2 =$	trace ?	
Heavy	metals		
of H <sub>2</sub> S	group =	trace ?	
		100.00	100.00

Pyrite does not seem so readily penetrated by sulphur vapor as covellite even at a much higher temperature. Covellite has a perfect cleavage, and lumps of it are always filled with seams while pyrite shows a smooth conchoidal fracture. For this reason, probably, pyrite dissociates much more slowly than covellite. Even after four or five hours heating the 100 mesh pyrite powder used in the experiments was only partially changed. The dissociated portion, i. e. the pyrrhotite, amounted to about one third to one-half of the original pyrite. It was of a somewhat darker tint and crystallized in mossy aggregations.

The magnetic test for pyrrhotite.—The difference in magnetic susceptibility between pyrite and pyrrhotite affords a fairly sensitive method for separating them. An ordinary horseshoe magnet however is unsuitable. We employed a strong electro-magnet for the purpose.

The glass apparatus containing the sulphide need not be opened for the preliminary magnetic test. After cooling, the bulb, C (fig. 1), is brought close to the poles of the magnet. Unless the quantity of pyrrhotite is small, some particles will show attraction very plainly. If the test is negative, it is necessary to open the bulb, remove and triturate the sulphide in an agate mortar and test it again. The magnet will now in some cases remove a little pyrrhotite. As a control on the results obtained with the magnet, a number of the products were also analyzed. The analyses were all carefully done in a platinum dish, the iron being twice precipitated with ammonian hydroxide which was prepared by saturating, with ammonia gas, water contained in a gold vessel. The following table shows the agreement between the magnetic tests and the analyses.

The percentage of iron in pure pyrite is 46.56. All the magnetic products contained more iron than this. (See Table VI.) The non-magnetic products which were analyzed gave 46.90, 46.73, 46.99, 47.39. The first three results are as close to pyrite as could be expected. The last is the only real dis-

TABLE	VI.
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Com	parison	of	magnetic	behavior	with	composition.
00111						o o and p o lor o a o and

Tom- Sure of					Analysis		
Tem- pera- ture of pyrite in C°.	pera- ture of sul- phur in C°.	sule of sul- phur in mm. of mer- cury	Magnetic behavior	Portion analyzed	Weight of sul- phide taken	Weight of Fe <sub>2</sub> O <sub>3</sub> found	Per- cent- age of iron
610	250	12	magnetic	magnetic portion	0.1043	0.0735	49.29
610	236	6	"	"	·1040	.0788	53.00
665	380	259	non- magnetic	the whole	·2030	·1361	46.90
665	378	243	magnetic	magnetic portion	•1048	·0825	55.07
680	418	505	"	the whole	$\cdot 0754$	•0514	48.43
680	418	505	66	٤٢	$\cdot 2145$	.1446	47.16
680	411	453	66	magnetic portion	·1353	·1068	55.22
680	424	554	non- magnetic	the whole	·2244	.1499	46.73
680	,421	530	66	"	·2047	.1375	46.99
595	209	3	magnetic	magnetic portion	·0792	•0557	61.94
595	228	4	non- magnetic	the whole	·1011	.0685	47.39

crepancy in the table, but even here the result involves an error of less than a milligram. For a rigorous comparison of the methods, more material should of course have been taken for analysis, but small quantities of pyrite were used in the pressure experiments because in that way a uniform temperature for the whole charge was more certainly attained.

Dissociation pressures.--The dissociation pressures established by the aid of the magnetic method are tabulated in Table VII and plotted in fig. 6.

These results are expressed by the equation:  $\log p = -\frac{A}{T} + B \log T + C$ , with about the same degree of accuracy, as are those with covellite. The values of log p at 595°, 645° and 672° were chosen for the computation of the constants. The values found were: A = +191942.61, B = -434.195075,

C = +1497.56707. A comparison of the values of p computed from the constants, with the values observed are given in Table VIII.

Tempera- ture of sulphide in C°	Tempera- ture limits of sulphur in C°	Correspond- ing pressure limits of sulphur in mm. of mercury	Mean dissociation pressure in mm. of mercury	Estimated error in mm.
680	418-421	505-530	518	$\pm 13$
672	393-395	337 - 349	343	$\pm 6$
665	378 - 380	243 - 259	251	$\pm 8$
655	363 - 364	166 - 170	168	$\pm 2$
645	$341 - 342 \cdot 7$	105-108	106.2	$\pm 1.5$
635	314-316	60-62	61.0	$\pm 1.0$
625	288 - 291	$35 - 37 \cdot 5$	36.3	$\pm 1.3$
610	250 - 255	12 - 15.0	13.5	$\pm 1.5$
595	209-228	3.0 - 4.0	3.5	$\pm 0.5$
575	167 - 183	0.5- 1.0	0.75	$\pm 0.25$

TABLE VII.

Dissociation pressures of pyrite from 575° to 680°.\*

\*The upper pressure limit was the lowest pressure actually found at which the product was entirely non-magnetic; the lower pressure limit was the highest actually found at which magnetic substance was detected.

#### TABLE VIII.

Comparison of observed and calculated values of p, the dissociation pressure of pyrite.

Abs. temp.	Temp. C°	p observed	p cal.	diff.
953	680	518	447	+ 71.0
945	672	343	343	0.0
938	665	251	264	-13.0
928	655	168	173	- 5.0
918	645	106.5	106.5	0.0
908	635	61.0	62.0	- 1.0
898	625	36•3	33.2	+ 2.8
883	610	13.5	11.7	+ 1.8
868	595	3.5	3.5	0.0
848	575	0.75	0.2	+ 0.25

In a former paper from this laboratory<sup>†</sup> it was stated that with hydrogen sulphide gas at 1 atmosphere pressure, pyrite and pyrrhotite appeared to be in equilibrium at 565°-575°. By an extrapolation of the curve of Preunner and Schupp,<sup>‡</sup> the par-

† Allen, Crenshaw and Johnston, The mineral sulphides of iron, this Journal, xxxiii, pp. 203-204, 1912.

‡Z. phys. Chem., lxviii, 161, 1909.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 255.—MARCH, 1917. 14 tial pressure of sulphur in hydrogen sulphide at this temperature was estimated to be about  $5^{mm}$ . The free hydrogen very likely has an influence on this equilibrium, for in pure sulphur vapor we now find the dissociation pressure of pyrite to be less than  $1^{mm}$  at the above temperature. In the same investigation a strong absorption of heat was found in pyrite between  $665^{\circ}$ 



FIG. 6.



and  $685^{\circ}$  which was attributed to the fact that the sulphur pressure had reached 1 atmosphere. This is confirmed by the present work. A short extrapolation of the curve plotted in fig. 6 indicates that a pressure of  $76^{\circ m}$  would be reached about  $683^{\circ}$ . One atmosphere pressure is evidently reached only at the *upper end* of this absorption interval ( $665^{\circ}-685^{\circ}$ ) rather than the lower as we then supposed.

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Heat of dissociation of covellite and pyrite.—The two cases of dissociation which we have studied are unusually complicated. Not only does the sulphur vapor change in density with change of temperature, but the solid products, pyrrhotite and covellite, vary in composition. The validity of the Van't Hoff equation:

$$\log \frac{p_2}{T_2} - \log \frac{p_1}{T_1} = \frac{Q}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

may be doubted here, but assuming that it applies, the experimental data are not sufficiently accurate for the calculation of satisfactory values of Q. An error of 1° in the temperature of the sulphur causes an error in p of 8–10<sup>mm</sup> in certain parts of the curve (450–500<sup>mm</sup>) which occasion a very large error in the calculated value of Q. Small errors in the temperature interval  $T_2 - T_1$  also cause large errors in the value of Q.

## IV. Advantages and Disadvantages of the Method.

1. The above method for the determination of dissociation pressures has the important advantage of approaching the equilibrium from both directions so that, if the temperature measurements are accurately made, the course of the curve within the limits set should be certain. It will be noted that the chilling of the glass tube as a consequence of its light weight and the method of manipulation, is very quickly accomplished. It is possible that at high pressures there might be some reversal of the reaction in this operation, but nothing of the kind has been observed in our experiments.

2. Either the sulphide or its dissociation product may be used and the presence of free sulphur would have no effect, advantages not possessed by the spiral gauge method. The influence of moisture or other foreign gases would probably be less serious than in other methods.

3. It is unnecessary to wait till the sulphur vapor has come to equilibrium with the sulphide; all that is needed is to know with certainty *the direction* in which the reaction is proceeding under given conditions. With the spiral gauge method it would of course be necessary to a correct measurement that the sulphide should be held at constant temperature until equilibrium was reached. This necessity would cause much trouble if the reaction moved very slowly, because the temperatures require constant watching. The dynamic method could not be used at all in such a case, for it depends on the assumption that the partial pressure of the sulphur in the stream of indifferent gas is *always* equal to the dissociation pressure.<sup>\*</sup> This

\* Wasjuchnowa proved that equilibrium under her working conditions was quickly established between covellite, chalcocite and sulphur vapor. advantage is quite important. The two mineral sulphides covellite and pyrite reach their equilibrium pressures very slowly under the conditions described in this paper. For example, 1 g. pyrite was crushed to a powder which passed a screen of 100 meshes to the inch. After 5-6 hours heating at a temperature of 672° and a pressure of  $320^{\text{mm}}$  of sulphur vapor, therefore very close to the dissociation pressure curve, about 10% remained unchanged while the rest contained 49.6% iron and had therefore lost only 3% sulphur. A portion of this dissociation product was heated a second time under similar conditions. Analysis showed that it now contained 57% iron. It had therefore lost 7.5% more sulphur in the second heating. Covellite also was found to move slowly to equilibrium, though not so slowly as pyrite.

4. The apparatus required is easy to construct, is not fragile, and is inexpensive.

5. The most serious disadvantage of this method is the time which it involves; it being necessary to make a number of experiments for the determination of every point on the curve. The adjustment of the furnace temperatures is also tedious, but it is difficult to see how this could be avoided in any method, for uniformity in temperature is a prime necessity in any solution of the problem.

6. The method is not adapted to the measurement of pressures of much more than an atmosphere, since the vapor pressure curve of sulphur in this region becomes so steep that a small error in temperature causes a comparatively large error in the pressure.

Other uses of the method.—In principle, of course, this method for dissociation pressures need not be confined to the sulphides; any compound which dissociates at accessible temperatures with the formation of a single volatile product which condenses at accessible temperatures could be investigated in this way. A further proviso is that glass (or quartz glass) should stand the chemical action of the vapor sufficiently well. The method also affords a convenient means for the synthesis of most\* sulphides and can be employed to advantage in certain instances where dissociation gives trouble. More important than this, the method promises to be a valuable instrument in 'the investigation of complex sulphides which can not be synthesized by simple fusion in an indifferent gas.

### Summary.

1. A new method has been devised for the determination of dissociation pressures at comparatively high temperatures in

\*Some sulphides like marcasite could probably not be made in the dry way.

cases where mercury gauges can not be used. It is intended especially for sulphides. It depends in principle upon balancing the dissociation pressure of the sulphide by the vapor pressure of sulphur at a known temperature; the pressure is not directly measured. The method applies to other compounds than sulphides provided there is a single volatile dissociation product which does not attack glass (or quartz glass) and which condenses at accessible temperatures. The method can not be used above about 1100° to 1200°.

2. By this method the dissociation pressure curves of covellite (CuS) and pyrite (FeS<sub>2</sub>) have been determined from about  $1^{mm}$  to 500<sup>mm</sup>.

3. The chief advantage of the method is that the equilibrium is approached from both directions and the experimenter is therefore not liable to be deceived by false equilibria. The method has the disadvantage of being slow and is inaccurate at pressures much above an atmosphere.

4. The method was devised as an instrument for the investigation of complex sulphide systems where the dissociation pressure is a factor in stability that can not be neglected. There seems to be no reason why it should not find a broader application to other systems of similar characteristics.

5. The method also supplies a convenient means for the synthesis of sulphides the dissociation of which causes difficulty.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., November 22, 1916.

# ART. XVIII.—Beecher's Classification of Trilobites, after Twenty Years; by PERCY E. RAYMOND.

In the February and March numbers of this Journal for 1897 appeared the two parts of Professor C. E. Beecher's short paper, on an "Outline of a Natural Classification of the Trilo-The classification there proposed, modified rather by bites." curtailment than expansion, appeared again in the Eastman edition of Zittel's Textbook of Paleontology in 1900. On this occasion, just twenty years later, it seems fitting to inquire how Beecher's work has stood the test of actual use and I wish also to present what follows as a slight tribute to the memory of my revered teacher. Beecher himself regarded this classification only as an outline, and often expressed the wish that he himself or some other person could find the time to elaborate the classification in the same manner that Professor Schuchert had elaborated his earlier outline scheme for the Brachiopoda.

Professor Beecher's untimely death just seven years after the first part of his "classification" was printed prevented his own return to the subject, and the studies and contributions of other writers on trilobites during these twenty years have dealt usually rather with single species, genera or families than with the subject as a whole. Numerous objections to the scheme proposed by Beecher have appeared, from Pompeckj, in 1898 to Swinnerton in 1915, the objections varying in strength from Wood's\* sweeping remark that "the only classification of Trilobites which can be adopted is a division into families" to Swinnerton's statement that the majority of new trilobites found since the publication of the classification "fit into it without difficulty and prove that to a large extent it is conceived on a sound basis. A few, however, do not fit in, and have therefore revealed its weakness."<sup>†</sup>

The most grave criticisms of the classification have been directed against the first of the three orders, the Hypoparia. It will be remembered that Beecher's classification was based upon observations drawn from a review of all that was known of the ontogeny of trilobites. Since the young of practically all primitive trilobites lack eyes on the dorsal side, Beecher grouped all trilobites in which absence of eyes was a primary characteristic, in his first order, Hypoparia. Recent studies and discoveries have led a number of investigators to the conclusion that blindness in the Agnostidæ, Eodiscidæ, Trinucleidæ, Raphiophoridæ and Harpedidæ is secondary and a degenerative, not primitive characteristic. If their position is well taken, then the order should disappear, and the families be distributed in the two orders which remain. A second change

> \* The Cambridge Natural History, iv, p. 244, 1909. † Geol. Magazine, Dec. 6, ii, p. 487, 1915.

which has been suggested is the removal of the Calymenidæ from the Proparia to the Opisthoparia. Not of any great importance in itself, such a change reduces an already somewhat small order to such proportions that nearly all the families of trilobites would be grouped in the Opisthoparia and we would truly have arrived at the pass which Woods has deplored. The arguments can probably be best set forth if we take up in order each family whose position in the scheme has been questioned.

#### Hypoparia.

Agnostidæ.—Beecher included in this family both Agnostus and Microdiscus (Eodiscus), but the remarks which follow exclude the Eodiscidæ. The members of this family were considered by Beecher as the most primitive of trilobites, though he recognized in them certain highly specialized and even degraded characteristics (see his paper, pp. 184–185). He stated that the free cheeks were continuous and ventral in position, and the suture marginal or ventral. He unfortunately furnished no definite proof of these statements, the truth of which has been denied by Jaekel,\* Lindström,† and Holm, and questioned by Swinnerton.‡

In his article Beecher states: "In Agnostus this feature (the suture) has escaped notice. The examination of extensive series of Agnostus in the National Museum and in the Museum of Comparative Zoölogy has proved that under favorable conditions of preservation this genus shows a distinct plate, separated from the cranidium by a suture, and it can be compared only with the free cheeks of other trilobites." Beecher neither mentioned the species in which he saw this plate, nor did he ever figure it.§ Acting on the above hint, however, I

‡Geol. Mag., Dec. 6, vol. ii, p. 490, 1915.

SAgnostidæ.—In regard to the presence of free cheeks in the Agnostidæ as seen by Beecher, the reason why he "furnished no definite proof of these statements" is as follows: Before he had printed his classification of the Trilobita he and I had gone over the material in the United States National Museum and I distinctly remember that he was especially desirous of seeing Hypoparia. Dr. Walcott had turned over to that museum much material that he had gathered under auspices of the United States Geological Survey and there was considerable material of the genus Agnostus. All of this material Beecher looked over, and among the American species of Agnostus preserved in shales there was one that seemed to show the presence of free cheeks. The evidence at first was not conclusive and he then went over the material again and finally succeeded in finding a free cheek in the form of an imprint lying alone among the heads and tails of Agnostus. The species is now unknown to me. This he showed to me and we agreed that it was actually a free cheek of a species of this genus. In width the free cheek was linear, almost no thicker than a human hair and without a trace of an eyespot or ornamentation. The reason why he did not figure the specimen was because the Cambrian trilobites were reserved for further study by Walcott, and it was expected that in the course of time the latter would come upon this specimen and figure it in his prospective monograph of Cambrian trilobites.-Charles Schuchert.

<sup>\*</sup>Zeitschr. Deutsch. Geol. Ges., vol. lxi, p. 387, 1909.

<sup>†</sup> Kongl. Svenska Vet. Akad. Handl., xxxiv, No. 8, p. 10, 1901.

have gone over the specimens in the Museum of Comparative Zoölogy, and I find that the facial suture and free cheeks are very well shown on many specimens of Agnostus nudus, can be plainly seen on a few specimens of A. integer\* and A. bibullatus, and rather imperfectly made out on a number of A. rex. Curiously enough, these free cheeks and sutures occur

FIG. 1.



Fig. 1. Agnostus nudus (Beyrich). Figure after Barrande, with the sutures and ventral plate added from a specimen in the Museum of Comparative Zoölogy. Enlarged.

on that portion of the animal which Angelin, Barrande, Jaekel and others have designated the pygidium, a fact which may have caused some investigators to overlook them. The specimens in which these features can be seen are all casts in a very fine-grained shale and are, of course, all from Bohemia. I think the structures can be seen by anyone who has access to a large collection of these species, the only preparation necessary being the flaking off with a fine needle of the cast of the doublure around the margin of the cephalon. Full grown specimens of Aquostus nuclus are of fair size, and so permit this development. Other species would probably show the features as well under favorable conditions of preservation, but I have looked through our extensive set of Swedish and American specimens without finding any examples showing the sutures. Aquostus nudus has

one shield evenly convex, and the other with a depressed brim. All authors seem to have considered the evenly convex shield the cephalon, because of the way in which the segments overlap one another. The facial sutures are not marginal, but intra-marginal. They meet in an obtuse angle at the front, and run backward just inside the margin, reminding one much of the course of the pre-ocular portion of the suture in an Homalonotus. The sutures keep within the angles, so that the fixed cheeks bear the genal angles, a Proparian characteristic. The sutures in this manner cut off a yoke-shaped area, bounded outside by the facial sutures and inside by a natural edge which follows the outline of the base of the elevated portion of the cranidium (the glabella). Both limbs of the yoke taper backward to a point, and it forms a continuous plate, with no vertical or epistomal sutures. The plate has the position and aspect of a large epistomal plate, but whether called an epistoma or free cheeks, the sutures which separate it from the cranidium must

\* It is shown in one of Barrande's figures of this species, on what he believed to be the pygidium. System Silur. Bohême, I, pl. 49, fig. 5b.

on the Beecher hypothesis be interpreted as the facial sutures. Each suture shows a slight outward bend near the anterior end, suggesting the presence of a small eye, but I am not prepared on present evidence to say that eyes were present on the ventral side. Jaekel's\* argument that because these trilobites had the power of closing the pygidium against the cephalon, they could not have eyes or facial sutures on the ventral side seems to be absolutely without point.

Swinnerton also cites in favor of his view that the Agnostidæ are degenerate Proparia with fused fixed and free cheeks and obliterated eyes, the fact that Walcott has placed his genus *Mollisonia*<sup>+</sup> "near the Agnostidæ" (really Eodiscidæ) and in describing it refers to indications of eyes and facial sutures on the dorsal side. I have only the published figures of *Mollisonia* by which to judge of its characteristics, but they seem to justify the rather incomplete descriptions which have been published, and I do not see that any importance can be attached to them in connection with the Agnostidæ. Indeed, it remains to be definitely shown that they are trilobites. The condition of preservation of the specimens indicates a test unlike that of the associated trilobites.

Summarizing what has been said about the Agnostidæ, it may be stated that interpreting trilobites in the generally accepted way these trilobites do possess facial sutures, that the sutures and free cheeks are ventral in position, and the position of the free cheeks is such that these trilobites, had they been of progressive stock, would have given rise to Proparian descendents. Since the free cheeks are not visible from the dorsal side they can not be placed in the Proparia, and Beecher's order Hypoparia is justified, even if this family only is to be included in it.

*Eodiscidæ.*— The discovery by Walcott of two species of Eodiscids with free cheeks and eyes seems to me a remarkable confirmation of the correctness of the position to which Beecher referred this family. *Pagetia*<sup>‡</sup> is an undoubted Eodiscid and has eyes very far from the glabella, i. e., near the margin, and the facial sutures are short and have a typical Proparian course. Now this is exactly what one would expect in the case of a trilobite in which the eyes had just migrated over the lateral margins and is in entire harmony with all Beecher's ideas. If *Pagetia* were the oldest known genus of the Eodiscidæ, one might argue with some plausibility that the other eodiscids were degenerate from such a state of development. The opposite is, however, true. The great development of the Eodisci-

\* Op. cit., p. 388.

†Smithsonian Misel. Coll., vol. lvii, p. 195, pl. 24, fig. 3, 1912.

‡ Ibid., vol. lxiv, No. 5, p. 408, pl. 67, 1916.

dæ was in the Lower Cambrian, and the specimens bearing the eyes are from the Middle Cambrian. Not only that, but these species are highly specialized eodiscids, as is shown by the reduction to two thoracic segments, the practical obliteration of furrows on the pleural lobes of the pygidium, and the great axial spines, especially in *Pagetia bootes*.

The discovery of a genus with two species which bear eyes very close to the lateral margins seems to be a confirmation of the previous supposition that the Eodiscidæ have ventral free cheeks. Since the great majority, including the most primitive of the genera and species of this family, do not show free cheeks on the dorsal surface and so come within the limits of the Hypoparia as defined by Beecher, it seems to me that the family should remain in that order. Like the Agnostidæ, the Eodiscidæ appear to have Proparian tendencies.

Shumardidæ.—These little trilobites are still too much of a puzzle to be discussed at any length, and the ultimate disposition of the family has no particular bearing upon the question at hand.

Harpedidæ.—Of this family I have no personal knowledge, but as its principal characteristics are even more primitive than those of the Trinucleidæ and as the organization of its cephalon is so closely parallel to that of the latter group, I do not yet see any particular reason to remove the family from the position in which Beecher placed it.

I have the paper by Richter mentioned by Swinnerton, and though I have the greatest respect for the work of Dr. and Frau Richter, still Middle Devonian species of Harpes can not be considered as exactly the ones to study in getting at the primitive characteristics of this group. There seems no *à priori* reason why simple or aggregate eyes should not develop on trilobites absolutely independently of the compound eye, and the presence of such eyes in a Silurian or Devonian trilobite whose ancestors were more nearly blind does not seem any proof at all that they are remnants of fully developed compound eyes.

Trinucleidæ.—It is in connection with this family that the principal objection against the order Hypoparia has been raised. The present opinion of a number of paleontologists, best summarized by Swinnerton, is that the Trinucleidæ are degenerate descendents of trilobites with eyes, that the free and fixed cheeks are coalesced with the obliteration of the suture, and that the ocelli on the cheeks represent the degenerate remains of compound eyes. These paleontologists believe that the facial suture of McCoy is the real facial suture and either deny the presence or question the morphology of the facial suture of Barrande. This idea is of course not new, but has been given especial impetus of late years by the reference by Lake of *Orometopus*<sup>\*</sup> to the Trinucleidæ. (Using Trinucleidæ in a broad sense, as including the Raphiophoridæ.)

The question of the facial suture may be taken up first. Reed is the latest writer on the Trinucleidæ, and his excellent series<sup>+</sup> of papers have added much that was new about the family. Dr. Reed seems, however, to have changed his mind about the sutures several times in the course of preparation of the papers, a thing for which anyone who has studied this puzzling family can readily forgive him. On page 170 of the concluding article he states :- "No satisfactory evidence of such sutures [across the cheeks and apart from the marginal suture round the fringe] in young or adult has been produced, and Mc-Coy's figures and description of their presence in his genus Tretaspis are not supported by the specimens which he used." Yet on the final page he concludes that the fixed and free cheeks are fused and the eyes degenerate. He does not anywhere deny the reality of the marginal suture, but offers two possible explanations of it, the second of which he adopts. Firstly, the ventral plate may represent a second underturned segment of the ancestral annelid, or secondly, the marginal suture may represent a secondary facial suture to assist in moulting and compensate for the one lost by fusion.

The first of these suppositions can not in our present state of ignorance of the ancestor of the trilobites be profitably discussed. It may be remarked however, that if Bernard was right in considering the oculiferous segment of the ancestral annelid to have been the first, then another ancestor for *Trinucleus* than for the remainder of the trilobites would be called for. The second point, however, needs further consideration.

If, as Reed claims, the marginal suture is secondary after complete fusion of the primary sutures, then this splitting must have taken place after the animal had become fully adapted to that mode of life which led to the obliteration of the true sutures. In other words, the fringe must have been fully developed before the splitting took place. Now whatever the primary functions of the perforations of the fringe, the numerous invaginations certainly greatly strengthen the brim and reduce rather than enhance the chances that it would split. Moreover, if the whole fringe were merely the doublure of the free cheeks, as would be necessary in his interpretation, why is the pattern of the lower side unlike the upper? The fact that the patterns are unlike certainly argues for the independent origin of the lower plate. Among Opisthoparian

\*British Cambrian Trilobites, Palaeontogr. Soc., vol. lxi, p. 46, pl. 4, figs. 6-10, 1907.

† Geol. Mag. Dec. 5, vol. ix, pp. 346 and 385, 1912; Dec. 6, vol. i. p. 349, 1914; Dec. 6, vol. iii, pp. 118 and 169, 1916.

trilobites there are two types of head structure : one in which the facial sutures are confluent around the frontal margin, and the free cheeks do not meet but are separated by an epistoma; another in which the free cheeks meet in a vertical suture and an epistoma is apparently absent. Now the first condition is very much more common than the second, and where the second condition is best shown, in the Asaphidæ, there is considerable evidence that proves that the epistoma is present, but that the epistomal sutures are obliterated and that the vertical suture is secondary. If, then, Trinucleus is a degenerate Opisthoparian, the plate in front of the hypostoma must be the epistoma, and the chances are that the part of the marginal suture directly at the front is a part of the true facial suture. If that be the case then the facial suture is not entirely obliterated, and we ought in the thousands and thousands of specimens which have been examined, to find at least one or two which show traces of the remainder of the facial suture or of the epistomal sutures. In no case among the Opisthoparian or Proparian trilobites where the cheeks are fused have the sutures become entirely obliterated.

It is probably permissible to say, without being accused of sectional pride, that the North American specimens of "Trinucleus" are more numerous and better preserved than those of any other region. We do not find the abundant entire specimens such as occur in Bohemia, but in our specimens the test is well preserved and the specimens are not flattened. And anyone who collects in our rocks readily becomes convinced that the ventral plate of "*Trinucleus*" is readily separable from the cranidium. One of these plates, naturally separated, when viewed from the inside, shows the first two rows of "hour-glass structures" broken across at the constriction, but the posterior rows of pits were not deep enough to connect across, so that they show from the inside as hemisphæric mounds. The angles of this ventral plate carry the genal spines, and where the cranidium is found without the ventral plate, the angles are smoothly rounded, showing that the suture becomes dorsal in position at least at those points. The fact that this ventral plate is entirely separable along well-defined sutures, and that it bears the genal spines, seems rather conclusive evidence that it is a primarily independent plate, and that the suture is not secondary. Reed has suggested a comparison with Limulus, but in that genus the crack extends only around the front and sides of the cephalothorax, does not extend to the angles, and does not cut off a separate plate. If the marginal suture in the Trinucleidæ were a similar makeshift cracking, there seems no reason why it should not be similarly incomplete. The marginal suture of Trinucleus

seems homologous with the ventral suture of Agnostus, and that, not being at an edge, can not well be explained as a secondary splitting.

There remains to be discussed the question of Orometopus. Why should it be included in the Trinucleidæ? It is so unlike any of the Trinucleids that the burden of proof that it belongs to that family should be upon those who have placed it there, but its present placing has been accepted with such avidity that it is necessary to make some comments. Lake says of Orometopus\*:—" The clavate glabella, the horizontal grooved pleuræ, and the broad triangular tail, are characters which it shares with those genera [Trinucleus and Ampyx], and which differentiate it from other families."

The characteristics which ally Orometopus with the Trinucleidæ and Raphiophoridæ are all to be found in the thorax and pygidium, and the result of the experience of all students of trilobites has been to learn that the thorax and pygidium seldom show characteristics of family rank. Within the same family the thorax and pygidium are often highly variable, and the thoraces and pygidia of some species in totally unrelated families are quite similar. The broadly rounded form, flat segments and wide short pygidium of Orometopus make it look like a trinucleid or ampycid, but those families share with Harpes and many of the Olenidæ the form of the thoracic segments, and the pygidium is olenid in outline.

Orometopus differs from the Trinucleidæ in the possession of compound eyes and large free cheeks on the dorsal side, in lacking a specialized glabella which enlarges forward, in possessing more than 6 thoracic segments, and especially in the form of the hypostoma, which is nearly square in Orometopus with a straight posterior border and nearly circular with a median tongue-shaped posterior projection in "Trinucleus." The similarities consist merely in the form of the thoracic segments and pygidium, and are of too little importance to outweigh the evidence of the other characteristics of the animals.

Orometopus can, I think, be quite definitely eliminated as a possible ancestor of the Trinucleidæ. From Barrande's work many stages in the development of "Trinucleus" are known. Although the protaspis has not been seen, specimens without thoracic segments and only  $1^{mm}$  long have been figured. The striking thing about the young "Trinucleus" is that the pygidium is nearly or quite as large as the cephalon. This is very unusual in the young of trilobites, and if we can trust the young as pointing toward the ancestral line, some isopygous group like the Agnostidæ or Eodiscidæ is indicated, rather

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than such a form as Orometopus. In fact, the row of pustules on the border of some species of Eodiscus foreshadows to some extent the Trinucleid fringe. The ontogeny of such a species as Cryptolithus ornatus (Sternberg) shows that in the youngest stages now known the cephalon of Cryptolithus has a narrow brim without pits, that at the same time as the development of the first thoracic segment a single row of pits is present, and with increasing growth the brim widens with successive rows of pits. It is interesting to note that the cephalon of the oldest of the Trinucleids, Trinucleus reussi Barrande, shows in the adult a form corresponding to the second stage in the development of Cryptolithus ornatus, having but a single well developed row of pits on its narrow brim, and showing the same large side lobes on the glabella. This form I propose to make the type of a separate genus, Trinucleoides.

To summarize for the Trinucleidæ then, it may be said : firstly, that there is no positive evidence that the free and fixed cheeks are fused, Reed having definitely shown that the suture of McCoy is not a facial suture.

Secondly, the ventral plate is an easily separable and independent plate, bounded by sutures which on Beecher's conception of the morphology of the head would be the facial sutures.

Thirdly, *Orometopus* does not in itself present any very strong evidence that it is the ancestor of the Trinucleidæ.

Fourthly, the ontogeny of the Trinucleids points to an isopygous ancestor with ventral free cheeks, of the same type as Eodiscidæ or Agnostidæ.

Until some stronger evidence of the degeneracy of the Trinucleids from an Opisthoparian ancestor is adduced, I think the family may safely be left in the Hypoparia.

Raphiophoridæ.—Professor Swinnerton is entirely correct when he states that the Raphiophoridæ "are presumably placed in the Hypoparia because of their evident relationship to the Trinucleidæ." It is no part of the function of a "natural" classification to force apart evidently related families merely to be consistent with the definitions. The more natural a classification is, the more impossible it is to frame definitions which are rigid. The word "generally" must be freely used or understood. That the highest families of one order should parallel the lowest of a more advanced order is to be expected, and may be construed as furnishing a proof of the success of a classification, rather than as militating against it.

The Raphiophoridæ furnish one point of considerable interest in connection with this discussion. It is generally accepted that the epistoma and the free cheeks are parts of the same segment, but it is possible to think of them as belonging to different segments, in which case the ventral plate of the Agnostidæ and Trinucleidæ might be thought of as simply an epistoma and not as undifferentiated free cheeks and epistoma. Free specimens of *Lonchodomas portlocki* (Barrande) show on the ventral side of the head a yoke-shaped plate like that of *Agnostus nudus*, but instead of being confined to the ventral side, it laps over the margins up onto the dorsal side, being separated from the cranidium by a suture which has the course of the ordinary facial suture. The absence of eyes makes the analogy with the ventral plate of Agnostus the more complete, and there can be no doubt that in this case the ventral plate has encroached upon the dorsal side, and there can also be no doubt that the plate represents the undifferentiated free cheeks and epistoma.



FIG. 2. Lonchodomas portlocki (Barrande). Figure, somewhat restored, of an enrolled specimen in the Museum of Comparative Zoology to show the continuous ventral plate of the cephalon. Enlarged.

All the families of the Hypoparia have now been reviewed and it hardly seems that there is strong evidence at the present time for removing any of the families from that order. Within the order there seems to be a tendency in two directions, in the Agnostidæ and Eodiscidæ toward the Proparia, and in the Trinucleidæ and Raphiophoridæ toward the Opisthoparia. That the Eodiscidæ should in the Middle Cambrian have produced a true Proparian, Pagetia, and that on the other hand the Opisthoparian Trinucleids should apparently hark back to another branch of the same stock, shows that we can not dispense with the order and relegate its families to the Opisthoparia and Proparia. The attempt to show that the Agnostidæ, Trinucleidæ and Harpedidæ are degenerate Proparia and Opisthoparia seems to fall from lack of evidence, while the evidence for their primitive position seems to increase with new discoveries.

### Opisthoparia.

Mesonacidæ.—The suggestions of Swinnerton in regard to this family and his proposed order Protoparia are certainly exceedingly interesting and attractive, and offer the only logical explanation so far put forward for the condition seen in the Mesonacidæ. Unfortunately, to accept Swinnerton's explanation involves a belief in the polyphyletic origin of the trilobites, which hardly seems probable, in view of the compactness of the group.

There can be no doubt, in spite of statements to the contrary, that a fair proportion of specimens of Mesonacids show distinct traces of facial sutures, particularly of the part behind the eyes. This posterior portion of the sutures is well shown in Walcott's<sup>\*</sup> figures of *Elliptocephala asaphoides* (pl. 24), *Mesonacis vermontana* (pl. 26), *Callavia bröggeri* (pl. 27), and *Callavia callavei* (pl. 42,—this shows anterior portion of sutures also). The fact that specimens often show the facial suture on one half of the cephalon and not on the other, and that the anterior portion may show on a specimen which shows no trace of the posterior portion, would seem to indicate that these sutures are vestigial and not rudimentary and in a state of symphysis and not synthesis (see Swinnerton, p. 492).

When Swinnerton states that the young Mesonacids do not show facial sutures, and that in the youngest known specimens the eyes are fully developed and on the dorsal surface, he is correct, for there is here an anomaly among trilobites. While the eyes come in at the margin and move (relatively) backward through the growth of the free cheeks during development there is no suggestion that they were ever ventral or came The facial sutures are much more in eviover the margin. dence in the adult than in the young. If the Mesonacids could be considered as highly specialized trilobites occupying a terminal position in their particular line of development, we might explain this as a case of "earlier inheritance," but all the evidence of the thorax and pygidium seems to point to the primitive state of development in the Mesonacidæ. + From a study of the young stages in the development of Elliptocephala and other genera of the family it is possible to develop a theory of

\*Smithsonian Misel. Coll., vol. liii, No. 6, 1910.

<sup>†</sup>The supposed possession by *Olenellus* of a telson in place of a pygidium has been used as an argument that the Mesonacidæ are specialized trilobites. Personally, I do not believe that the spine seen at the termination of *Olenellus* is a pygidium, or takes the place of the pygidium, but that this spine is the normal spine seen on the 15th segment of all species of Mesonacis and Paedeumias. In other words Paedeumias seems to me to be a complete specimen of Olenellus. This belief is of long standing, as may be seen by my wording of the definition of Olenellus in the '' Eastman-Zittel " textbook, and has just received an interesting confirmation in the discovery by Walcott that *Olenellus gilberti* is a *Mesonacis* (Smithsonian Miscl. Coll., vol. iv, p. 406, pl. 45, fig. 3). the secondary origin of the free cheeks on a plan quite different from that set forth by Professor Beecher.

The study of the young specimens of Mesonacids figured by Ford,\* Beecher, and Walcott indicates that the cephalon of these trilobites is made up of six similar segments each consisting of an axial and pair of pleural portions. The axial portions are ranged one behind the other in a straight line, while the pleuræ are bent abruptly backward so that the anterior ones closely envelop and crowd those behind. The effect of this crowding has been to eliminate the greater part of the pleuræ of the last segments, though these three segments combined produced one pair of spines which project beyond the posterior border. The first two segments of the cephalon are more or less coalesced, and their pleuræ also unite to produce

#### FIG. 3.



FIG. 3. Elliptocephala asaphoides Emmons. A very young specimen, representing one of the earliest stages known in the development of a Mesonacid. After Walcott. Much enlarged.

a pair of free spines. In the smallest specimens known these spines are very close together (Walcott, loc. cit. pl. 25, figs. 1, 2) or may even be coalesced (pl. 25, fig. 22). On further growth, there is a spreading out along the posterior margin, as is shown by the fact that the spines move outward. The spines of the first two segments separate, so that the spines of the first segment move to the genal angles, or in some cases, even around to the front of the cephalon (Walcott, loc. cit. pl. 36, fig. 14; pl. 7, figs. 9-11); the spines of the second segment move outward to form the intergenal spines, or where the 3 pairs of spines remain, the genal spines; and the inner spines of the young are either suppressed or, in exceptional cases, become intergenal spines. If then, we think of the dorsal surface of the head of these trilobites as consisting of 6 united segments, the first act in forming the head was the sharp bending back of all the pleuræ to form an oval head

\*This Journal (3), vol. xiii, p. 265, 1877; vol. xv, p. 129, 1878; vol. xxii, p. 250, 1831.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 255.—MARCH, 1917. 15 shield, and then by secondary growth of interstitial tissue at the back, the pleuræ were again forced around into nearly their original position, but as the pleuræ of the third, fourth, and fifth segments had been largely obliterated in the turning backward, the new cheeks were composed principally of the pleuræ of the first and second segments. Unless one believes with Lindström that the Mesonacidæ were blind, it follows that even in these young forms the inner edges of the pleuræ of the first (dorsal) segment carried the visual surface of the eye, and the pleuræ of the second segment formed the palpebral lobes.

In order to facilitate moulting there should have been some sort of a suture in the Mesonacidæ, and seemingly there was a ventral suture, at least in the young, very similar to the suture in the Agnostidæ. Walcott has figured several specimens in which the hypostoma is attached to a narrow "doublure", and one remarkable specimen from Pennsylvania in which the hypostoma attached to a narrow "doublure" has swung back so that it presents its ventral face to the observer on the same block with and still attached to the head shield. This doublure is analogous to the ventral plate of Agnostus, and that the suture along which it separated was not marginal is shown by the fact that the plate is attached at the intergenal and not at the genal spines. If this plate is not accidentally separated, then it is an epistoma, and constitutes the seventh and anterior segment which made up the head of the trilobite, the hypostoma being its appendage.

It would be easy to conceive that, to facilitate the removal of the covering of the eye in moulting, dorsal facial sutures should be secondarily developed. Beginning at the front of the eye and running back to the posterior margin of the head, there was a natural line of weakness, because it was the line of division between the original first and second segments of the dorsal side. And it is known that the posterior portion of the suture does follow this line, as, when present, it comes out at the intergenal spine. Forward from the front of the eye, the course of the facial suture had no natural line to follow, but in most cases seems to be guided by the outline of the hypostoma, hence the outward curve. Following this line of reasoning it would follow that the lines which are seen on the heads of Mesonacids are rudimentary sutures, and that Swinnerton was right in regarding the ancestral trilobite as being without free cheeks. And, further, it is conceivable that in the process of evolution, the free cheeks crowded upon the epistoma so as to greatly reduce its size, or even force it out entirely.

In this way of thinking of the trilobite head, the anterior segment was not oculiferous, the eyes would never have been ventral in position, and there is no reason why in development they should travel backward. This seems the greatest argument against Swinnerton's view, for in practically all trilobites except the Mesonacidæ, the eyes appear first at the margin and do travel backward. Beecher's theory seems to explain all trilobites except the Mesonacidæ, while Professor Swinnerton's applies to the Mesonacidæ principally, and unless it can be shown that the Trilobita are polyphyletic, it seems better to adhere to Beecher's idea, and await an explanation of the Mesonacidæ which is in accordance with our notions of other trilobites.\*

As a matter of fact, if Swinnerton's suggestion of the Protoparia were logically carried out, it would affect the present classification but slightly. He would probably remove the Raphiophoridæ to the Opisthoparia, but the remaining Hypoparia would become Protoparia and the Mesonacidæ would replace the Raphiophoridæ as the highest of the Protoparia. It is not at all a consequence of his definition of the Protoparia that the Agnostidæ and Trinucleidæ should be considered degenerate animals, On the contrary, as they possess a large ventral plate (epistoma) and no visible free cheeks, the traces of eyes which they possess may well be considered rudimentary instead of vestigial, and when, as in Pagetia among the Eodiscidæ, eyes become fully developed, facial sutures and free cheeks are formed. At first sight, this method of the formation of the free cheeks would seem to apply only to the Opisthoparia, but in the secondary forward movement of the pleural portions of the head, as evidenced by the forward migration of the spines, is seen a modus by which the posterior portion of the facial suture may be brought to terminate in front of the genal angle, and so produce the Proparia.

I have thus developed Swinnerton's scheme at greater length than did its proposer in order to show how attractive it is, and how well it explains conditions which obtain in the Mesonacidæ, and at the same time, how little change its adoption would make in our present classification. Little is known of the morphology of the head of the trilobite, and it is entirely possible that the free cheeks may be a part of the epistomal segment in one group of them, and a part of the first dorsal segment in others. The problem is well worth keeping in mind in future investigations. Until more is known, however, it seems as though the Mesonacidæ were in as secure a place

\* Beecher pointed out that the actual protaspis of *Elliptocephala* is not yet known, and when discovered it may prove to be eyeless, and in conformity with other young of Cambrian trilobites.

† See in this connection Dr. Clarke's figures of *Proboloides cuspidatus* from the Devonian at Ponta Grossa, Brazil. Monographias do Serviço Geologico e Mineralogico do Brazil, 1, 1913, pl. 7. near the base of the Opisthoparian pyramid as high in the Hypoparia (Protoparia).

#### Proparia.

Calymenida.—When I was preparing the revision of the families of trilobites for the second edition of the "Eastman-Zittel" Textbook I was at first inclined to follow the suggestion of Pompeckj\* and others and place this family near the Olenidæ in the Opisthoparia, but after considerable study of the evidence for and against, left the family where Beecher placed it. I remember, as a student, asking Beecher why this family was placed in the Proparia rather than in the Opisthoparia. He replied that while as a group, the post-ocular portions of the facial sutures cut the genal angles, in Pharostoma, one of the geologically older and presumably primitive genera, (also so considered by Pompeckj) the genal spines were borne by the fixed cheeks and the free cheeks were decidedly Proparian. This seems a proper reason, and if this Proparian family can be derived from an Olenid stock, so much the better for our general knowledge of trilobites. In addition to the statement in regard to the condition of the cheeks in *Pharostoma*, it may be mentioned that the cheeks in the earlier stages of the development of the common *Calymene senaria* of the American Trenton are also distinctly Proparian, so that the parallelism of the adult with *Triarthrus* in this matter is a secondary affair.

With this I shall close my remarks on the objections which have been raised to the Beecher classification. I think that Professor Swinnerton has sufficiently shown the very inadequate basis of Gürich's classification, and the same remarks with which an eminent investigator has dismissed Professor Jaekel's suggested classification of the reptiles may be applied to the result of his endeavors in behalf of the trilobites. To discuss at the present time Professor Swinnerton's proposed sub-orders and families would not be appropriate. The samples which Dr. Walcott has recently been giving us of his wonderful store of Cambrian trilobites indicate clearly the futility of proceeding to the refinements of classification until that fauna is quite fully described.

Museum of Comparative Zoölogy, Harvard University, Cambridge, Mass.

\* Ueber Calymmene Brongniart, Neues Jahrb., vol. i, 1898, p. 187.

## ART. XIX.—Origin of Formkohle; by JOHN J. STEVENSON.

A PECULIAR type of brown coal, called Form-, Fein-, Klaror Rieselkohle, occurs in parts of Sachsen, Brandenburg, as well as in the Cologne region, and similar coal is found in It is an incoherent brown coal, apparently without Texas. cementing material; it may constitute the whole of a bed at one locality, while elsewhere in the same bed only Knabben- or Knorpelkohle, lump coal, is found; or it may be confined to a single bench, even to a portion of a bench. Usually it is converted into briquets for fuel, but in Sachsen it is associated with pyropissite, which is utilized in the paraffin industry. This type of brown coal has acquired new interest to geologists because of recent discussions respecting its origin and mode of accumulation. Potonié\* has asserted that it is secondarilyallochthonous in origin, signifying by that term that it must be regarded as an autochthonous coal, removed from its original place of accumulation and redeposited. The transporting agent was running water and the process of redeposition was affected by selective influence of gravity.

Potonié remarks that autochthonous and primarily-allochthonous coals are hard and homogeneous; if they have numerous cracks, they be Rieselkohle, but in that case the fragments fit together as in a mosaic and the clefts are commonly filled with inorganic material, such as calcite. The coal had been Knabbenkohle; he had seen such coal in the Oligocene of Sachsen. The condition is wholly different in coal of secondarily-allochthonous origin, as is seen in the Emma mine, near Streckau in Sachsen. There the individual pieces are less closely united and the larger ones are embedded in fine material, so that, when struck by a pick, the mass falls into a dustlike or crumblike heap. Pebbles of coal are rare in such deposits, because the brittle coal would break into angular fragments during transport. This is proved by the constant occurrence of crumb or dust coal. The farther the coal was transported, by so much finer would be the particles; thus one finds at times, as at the Voss stripping near Deuben, very fine coal throughout, evidently dustlike when deposited. In this connection, Potonié remarks that this specific structure would disappear with increasing age of the coal, as advancing selfdecomposition would induce homogeneity.

To determine whether or not a coal is secondarily-allochthonous in origin, one must have an unweathered pile for study, since weathered autochthonous is very similar to the other.

\*H. Potonié, "Die Entstehung der Steinkohle," 5te Aufl. 1910, pp. 137-142, 205-211. Drifted fuel materials necessarily take up mineral substances, which accompany them in the water, and this inorganic matter may be in excess. He has instances from the lower Rhine region, where clay beds intervene in secondarily-allochthonous coal and contain scattered fragments of coal. Similar scattered bits of coal occur in rocks between beds of brown coal in southern Sachsen and in Anhalt, as well as in the underclay at the Emma mine.

Drying-cracks indicate secondarily-allochthonous origin, since autochthonous coals must be compared with moors, which develop under constant cover of water. If a dry period come to these, the humus masses sink together in consequence of their water content, so that extreme drying would be needed to produce the shrinkage cracks. It is very different with unstratified humus, transported by high water and therefore easily carried to areas with only a slight cover of water. So, he knows of drying-cracks, up to this time, only in secondarilyallochthonous coals. It must be recognized also that certain features, which elsewhere indicate autochthonous origin, may occur also in secondarily-allochthonous coals. In study of a particular area, one must not forget that a deposit of transported material, organic or inorganic, can produce in times of quiet an autochthonous vegetation-trees, reed-banks and the rest—and that this in turn may be covered by an allochthonous fuel-material. In illustration, be cites conditions observed by Zimmermann, who stated that in the Culm near Landeshut, between the many meters thick layers of cemented gravel and conglomerate (allochthonous) there occur thinly-layered clay beds (allochthonous) with Stigmaria spreading in all directions, therefore the foundation of a coal bed and autochthonous. Zimmermann saw this condition repeated thrice in a single quarry-but the coal beds there are few and thin. Potonié adds that this is a familiar occurrence in all productive coal areas. Erect trees and reed-beds are not always evidence that the coal is autochthonous. The belief that the secondarilyallochthonous coal of Cöln must be autochthonous, because trees grow on it, is absurd. Logically, on the same basis, the North German sands must be autochthonous because firs grow on them. He is inclined to regard bursting bogs as a by no means unimportant agent is causing distribution of the organic material. The great Sumatran bog, described by Koorders, is pulp-like; it could be torn away by high water and redistributed.

The manner in which pyropissite occurs affords additional evidence to Potonié. He uses this term to designate the clean material, composed essentially of resinous and waxy substances; pyropissite-brown coal is a mixture with fuel coal and often has marked resemblance to pyropissite; no sharp line of separation exists. Schwelkohle is the technical term for pyropissite-brown coal, which is utilized now in manufacture of oils and paraffin, since the purer material is almost exhausted. Potonié cites v. Fritsch, who regarded coals as allochthonous, to the effect that the flora, providing substance for the brown coals, was very rich in resins; and he looks upon pyropissite as consisting essentially of resinous matter. "Necessarily, the light resin would float and would be set off in special layers, while the somewhat heavier vegetable coal, brown coal proper, was forming its layers." He gives the gravity of brown coal as 1.2 to 1.4, and that of pyropissite as 0.9 or, when pure, even less.

The features observed near Halle in Sachsen agree, in Potonié's opinion, wholly with his conception of origin. Some of the coal is clearly autochthonous, but in chief part it is secondarily-allochthonous. Between Weissenfels and Altenburg, autochthonous coal is mostly in the southeastern part of the area and the other type is in the northwestern part, where pyropissite especially abounds—a fact, which suggests that the transportation was from southeast to northwest; but he feels that closer investigation must be made before the areas can be delimited definitively. It is certain that many mines have autochthonous coal in the Liegende and allochthonous in the Hangende; also that, at times, both kinds appear together, as in the deep works at Preussengrube, which shows that the transporting stream, as in the district west from Cöln, had afterwards filled with coal its channel way through the coal bed.

The autochthonous coal of the region is characterized macroscopically by numerous irregularly mingled larger and smaller pieces of resin (retinite) or by well-distributed pulverized resin. This contradicts the opinion that all the coals of this region have undergone a separation of the humic and resinous constituents, while it makes clear that the brown coals are from a flora rich in resins. These autochthonous coals were attacked, in part, by the waters; in going northwestwardly through the region, one finds more and more abundant that type of brown coal which shows by the finely broken material that it has been transported. During that transport, there occurred through gravity a separation of the constituents; pyropissite increases toward the northwest, where also Rieselkohle and pyropissite-brown coal prevail.

More or less of pyropissite, in layers or smuts, can occur in autochthonous coal; on drier portions decay would take place and there would be corresponding enrichment in resinous materials, just as one recognizes a corresponding similar enrichment in recent peats. When the upper part of an already hard bed of brown coal is so exposed to the atmosphere that a greater decomposition becomes possible and the coal becomes a Schmierkohle, an enrichment of the same kind must occur. But in so far as Potonié has investigated the conditions, evidence favors the belief, that separation of the substances by running water under influence of gravity explains the difference in structure and composition.

Potonié's conclusions were opposed by Raefler,\* who based his arguments upon a close study of more than one hundred mines and strippings within that part of Sachsen whence Potonié had drawn his illustrations. He recognizes that when one considers the characteristics of Potonié's typical autochthonous coal and contrasts them with those of that author's secondarily-allochthonous, the temptation to seek different modes of origin is very great; but he maintains that one must not neglect consideration of certain agents which are efficient in causing changes in structure.

The character, constitution and thickness of materials covering the coal are very important. There is one workable coal bed in the district under review, with extreme thickness of 15 to 20 meters and accompanied locally by one or more beds higher in the section. The whole region is covered with Diluvium, which rests now on Lower Oligocene sands and clays, but again directly on the coal. Under clay cover, the coal is Knorpel, i. e., lump coal; under sand, it is Klar or incoherent coal. He gives many instances showing the conditions as shown in a single stripping. The manner in which the roof material originated is important. A thick cover of ice had serious effect on coal separated from it by only a thin layer of Oligocene. Pressure, thrust and the water from melting ice combined to bring about change. The proof is beyond dispute in all mines where the coal directly underlies Diluvium, for there the coal is very different from that in those where Tertiary beds form the roof. Even in the Emma stripping, on which the doctrine of origin was based, coal covered by Tertiary rocks is Knorpel, but under other cover it is not. Following from south to north the gradual disappearance of Tertiary cover in that great open work, one sees the equally gradual passage from lump coal to, in the area of diluvial contact, a typical Rieselkohle. The same condition appears in other mines described by Raefler, whose notes are in such detail as to leave no room for doubt. Even thickness of cover seems to have far reaching influence, for in the old stripping near Fichtenhainichen as well as in

\* F. Raefler, "Die Enstehung der Braunkohlenlager zwischen Altenburg und Weissenfels," Jena, 1911, pp. 9, 17-30, 50-70. several others, the passage from one type of coal to the other coincides with decreasing thickness of cover. Raefler maintains that the relation between character and mass of cover, on one side, and the character of the coal, on the other, is so intimate, that study of maps recently published by the Prussian Landesanstalt should enable one to determine beforehand the kind of coal likely to be found at any given locality. He finds no evidence to support the suggestion that the Formkohle of Sachsen is other than autochthonous.

Raefler recognizes that the geographical distribution of liptobiolithic\* materials is an important element in the discussion. As the records of only three concerns making Montanwachs were available, he gathered material for direct study from 110 localities, representing all parts of the region. The liptobiolith content was ascertained in part by extraction of the bitumens and in part by determination of the tar-yield. He does not regard distillation as the proper method of determining the quantity of "bitumen," though that was chosen by Potonié and other students. Tar and "bitumen" are not equivalent terms; filter paper yields tar by dry distillation, but it is not a bituminous substance. He prefers Graefe's definition, that " bitumen" is the material extracted by an organic solvent, such as benzol.

One must agree with Raefler in accepting this definition, for it distinguishes sharply between substances actually existing in the coal and those produced by decomposition during destructive distillation. The necessity for this distinction was emphasized long ago by Mulder and by Angus Smith in their study of peats.<sup>+</sup> Balfour, many years ago, showed that the products of distillation depend very largely upon varying conditions during the process; and the matter has been made abundantly clear in recent years by the studies of Porter and Ovitz,<sup>‡</sup> who analyzed gases obtained at different temperatures. Their experiments confirm the conclusions reached by Emerson McMillin and Henry L. Doherty, who have tested all types of coal in their great gas plants in many cities of the United They assert that reported results of investigation are States. not comparable, unless all conditions under which the work was conducted are known. Raefler states that coal, from which the "bitumen" has been removed by benzol, yields

\* A term introduced by Potonié to designate "Harz-, Wachsharz- and Wachs-bildungen, die bei ihrer schwerer Zersetlichkeit nach der Verwesung von Pflanzenteilen, die diese Produkte enthalten, zuruckbleiben." ("Entstehung," p. 3.)

hung," p. 3.) † See "Interrelations of the Fossil Fuels, I," Proc. Amer. Phil. Soc., vol. lv, 1916, pp. 103, 104.

<sup>‡</sup> H. C. Porter and F. K. Ovitz, "The Volatile Matter of Coal," Bureau of Mines, Bull. I, p. 26.

much tar and even some paraffin. He remarks also that one cannot represent graphically the distribution of bitumens, because the coal of any bed varies in content of tar and "bitumens," both horizontally and vertically; and the composition of those products varies in like manner.

Potonié believed that, in the Zeitz-Weissenfels area, the tar and bitumen content increases from southeast to northwest: but a study of Raefler's map shows that the increase is equally notable from east to west in the basin north from Zeitz (23) miles southwest from Leipzig). At Teuchern, about 10 miles northwest from Zeitz, the coal is very rich, but within 4 miles toward the east, the yield is so small as to be unprofitable. The most important area is a series of small isolated basins, within a space of little more than a square mile, lying west from the Rippach river and north from Teuchern. Here are the well-known properties of Gesterwitz, Granschütz and Teu-These patches occupy independent basins, of Prechern. Tertiary origin, and their coal is wholly different from that east from the Rippach. Bitumen content of 25 to 30 per cent is by no means rare. In these basins the coal is richest toward the borders, where it contains so great proportion of pyropissite that the monthly yield at the works was from 7.3 to 9.5 kilogrammes of tar per hectoliter.

Aside from deposits on the borders, pyropissite occurs in great isolated nests, mostly in the upper part of the bed; usually, however, Feuer- and Schwelkohle are found in alternating layers. At most localities, the best Schwelkohle is in the lower part of the bed and it is often wanting at the top. Coal from two properties, one near Gaumnitz south from Teuchern, and the other from Webau north from that village, gave the following results of bitumen analysis in successive layers from the bottom upward:

Webau	21.0	27.2	18.1	9.1	21.3	3.5
Gaumnitz	19.3	21.4	25.6	6.6	17.9	5.9

the calculation being based on pure coal. The bed is from 15 to 20 meters, extreme thickness. Raefler regards the distribution of liptobioliths, the undisturbed and regular appearance of the pyropissite-brown coal, the stratigraphical relations of the independent basins of the western border as all-important in any discussion respecting accumulation of this material and as wholly antagonistic to the conception of secondarily-allochthonous origin. As the petty basins at the northwest are of Pre-Tertiary age and in all probability always isolated, their pyropissite cannot be regarded as the collected resin of coals at the east. He makes the positive assertion, based on analyses, that Klarkohle, the transported coal of Potonié, is not richer in tar and bitumen than the adjoining coal, which is recognized by that author as autochthonous. He finds that the alleged separation of original materials according to specific gravity has not taken place, the specifically lighter coal being for the most part in the lower part of the coal deposit. In districts with Klarkohle, bitumen-rich and bitumen-poor coal alternate just as they do in districts containing knorpelig coal. Even in the Emma mine, the pyropissite layers are regular. Still more important is the fact that on the southeastern side of the region, on the outcrop of the beds in that direction, as well as in independent basins, analogous to those of the northwestern side, one finds a bitumen-rich coal with nests of pyropissite.

Raefler believes that wax-producing plants gave the pyropissite material; by decay of cellulosic and other constituents, there would be enrichment of waxy matter, but unless the wax were already present no pyropissite or Schwelkohle could be formed. The careful chemical studies by Graefe\* are important in this connection. The prevalent opinion has been that pyropissite is probably a fossil resin; but in consequence of the contrast between that substance and retinite, Graefe cannot regard resin as the source of bitumen. After consideration of the gravity, fusion point, optical conduct, the characteristics of the tar-output and of the acids, he concludes that wax-like secretions were in chief part the original material of pyropissite.

Potonié's hypothesis is an assertion that by structure and composition Rieselkohle—Form- or Klarkohle—is proved to be autochthonous material transported by running water and redeposited, measurably under selective influence of gravity.

Running water, aided by gravity, does exercise selective influence upon transported materials. The process is continuous along streams, and it is so characteristic that one finds no difficulty in recognizing stream-action, even the courses of streams in the older rocks. Particles of coal are like other débris. The writer, in following streams within areas of coal mining, has often seen patches of mud and sand with much fine coal, which had accumulated in the curves. Students of coal bearing rocks, in every period, have observed fragments of coal in sandstones, clays, even in limestones. But such occurrences have no significance in this connection, for here one has to consider great deposits of commercially clean coal, not patches of sand or clay containing more or less of distinctly transported coal.

The accumulation of Knorpel- and Formkohle was contemporaneous, in the strictest sense of that term, at many places in Sachsen. Both types, at times, are continuous in a bed or bench, passage from one to the other being so gradual that

\* E. Graefe, "Bitumen und Retinit," Braunkohle, vol. vi, p. 226.

the continuity is as positive as that in a vari-colored sheet of The coal throughout shows little more than ordinary paper. differences in composition, except that the moisture of Formkohle is apt to be greater owing to the greater porosity; the only positive distinction is in degree of coherence. The profiles by Raefler and the earlier observations by Stohr and Russwurm<sup>\*</sup> confirm these statements.

When one considers the hypothesis of origin by transport, he finds serious difficulties at once. Allusion has been made to relations of the types in a single bench; but a more perplexing condition is the immense mass of the material; Davist gives a measurement of 328 feet near Cologne; Plettner<sup>+</sup> has shown the great abundance of Formkohle in parts of Brandenburg, while Raefler, Russwurm, Stohr, Laspeyres and others have made certain its prevalence in much of Sachsen and the adjoining region; v. Ammon§ found it the prevailing type in southern Bavaria; and closely allied coal is present in much of the Texas region. The physical character varies; sometimes the mass is a confused intermingling of large and small pieces in a matrix of incoherent, more or less dustlike or crumblike coal; but at others, as at Voss according to Potonié, coarse fragments are absent. Stems of trees, occasionally very large and often very numerous, are found in the Formkohle. The Knorpel- and the Formkohle of a given bed or bench are of the same age throughout, Oligocene or Eocene as the case may be, for the plant remains are the same in both. The important deposits of Sachsen, Brandenburg and the Cologne region are Oligocene and there is no Eocene coal in those areas. The brown coal basins are small and many of them appear to have been wholly independent from their beginning.

The hypothesis of secondarily-allochthonous origin appears to require as a basal postulate that the coal had become hard prior to removal. One is told that the large fragments are all angular, as they ought to be, because rounded pebbles are not to be expected, for coal is brittle. But the cutting and transportation must have been done while the Knorpelkohle was still exposed, for the statement is made that channels in the coal bed were filled with transported coal. This certainly involves the conception that the coal was already hard before it had received a cover of inorganic material, since there is no coal of earlier age in the districts. The question respecting the time

\* E. Stohr, "Das Pyropissit Vorkommen in den Braunkohle bei Weissen-<sup>a</sup> E. Stohr, "Das Lyropissit vorkönnen in den Draumonie ber Weissen fels und Zeitz." Neues Jahrb., Jahrg. 1867, pp. 407-409: P. Russwurm, Zeitschr. f. prakt. Geologie, Jahrg. 17, 1909. pp. 93. 94.
<sup>†</sup> C. A. Davis, U. S. Bureau of Mines, Techn. Paper 55, 1913, pp. 5, 6.
<sup>‡</sup> Plettner, Zeitschr. d. d. geol. Gesell., IV Band. 1852, pp. 249-483.
<sup>§</sup> L. v. Ammon, "Bayerische Braunkohlen und ihre Verwertung," Mün-1011

chen, 1911.

required for conversion of peat into hard coal may still be open to debate; but in this case the speed of conversion exceeded that conceived by the most earnest advocate, since the change must have been complete before the bog ceased to grow.

But the author of this hypothesis is not wedded too firmly to a belief that the coal was already hard. On page 142 of his work, one finds two paragraphs which seem to represent an after-thought. It would appear that bursting peat bogs might give material for a layer of coal; the great bog of Kampar river in Sumatra, described by Koorders, is pulpy, so that its material could be removed by high water and be deposited elsewhere. But the difficulties are no less along this path.

The basins, in which Formkohle occurs, are small and many of them seem to have been isolated throughout their existence as coal basins. Their distribution suggests conditions such as exist in some of our northern states, where one finds swamps, large and small, scattered over the several areas. As these basins of Sachsen cannot be brought into relation with any general system of Oligocene drainage, it would seem that one who asserts the doctrine of transport must seek the source of the material as well as an explanation of the phenomena within the area of local drainage—which, in some cases, was much less than 30 or 40 square miles, including the space now occupied by the coal itself. It is possible that enough vegetable matter might accumulate on the low hills surrounding the present coal area; enough to give, for example, the lower or Formkohle division of the bed at Orebkau, described by Russwurm. There would still remain the difficulty of accounting for the uprooting and transferring of the more or less forested bog to the lower forested part of the basin. The extreme toughness of recent peat and its strenuous resistance to eroding agents are among the most familiar facts—and one must emphasize anew that only bog material can be considered in this connection, as there are no Eocene coals in the districts under consideration. To remove the mass of peat there would be required a series of cataclysmic cloudbursts, possessed of more than ordinary discrimination, so as to end their destructive work with removal of the peat and to carry out none of the underlying inorganic matter.

The importance assigned to shrinkage cracks seems to be excessive, for it is not clear that the crevices are actually shrinkage cracks. If the transported material were coal and deposited under even the slight cover of water imagined by the author, drying cracks would be insignificant. If the material were still peat and there were a similar thin cover of water, the probabilities are almost certainties that the peat would become a living bog. In any case, there is no reason for supposing that pulpy peat, when transferred and kept under a water cover, would undergo changes so different from those which would have occurred on the original site as to give pulverulent coal instead of solid coal. If there were no cover of water, the saturated peat would dry on the surface, would be oxidized and would be blown away. This condition of wasting would be the same if the material were a powdery imperfect brown coal.

There is little evidence of selection by gravity in deposits of Formkohle. Some beds have incoherent coal in the upper bench and lump coal in the lower, while in others the positions are reversed. Raefler has shown that passage from one type to the other is gradual and within a space so small as to render the hypothesis of selection incompetent. Indeed, the relation is so indefinite that miners use the terms arbitrarily, coal from one mine being called Knorpel-, which in adjacent mines would be called Formkohle. The presence of logs in the fine coal is evidence that there was little selection, for those are often large and very numerous.

Pockets, even layers of sand, gravel and clay are not evidence that the mass consists of transported matter. Such pockets and layers occur in peat deposits generally and one can see them on the surface of growing bogs, where their origin is evident, and where no one would dream of utilizing them to prove that the peat is allochthonous.

The distribution of pyropissite and Schwelkohle gives no support to the hypothesis. Pyropissite material is supposed to have been carried farther than that of the brown coal and to have reached the place of deposition at the northwest. Raefler's study, not of a single property but of the whole region, has shown that the concentration is certainly notable in the northwest, but not in such way as required by the hypothesis. The richest localities are several small basins, independent and probably always so, in which the concentration is along the borders, not in the central portion Pyropissite occurs in nests, streaks and layers within Knorpelkohle (autochthonous) as it does in Formkohle (secondarily-allochthonous). Stohr and Fiebelkorn\* have shown that the Schwelkohle is confined to no particular position in the bed. It is certain that the coaly material must have been in advanced stage of conversion so as to make possible separation of pyropissite from other substances borne by the moving water; but whether the material were well advanced or not, one cannot well conceive how the pyropissite could be deposited by a current, slow or swift, since its gravity is less than that of water. Deposition could come only through evaporation.

\* M. Fiebelkorn, Zeitschr. f. pr. Geol., Jahrg. 1895, pp. 360, 403, 404.

The hypothesis that Formkohle is transported coal or peat appears to be a generalization based on conditions in portions of a few mines. It is supported merely by a priori reasoning dependent on postulates, which themselves are hypothetical. No evidence is presented to show that the supposed process of removal and redeposition is probable, though such evidence is necessary; since this supposed process is not only unlike anything known in the present era but also is contradicted by all that is known. The author appears to have been so convinced by his logic as to suppose that nothing was essential beyond mere assertion in order to secure immediate acceptance. But one should be grateful for the delicate reminder that sand is not necessarily autochthonous when it happens to be covered by a forest of firs.

There are features in Formkohle that are perplexing and no one explanation, thus far, seems to be sufficient. But it is certain that some are explicable by the well-known process of weathering, which is protean in manifestations. Potonié well says that for determination one must have a pile of freshly mined coal, since exposure to the weather changes lump to fine coal. Weathering may be induced by change in character or thickness of cover as well as by disturbance, which by crushing increases the porosity and aids access of surface water. The Emma mine in the Zeitz district is that on which the transport hypothesis had its birth; but even there the influence of changing cover and of increasing disturbance is distinct. Where the cover is only slightly pervious clay, the coal is lump; but pulverulent coal appears in greater and greater proportion with change of roof to pervious diluvium and with increasing disturbance. The relations are exposed fully in that extensive stripping. Stohr's section is equally to the point. The upper bench is lump coal and has a roof of clay to sandstone; it is best under the clay. The lower bench, separated by a parting, is fine coal. Its cover is very thin and represents a period during which the underlying coal or peat was exposed to the action of leaching waters. Heusler,\* in describing the Cologne area, says that the coal often has a diluvial cover, through which pluvial waters gain access and pass even to the bottom of the mass, affecting the quality. In that region, the top portion of the deposit has been converted into Schmierkohle, a soft, greasy substance, which is said to yield a greater proportion of distillation products than is obtained from the underlying coal. Potonié has suggested that this Schmierkohle is allied to Schwelkohle; but it is unquestionably due to weathering and the ash as well as moisture content decreases

\* C. Heusler, '' Beschreibung des Bergreviers Brühl-Unkel und des Niederrheinischen Braunkohlen-beckens,'' Bonn, 1897, pp. 149, 163. below it. Potonié recognizes the efficiency of weathering upon peat and explains by it the nests and streaks of pyropissite in lump coal, though he does not apply the same explanation to the similar nests and streaks in Formkohle.

The cementing substance of brown coal, related to the dopplerite of peat, can be removed by solution, as Pishel\* has shown. In describing the conditions on an Indian reservation in North Dakota, he says that much "hydrocarbon" can be removed during the lignite stage and that a great quantity is carried out from lignite beds by springs. The larger springs are but slightly discolored but those of less size are decidedly dark. The substance is dissolved, it is not in suspension, for water in pools becomes darker on evaporation and leaves no precipitate until wholly removed, when some dry scales remain. The water of this region contains some alkaline matter. Wilder states that sometimes the upper part of a lignite bed is "slacked" and does not improve away from the outcrop. The condition is such as would result from exposure of the upper portion while the lower portion was protected. At times the whole bed has been reduced to "slack" or pulverulent coal. The change in structure, judging from Wilder's descriptions, may have begun before the deposit was covered.

While in some districts weathering appears to have been the cause of change, still there are others in which there is no proof that it was the sole or even the dominant cause. But whatever the cause may have been, the hypothesis of origin by transport fails to offer an adequate explanation. As presented, the supporting arguments are contradictory, while the basal postulates are inconsistent with all known existing conditions.

\* M. A. Pishel, "Lignite in the Fort Berthold Indian Reservation," U. S. G. S. Bull. 471-C, 1912, pp. 9-11. <sup>+</sup> F. A. Wilder, "The Lignite Coals of North Dakota," Econ. Geol. vol. i,

1906, pp. 676, 677.

## ART. XX.—On the Etching Figures of Beryl; by ARTHUR P. Honess.

This paper embodies a brief discussion of the etch figures of beryl, both artificial and natural. It was the desire of the writer, in beginning this work, to etch all of the fundamental forms, but, owing to the fact that the rarer faces occurring on the available material were so slightly developed or corroded this could not be accomplished. It is hoped, however, that, in the future, these less common forms may be obtained and the etchings described and illustrated in one of the subsequent papers, the contents of which will embody the results of the writer's work on other crystal types.

Perhaps one of the most interesting minerals studied, in connection with investigation of natural and artificial etch figures, is the holohedral mineral beryl. It has been described from various localities and a variety of etch forms discovered. which serve conclusively to illustrate the holohedral character of the mineral. W. Peterson\* has described the natural figures on beryl from Mursinka, the prism etchings of which are rhombic and hexagonal forms with the longer axis at right angles to the vertical axis, c. These forms are similar to those described on one of the Miask crystals by the writer. On the second-order pyramid Peterson observed deep and shallow rhombic and hexagonal forms, while those on the first order pyramid were triangular with their edges parallel to the edges  $0001/10\overline{1}1$  and  $10\overline{1}1/11\overline{2}1$ . The base was covered with regular hexagonal pits. Carl Vrba, + by means of casts, was able to measure the angles of the etching faces on beryl from Pisek and to identify them with known forms. A. Krejci, t in his study of the beryl crystals from the Pisek State Museum, likewise identified several forms,  $40\overline{41} - 20\overline{21}$  on the negative pyramid. F. J. Wiik§ has described rectangular forms from the beryl crystals from the Urals. A. Arzruni described natural etchings on crystals from Mursinka similar to Peterson's. S. L. Penfield, in his study of beryl from Willimantic, Conn., attributes the origin of certain crystals showing rare faces to the etching process alone.

Hans Kohlmann,\*\* working on Brazilian beryl crystals, belonging to the collections of Giesen Mineralogical Institute

AM. JOUR. SCI.-FOURTH SERIES, VOL. XLIII, No. 255.-MARCH, 1917. 16

<sup>\*</sup> W. Peterson, Bih. Svensk. Vet. Akad. Handl., xv, II, No. 1, 1, 1889.
† Zs. Kr., xxiv, 104, 1894.
‡ Zs. Kr., xxix, 399, 1904.
§ F. J. Wiik, Finsk. Vet. Soc. Förh., xxvii, 1885.
[] A. Arzruni, Verh. K. Russ. Min. Ges. (2), xxxi, 155, 1894.
¶ S. L. Penfield, this Journal, xxxvi, 317, 1888; xl, 488, 1890.
\*\* Kohlmann. Ib. Min. Beil. xxw. 125, 1908.

<sup>\*\*</sup> Kohlmann, Jb. Min. Beil., xxv, 135, 1908.

at Marburg, and the University of Kiel, has prepared a very elaborate discussion of natural etch figures. Five forms were etched; the prism is marked by rectangular pits, elongated at right angles to the prism edges; the figures are three mm. long, one broad and one-third mm. deep and composed of four triangular faces meeting in the center of the pit. Smaller figures representing other stages of development are also described. The second-order prism reveals long, slender, spindle-shaped etchings, parallel to the prism edges; other forms are elongated octagons. The first-order pyramid has triangular pits with the apex turned downward. Occasionally the apex is truncated producing a four-sided figure, symmetrical to a vertical plane. The second-order pyramid has many well-defined shield-shaped figures, very shallow, with point downward. On the base are hexagonal and dihexagonal etchings: some have a base, others are pyramidal, but all are symmetrical to six vertical planes. Traube\* has etched beryl crystals from Elba with potassium hydroxide. On the base are regular six-sided forms with the edges parallel to  $0001/10\overline{10}$ . On the first-order pyramid are triangular figures, apex upward and the longer side parallel to 1011/1010. The second-order pyramid is marked by foursided pits, with boundaries curved and elongated horizontally. Three or four different types of figures are represented on the unit prism : some are rectangular with the boundaries straight and the long axes parallel to  $\dot{c}$ , others are similarly oriented but have curved bounding lines; still others are quite oval having five faces and elongated parallel to c. All of the figures on the various forms indicate the symmetry of the type. With potassium fluoride the figures on the base and pyramid faces do not differ essentially from the potassium hydroxide figures. but the unit prism contains hexagonal forms elongated parallel to the prism edges; other figures appearing on the prism are rhombic. The potassium hydroxide etchings of Traube may well be compared and contrasted with the potassium figures of the writer as subsequently described and illustrated.

The beryl crystals used for etching were small transparent crystals from Elba. They occur in a matrix of feldspar, associated with topaz and tourmaline, very often intimately attached to the topaz crystals, which they resemble very closely in form and luster. The crystals are not over four or five mm. in length and are very simple in form, possessing the unit prism  $10\overline{10}$ , the first order pyramid  $10\overline{11}$ , the second order pyramid  $11\overline{21}$ , and the base 0001.

Various solvents were used for the purpose of etching, but the best results were obtained with the alkalie hydroxides and a mixture of the same. Hydrofluoric acid, which ordina-

\* Traube, Jb. Min. Beil., x, 464, 1896.

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rily acts slightly upon beryl, failed to produce the slightest trace of etch figures on any of the forms, although the crystal was immersed in the boiling acid for an hour or more. When plunged into fused sodium hydroxide for only a few seconds, the crystal was well etched with distinct figures. The base and prism etched with equal rapidity, the base figures appearing circular in their primitive stage of growth, but gradually becoming hexagonal as solution continued. (See fig. 1.) The figures are of two kinds; the first are hexagonal pits meeting in a point and formed by six faces lying in the zone of the first order pyramid and the base; the second are similar six-sided forms possessing a basal plane. The figures are regular hexagonal forms with their margins parallel to the intersection  $10\overline{11}/0001$ , and are symmetrical to six vertical planes.

# Etching with Sodium hydroxide.

Prism.—The unit prism, 1010, was beautifully etched after immersion in the fused sodium hydroxide to the extent of fifteen seconds. Etchings could be distinctly seen after the first few seconds, but they appeared as tiny cubical forms, very similar to the natural etchings on the  $10\overline{10}$  form of beryl from Columbia, S. A., and evenly distributed over the face. The ultimate stage, reached after the solvent had acted upon the face for about fifteen seconds, revealed well-defined regular quadrilateral pits, elongated in the direction of the c axis (fig.  $\hat{2}$ ). The two longer sides are slightly bulging, while the ends of the figures are bounded by two short straight lines, in most cases, extending at right angles to the c axis of the crystal and the longer boundaries of the figure. In a few cases, these shorter lines are slightly inclined to the prism edge, but this is exceptional and is probably due to surface irregularities. The figures occurring on the unit prism, 1010, are of two kinds,those terminated by a plain parallel to m 1010, and those terminated by an edge. The former are bounded by two long faces parallel to the prism edges, and by two shorter planes in zone of the base and first order pyramid. The lateral faces are truncated by a fifth plane parallel to the prism face etched; this face is also quadrilateral, very much like the outline of the figure, except for the fact that its longer boundaries are not curved as are those of the figure itself. The figures are symmetrical to two planes, one vertical, and one horizontal, which accords with the type.

*Pyramids.*—The unit second-order pyramid, when immersed in fused sodium hydroxide, turned glassy in appearance and gradually disappeared, but not the slightest trace of an etching could be detected, although the face was repeatedly examined under the microscope. No attempt was made to etch the unit first-order pyramid with sodium hydroxide, as its surface was rather irregular, but undoubtedly the form would yield distinct figures if a more perfect surface could be obtained. In general, then, the figures produced by sodium hydroxide are very distinct and easily and quickly produced, and are perhaps more simple in form than those produced by the potassium hydroxide fusion next to be considered.

# Etching with Potassium hydroxide.

After immersion in the fused potassium hydroxide for fifteen seconds, the unit prism 1010 was densely pitted with etchings of sufficient size as to permit detailed study. The base, 0001, was also perfectly etched with a countless number of circular pits, so small that they revealed no angles under high magnification. The first and second-order pyramids were not etched as yet, but repeated immersions for two or three minutes gradually developed distinct forms on the first-order pyramid, but those of the second remained imperfect and dim.

Prism.-The prism figures, like those of the sodium hydroxide, are of two kinds, and in general resemble them. There is noticed, however, under high magnification, a distinct difference in the etch figures of the two solvents; those produced by sodium hydroxide are simple in form, while those produced by the potassium hydroxide fusion are complex. The more simple type of potassium hydroxide figures (b, fig. 5) are very shallow and bounded by three planes, the largest of which is curved, forming the base and ends of the pits. The lateral bounding faces, slightly bulged, descend very abruptly to meet the base, forming a simple quadrilateral figure, with the extremities slightly rounded. The forms are elongated parallel to the *c*-axis of the crystal and are symmetrical to two planes. The more complex etch figures are apparently made up of two pairs of lateral faces (d, fig. 5). The first pair, which gives the figure its general form, is much curved, and descends quite abruptly to the edge of a deep pit, produced by the second pair of lateral faces, which seem to meet the base of the figure almost perpendicularly. The deeper part of the pit is bounded by faces extending parallel to the long axis of the figure; the ends are modified by two faces meeting in a point at a very sharp angle, and these, like the lateral faces, extend upward to meet the more gently sloping planes, which give the figure its shape and which, in reality, are the uppermost lateral planes partly enveloping the ends of the pit. It is not an uncommon thing to observe on a single prism face, figures which are representative of four different stages of development, or a change from the simplest to the most complex, as is indicated



 $\times 190$ 

FIG. 3.



 $\times 190$ 





× 310





 $\times 310$ 





 $\times$  310

Fig. 6.



 $\times$  123

Fig. 1. 0001 etched by fused NaOH; Fig. 2,  $10\overline{10}$  by the same; Fig. 3, 0001 by fused KOH; Fig. 4,  $10\overline{11}$  by the same; Fig. 5,  $10\overline{10}$  by the same; Fig. 6,  $10\overline{10}$  and 0001, showing relative solubility.

by: a, b, c and d of fig. 5. All of the figures are symmetrical to two planes, and reveal very clearly the symmetry of the unit prism.

Base.—Immersion in the fused potassium hydroxide for approximately one minute, etched the base very successfully. The figures as they first became visible were circular, identical with those produced by the sodium hydroxide, and very shallow. As they became larger, through repeated immersions in the solvent, small faces began to appear; a few pits became dihexagonal, others appeared to possess twenty-four faces, and still others appeared to be bounded by a large number of very small planes. As solution continued, this series of small faces gave rise to six well-formed planes, forming perfect hexagonal pits, similar to those produced by sodium hydroxide, but differently oriented (fig. 3). Instead of occupying a position with their edges parallel to the edge  $10\overline{10}/0001$ , they are turned through a revolution of thirty degrees, about a vertical axis, thus the one hundred and twenty degree angles of the figures are symmetrically turned toward the edges of the face. This is not the result obtained by Traube\* in his investigation of the etchings on beryl.

Pyramids.---The first-order pyramid etched with considerable difficulty, in fact, only after repeated immersions in the potassium fusion for five minutes could distinct forms be observed and these were exceedingly rare, possibly four or five figures scattered over a considerable surface. After only a brief immersion in the fusion, the entire face assumed a fused, glassy appearance, which did not seem to change as the figures developed; the other forms, especially the base, 0001, and firstorder prism, 1010, became beautifully etched, and due to continued immersion, consequently corroded (fig. 6). The solution, eating into the first-order pyramid on all sides, caused the edges to appear rough and deeply notched, while the surface maintained that fused, glassy appearance (fig. 4), and even the figures themselves had rounded, glassy-looking margins. Nevertheless, the etchings are distinct and bounded by three faces, the intersections of which with the crystal face are The figures appear as flattened isosceles triangles, havcurved. ing but little depth, with the apex turned upward, the longer side extending parallel to the edge  $10\overline{1}1/10\overline{1}0$  and the larger plane of the figure lying in this zone. (See diagram E, fig. 15.) The angle at the apex measures approximately one hundred sixteen degrees. These figures are quite similar to those described by Traube, † and although his figures possess a fourth plane, extending from the deeper part of the pit to the apex,

\* L. c.

†L. c.

•:



Fig. 9.









 $\times 190$ 

FIG. 10.



 $\times 190$ 

FIG. 12.



Fig. 7, 1010 etched by 1:1 sodium-potassium fusion; Fig. 8, 1010, imma-ture figures of Fig. 7; Fig. 9, 1010, natural etchings; Fig. 10, same highly magnified; Fig. 11, 0001, natural etchings; Fig. 12, 0001, dihexagonal etching.



 $\times 123$ 

this is only a slight modification and may represent a different stage of development, or a potassium solvent slightly different from that used by the writer. The figures produced by the writer also resemble natural etchings found on the secondorder pyramid of a light green, transparent beryl crystal from Topsham, Maine. The figures occurring on this form are symmetrical to a vertical plane.

The second-order pyramid was not well-developed, consequently the figures obtained are rather indefinite but resemble very closely those produced by Traube on the same form. They are elongated oval forms (diagram E), extending



parallel to the crystalline edge  $11\overline{2}0/11\overline{2}1$ , widest in the center and tapering at each end. Four planes comprise the figures, the two larger planes meeting in the bottom of the pit and extending almost the entire length; at the ends, right and left, a small face descends rather abruptly to the bottom. The figures are also symmetrical to a vertical plane, which accords with the symmetry of the type. Thus the four forms etched serve conclusively to illustrate the holohedral character of beryl.

While the etch figures produced by the separate alkalic hydroxides are distinctly different, those produced by a one to one mixture of sodium hydroxide and potassium hydroxide are strikingly similar to those of the pure sodium fusion. Solution was stopped after six or seven seconds, in order to prevent intergrowth, hence a slight difference might be expected, as the sodium hydroxide figures, and also the potassium

 $\mathbf{230}$ 

figures, were immersed for fifteen seconds. Nevertheless, large, well-defined etchings were obtained, which may be easily compared with those previously described. These figures, as before mentioned, do not resemble the potassium figures to as great a degree as they do those produced by sodium hydroxide, and a comparison will eventually evolve into slight modifications of the sodium forms. In the first place a detailed study of the sodium-potassium etchings (fig. 7) reveals four slightly curved bounding lines instead of two, as described in the sodium figures. Also these figures are deeper with a larger plane lying parallel to the prism face; in most of the larger figures the basal groove so prominent in the sodium figures is noticeably absent. These characteristics reveal the presence of the potassium molecule, in the mixture, as they are quite common in the forms produced by that fusion. It is possible that they are shorter and thicker than either of the others. But. on the whole, the shape of the figures and their orientation resemble very closely the sodium figures. Other etchings appear on the same face representing various stages of growth, and even these bear much resemblance to the sodium forms. They are not so deep and possess a large plane parallel to the unit prism 1010; oftentimes they are so shallow as to be barely visible under the microscope, and still they are about the size of mature figures. Etchings of this kind have little detail, revealing practically nothing to the observer, except a broad flat plane, which gradually diminishes in size as the figure deepens, due to the development of the lateral bounding faces. In the mature figure, these lateral faces are much more prominent than the plane forming the base of the pit. Occasionally among the smaller figures, well-defined pits occur, which are bounded by four triangular faces, the apices of which meet in a common point, at the center of the figure (see fig. 8). These smaller forms appear to be identical with natural etchings on Brazilian beryl crystals described by Kohlmann.\* There is, then, a very noticeable resemblance in the two types of etch figures; those produced by the pure sodium hydroxide and those produced by the one to one mixture of sodium and potassium hydroxides; and, although the figures of different size and shape occur on the same face, which merely indicates a variation in conditions of etchings, each form reveals very clearly the symmetry of the face upon which it occurs, and the several fundamental forms etched serve conclusively to illustrate the holohedral character of beryl.

## Natural Etchings.

*Prisms.*—The writer, in his investigation of the beryl crystals from some of the more important localities, has been

successful in establishing the symmetry of the mineral by means of several different natural etchings hitherto undescribed. While but three or four different forms have been etched on the crystals present, these are, in every case, so distinct and so well defined as to reveal very clearly the symmetry of the face upon which they occur.

The first to be described is a light green crystal almost transparent, with the forms 1010, 1120, and 0001 well developed, collected near Hiddenite, North Carolina (diagram A, fig. 13).



The unit prism 1010 contains many small pits, more or less quadrilateral, extending across the face, with their long axes at right angles to  $\dot{c}$ . The figures are bounded by straight and curved lines, the smaller forms having rounded terminations. The quadrilateral outline of the larger figures is more apparent as they are composed of upper and lower faces (diagram A), and occasionally right and left faces, very rarely a plane parallel to the prism face. Figures of various shapes are represented upon a single face, indicating various developmental stages of growth. The figures are symmetrical to one vertical and one horizontal plane.

The second-order prism  $11\overline{2}0$  is a very narrow face and contains but few distinct forms. These are perfect spindle-shaped pits elongated parallel to the vertical axis of the crystal, and resemble very closely the natural figures occurring on the  $11\overline{2}0$  form of Brazilian beryls, as described by Kohlmann.\* The six-sided forms described by Kohlmann as primitive figures are absent on the North Carolina crystal.

*Base.*—On the base are beautifui, regular, hexagonal pits, with the sides parallel to the edge  $0001/10\overline{10}$  (see 1 and 2,

FIG. 14.

diagram F, fig. 15); some are terminated by a basal plane, others are pyramidal with the six bounding planes lying approximately in the plane of the first-order pyramid; both forms are symmetrical to six vertical planes, which conforms to the symmetry of the type.

Another form of natural etch figure occurs on a beautiful emerald from Musa Valley, near Bogota, United States of Columbia (diagram B, fig. 13). Three forms are etched.



Prism.-The unit prism 1010 is beautifully pitted with quadrilateral figures, many of them being perfect squares with four sloping planes; others are slightly elongated at right angles to the vertical axis of the crystal, but all angles are ninety degrees, as in the more regular type. The right and left faces of the figures lie in the prism zone, the upper and lower faces lie in the zone of the first-order pyramid and the The position as regards the intercept could not be base. accurately determined as these pits would not yield casts of sufficient size for measurement. The figures are very interesting from a genetic point of view, as they are identical in form with the artificial figures produced by the writer on the unit prism of a North Carolina beryl, by sodium hydroxide; they are perfect duplications at this state of growth. This is to be noted, however: if the artificial figures are allowed to develop to a more mature stage, they assume an elongated appearance exactly as do the natural etchings on the emerald from Musa Valley, South America, but they differ in orientation; the former have their long axes parallel to d, the latter

at right angles. This seems rather suggestive, for may we not assume a solvent rich in soda, and is it not probable that the beryl was associated with rocks and minerals with a high sodium content? At least the form of the figures would indicate this. The etchings are symmetrical to two planes.

*Pyramid.*—The second-order pyramid  $11\overline{21}$ , so well developed on this crystal, reveals one or two etched faces. The figures are too small to permit of detailed study, but they appear as top-shaped forms, with the point downward and divided symmetrically by a vertical groove (diagram B, fig. 13). They are, therefore, symmetrical to a vertical plane.

Base.—The figures on the base are similar to the natural figures on the North Carolina crystals, with the exception of a trigonal form (see 3, diagram F, fig. 15). The base, the second-order pyramid and the unit prism, then, reveal the symmetry of the type, as illustrated by natural etchings.

As a usual thing the etch figures are alike upon the same form in the same locality, but crystals from Miask, Russia, reveal the presence of two different solvents. The change in form and orientation may be due to increase in concentration or temperature, possibly both, but very evidently there has been a decided change in the nature of the solution, for the difference in the figures is not only orientation, but size and shape as well. For comparison two crystals were examined and described; these crystals are very clear and a greenish yellow, the surfaces being very bright and in every way suitable for the study of the etchings; they are of the same size and similarly developed with 1010 as the dominant form, and upon this face the figures appear. Upon the one crystal most of the figures are hexagonal, due to the replacement of the acute angle of the rhomb by a small face lying in the prism zone; the larger angle is approximately a hundred and thirty-five degrees (diagram C-I, fig. 14). Other figures occurring on the same face are very shallow and perfectly diamond-shape in The pit is so shallow that the four lateral planes are outline. reduced to mere lines. The base of the pit is very large and also diamond-shaped. The long axis extends at right angles to the prism edges.

The figures of the second crystal are diamond-shaped; measuring one and one-half mm. wide and three mm. long. The long axes of the figures are parallel to the prism edge, the reverse of the position of the figures on the first crystal. Occasionally the obtuse angle is replaced by a curved lateral boundary, producing a hexagonal form (diagram C-II). Although these crystals are from the same locality this would indicate two different solutions. As to the nature of the solvents, the writer has not been able to arrive at any conclusions, although several attempts were made to duplicate the figures with laboratory preparations.

Perhaps the most elaborate figures occur on a beautiful light green beryl from Topsham, Maine. The crystal possesses three of the fundamental forms, the unit prism, the base and the pyramid of the second order, and all faces are distinctly etched.

*Prism.*—Upon the prism three stages of development are manifest (figs. 9 and 10). The primitive form is the shallow diamond-shaped pit, very simple and distinct, with very often a small pit in the center, just discernible in some figures and quite well developed in others. The pit, having reached an advanced stage, completely fills the diamond form, producing a second stage in development. The mature figure possesses a deep groove at right angles to the prism edge and passes the entire length of the figure. These two planes as they ascend quite suddenly diverge at a much larger angle and intersect the surface in a curved line and in some cases a straight line. This gives the figures an hexagonal appearance, elongated at right angles to C; the acute angles at the ends of the pit measure approximately forty-five degrees, and are formed by the intersection of two small faces, lying in the zone of the second-order pyramid and the first-order prism.

Base.—The base reveals two different figures, one the outgrowth of the other; one is hexagonal, the other twelve-sided and both regular with the edges of the hexagonal form parallel to  $0001/11\overline{2}0$ . (See 4 and 5, diagram F.) The dihexagonal figures (fig. 12) ultimately become hexagonal as was observed in the case of the artificial figures produced by sodium hydroxide on beryl, where the figures were composed of so many small faces as to appear circular, but which gradually became hexagonal as solution continued. This well-defined figure (fig. 12) possesses twelve triangular faces meeting in a common point. All figures on the base are symmetrical to six vertical planes.

*Pyramid.*—Upon the pyramid of the second order are three or four well-defined triangular figures; they are isosceles triangles with the large angle turned upward and the base parallel to the edge  $11\overline{2}1/0001$ . The larger forms often appear pentagonal (diagram D, fig. 15) and all are symmetrical to a vertical plane.

The artificial etchings produced by the alkalie fusions are represented in diagram E, where the relation of the figures to the crystalline edges may be observed. Forms on  $10\overline{1}1$  and  $11\overline{2}1$  are produced by potassium hydroxide and on  $10\overline{1}0$  and 0001 by sodium hydroxide. Diagram G (fig. 15) represents the natural etchings found on a light green beryl from Mt. Antero, Chaffee County, Colorado. The figures are very large and simple, considerably intergrown, but occasional individuals may be readily detected with the unaided eye. The more common type of etching is represented by 1 and 2 of diagram G. In every figure there is present the two long faces lying in the prism zone, which either intersect at the base of the figure, or extend downward, intersecting the third long face, forming the bottom of the pit. Very often the larger figures possess narrow depressed areas extending lengthwise the pit and which, when observed in number, give the crystal face a striated appearance, parallel to C. The small face at each end may or may not be present. The figures are symmetrical to two planes at right angles.

A few well-defined natural etchings, which were observed on the base of a light green beryl, from Mursinka, Siberia, are shown in fig. 11.

Hence the various forms, naturally etched, conform to the symmetry of the type. And from the foregoing investigation, it is readily observed, that the etch figure, be it produced in nature or in the laboratory by solutions of various constituents, concentrations and temperatures, the result is always an accurate outward reflection of the interior structure of the crystal.

Princeton University, Princeton, N. J.

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J. M. Blake-Plotting Crystal Zones on the Sphere. 237

# ART. XXI.—*Plotting Crystal Zones on the Sphere;* by JOHN M. BLAKE. (Article 4.)

In the early sixties the writer made use of plotting on the sphere in the solution of certain crystal problems. Some preliminary trials were made with a nine-inch wooden slate-coated sphere, and the results were so encouraging that a hollow cast zinc sphere was made of about twelve inches diameter. This sphere was accurately turned in a special lathe, and was then



FIG. 1.

FIG. 1. J. M. Blake's Plotting Sphere.

coated with a liquid slating compound, and its spherical figure was perfected by recoating the low portions and then grinding the surface with a pumice stone mould of the same curvature. A hard, smooth, true surface was thus secured. It was provided with a graduated equatorial ring. On this ring a rightangled spherical triangle could be rested while plotting.

The base of the sphere rotates on rollers set with the axes radial. The sphere can be turned independently of the base by slackening three leather-tipped centering screws; and it rests in a shallow leather-lined cup which turns on a central adjustable screw point.

The main value of the sphere when used in connection with crystal work is dependent upon its adaptability for the retention of data relating to plane positions. It is obvious that plotting on the sphere cannot be performed with as great accuracy as upon paper; but if we refer to the measurements that have already been made with the goniometer, and keep the plotting work corrected, we can attain sufficient exactness to enable us to perform valuable work having crystal description for its object. This work can be done by such aid with economy of time and labor. In fact, we can perform work that would hardly be attempted if dependent on the methods that have so long been in most frequent use.

In order to secure the greatest degree of accuracy that a given crystal will yield, we make use of the best average zone tangent spaces that can be obtained from a measurement of the whole crystal. It will follow from this that the greatest number of planes we can develop on a salt, or the greater number of trustworthy reflections we can obtain from a mineral, will tend to a more accurate determination of the length of the crystal axes.

With these few hints relating to the hoped-for, eventual, exact determination of crystal laws and constants, we will turn our attention to some practical methods of collecting and presenting data in available form for future generalization and mathematical treatment. In so doing we will endeavor to make it apparent, that graphic and mechanical methods can, with advantage, be substituted for a great mass of the work commonly undertaken by algebraic and analytical methods. These algebraic attempts are many times founded on uncertain measurements, and mathematical precision cannot, therefore, be expected on such a basis. By the methods here advocated, the matter of collecting useful data is much facilitated, and the work can be undertaken by a larger number of observers.

If we examine a tangent-plane projection of the normals made from a suitable view-point, we will have a series of points arranged in parallel rows. Another set of rows having a different spacing length may cross the first set through the center at right angles, as in the orthorhombic forms, or they may pass obliquely at one side of the center, as we find with the oblique systems.

In addition to these rows of points, which are the intersections of the normals with the projection plane, there are planes whose normals do not pierce this plane, but lie parallel to it. These may be called the prismatic planes. These latter have their part in the growth and shaping of the crystal, and they

# J. M. Blake—Plotting Crystal Zones on the Sphere. 239

conform to the same laws. When we deviate from this best view-point, the rows converge to some point in the distance.

The planes of a fully developed crystal may be regarded as forming a mutually dependent whole. We may find certain planes undeveloped on one crystal which may be present on another crystal identical in composition; and also, a crystal may present a perfect microscopic edge where there should be a truncation by a frequently occurring plane. We will assume that each species has a limited number of planes, all of which may be developed under favoring conditions.

By growing a polished sphere of a salt to a proper degree, reflections may be obtained from its surface for all developable planes. Such a sphere, when grown, has distinctive markings brought out on its surface. With the same end in view, a corner, or an edge of a crystal, can be rounded and then grown.



In the latter case, we have some of the original planes left to aid in locating any less frequently occurring planes that may be developed by the treatment.

The system of measuring crystals by complete zones was originally suggested by the serious need of such a plan for use in the ready plotting of the planes on the sphere. The expedient of attaching the crystal by a short piece of lead wire, while measuring, was proposed in 1866 by the writer. This wire support will allow of making a complete zone reading for each adjustment.

The Gnomonic Projection.—We would here draw attention to the value of the gnomonic projection of crystal planes, as an important first step in the study of crystals. An objection has been made that some of the tangents are liable to become too seriously extended, and hence, a very general resort has been

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made to the stereographic projection which involves the use of the tangent of the half angle. By such a substitution we lose some important advantages which can follow the use of the gnomonic projection. The objection alluded to can be overcome in the case of the orthorhombic and oblique species by taking care in selecting the proper projecting point.

There is a certain position on a crystal which gives the most compact projection of the planes. This position will furnish the least complicated set of indices. A projection made at right angles to this, will probably show the planes less compact but still within reasonable bounds. A third position at right angles to the other two is apt to give a very widespread projection of the planes. This third position is to be avoided as a rule. If the drawing were made from this third view-point some of the planes would be seriously foreshortened.

Fig. 3 gives three projections of humite, type I, an orthorhombic species. It shows a remarkable segregation of planes in projection 1 at right angles to the c axis. The projection shown in 2 is also made at right angles to the c axis and is also at right angles to the 1 position. The projection on the cplane given in 3 is made at right angles to the 1 and 2 positions. It is, on the contrary, very diffuse, and for this reason the drawing 3 has been made to include only one quadrant. The radiating short lines in 1 and 2 represent the normals of the prism planes according as we adopt one or the other position. The humite series of minerals are unique in having forms bounded by a multiplicity of planes.

Oblique crystals may give several projections in which the planes are not widely scattered. Fig. 4 represents a triclinic crystal of albite. It is selected to show an inclined crystal in which the projection can be made from several view-points without wide-spreading the plane positions. The upper cut represents a crystal laid flat on the b plane and the numbered lines pointing towards its center give the direction of each projection. The middle figures show the crystal in several positions while being rotated on the b axis. The favored positions are selected with reference to giving an edge-on position to certain planes. The lower figure shows the several projections corresponding to the different positions. Radial lines at the margins indicate what are temporarily the prismatic zones. The triclinic character of the crystal is shown in measurable quantity on the original drawings which were made to a two inch radius, but is not plainly shown on the greatly reduced scale.

Plotting the Planes on the Sphere.--The planes of a single selected zone are first plotted on a great circle drawn on the sphere with a pencil guided by the equatorial ring. If we have a crystal with two rectangular axes, a second great circle can be drawn at once at right angles to the first circle at the intersection of the two zones. Preliminary zone plots on paper are useful as a guide in this work. The cross zones can be added in turn, and we eventually secure all the planes by this



process. In case of a triclinic crystal, it may be required to triangulate with the dividers to attain a first approximation in locating the second zone. The balance of the cross zones can then take their proper places.

The next step is to obtain a record of the position of all the planes that occur in one hemisphere. The reading of the equatorial circle will be from 0 to  $360^\circ$ . The reading of the vertical leg of the triangle will be from 0 at the point of contact of the tangent plane at the top of the sphere down to  $90^\circ$  where the triangle rests on the equatorial ring.

We shall require a record of the horizontal or equatorial reading, and of the corresponding vertical angle. It will facilitate this plotting if we prepare a suitable drawing board. This need not exceed twenty inches square. A hard-wood peg is inserted in its center and is cut off flush with the surface of the board. From this center a circle is drawn, and is divided into degrees. The graduation marks should extend sufficiently outward so as not to be covered by the square of the drawing paper. There should be two sets of numbers in reverse order both on the ring and on the board. The graduation marks on the board correspond to the divisions on the ring of the sphere.

We next mark on a paper strip a series of natural tangents up to eighty degrees. This scale of tangents can be one calculated for a two-inch radius. A shorter radius is sometimes used, but requires more exactness in drawing. We pin this paper strip by its zero point to the center of the drawing board. The graduated edge of the strip should be radial. A bit of paper is pasted to the strip to receive the pin through the zero point of the scale as this will bring about the radial position of the scale edge.

We can now go on and plot the position of the normal intersection points on paper, and we thus make the gnomonic projection. The equatorial zone will appear only as radial marks. The radius of the tangent scale can be shown by a circle drawn about the center.

The normal lines used in projecting start from the center of the sphere. When we use the projection for our purposes we look down upon it from the outside as we would upon a crystal. If we also project the back planes, these should appear as though we looked through the crystal and should be in reverse.

When we have made our tangent plane projection from the proper view-point, the indices of the planes can be obtained by inspection without calculating them.

It will be gathered from these articles that there has been a constant aim throughout to penetrate an almost untrodden field, which we know instinctively must lie just beyond our reach. It has also been the aim to improve the means for securing as reliable data as possible to be used in making further advances in the desired direction. The present article treats of a means of making the gnomonic projection, and gives a few illustrations of its application to crystal work. There remain at least two other methods to be described. These latter are needed to place the whole series on a complete and practical working basis. We should then be able to describe a crystal with little dependence upon algebraic methods, and the results of our work should pave the way for really effective mathematical treatment in the future.

New Haven, Conn., Jan. 1917.

Richardson—Note on the Age of the Scranton Coal. 243

# ART. XXII.—Note on the Age of the Scranton Coal, Denver Basin, Colorado;\* by G. B. RICHARDSON.

In the course of a reconnaissance in the Denver Basin, Colorado, in 1910–11, I traced, over a considerable area on the plains east of Castle Rock, a zone of coal beds carrying fossil leaves which Knowlton considers to be of post-Laramie age. On stratigraphic evidence I correlated this coal zone with the Scranton coals, which a number of years ago were mined in a shaft 20 miles east of Denver, and which, ever since the publication of the Monograph on the Denver Basin,<sup>+</sup> in 1896, have been referred to the Laramie formation. This discrepancy in age assignment prompted the desire that more field work be done before publication of the results, but the opportunity not having arisen it seems desirable, considering that the Denver Basin is the type area of the much-discussed Laramie formation, to publish the evidence now.

The coal zone referred to occurs between 900 and 1200 feet above the base of the Laramie formation. It crops out over a considerable area and has been prospected in a number of places, especially in the vicinity of Calhan and Fondis. Only here and there the coal is pure enough to warrant opening country banks, such as the Purdon mine in sec. 27, T. 11 S., R. 61 W., and the Moseby mine in sec. 18, T. 13 S., R. 62 W. The coal is a low grade sub-bituminous variety. I have traced this coal zone to within 15 miles of Scranton, in sec. 16, T. 3 S., R. 65 W., and although actual connection with the Scranton coals by following the outcrop is impossible, because of the cover of later deposits, it is evident from the field relations that the Scranton beds are in the zone traced.

The following list of fossil leaves from this coal zone were collected by the writer and C. W. Cooke in 1910 at the localities mentioned : Sec. 30, T. 9 S., R. 60 W.; secs. 7 and 33, T. 9 S., R. 61 W.; sec. 27, T. 11 S., R. 61 W.; sec. 18, T. 13 S., R. 61 W.

List of fossil leaves from upper coal zone, Denver Basin; by F. H. KNOWLTON.

> Pteris undulata Lx. Ficus spectabilis Lx. Laurus socialis Lx. Platanus Haydenii Newb.

\* Published by permission of the Director, U. S. Geological Survey. † Emmons, S. F., Cross, Whitman, and Eldridge, G. H., Geology of the Denver Basin in Colorado, U. S. Geol. Survey Mon. 27, pp. 373-375, 1896. Platanus rhomboidalis Lx. Platanus raynoldsii Newb. Populus nebrascensis Newb. Vitis olriki Heer Cissus lobatus-crenata Lx. Fraxinus eocenica Lx. Sequoia longsdorfii (Brgt.) Heer Lygodium kaulfussi Carya antiquorum Lx. Salix augusta Al. Br.

Knowlton reports that these leaves are of post-Laramie (Denver) age. They indicate, therefore, a reassignment of the age of the Scranton coal and the consequent modification of the constitution and delimitation of the Laramie formation in the type area.

This conclusion is corroborated by the record of a well sunk in search of oil near Sable Station on the Union Pacific Railroad in sec. 24, T. 3 S., R. 67 W., about midway between Denver and Scranton. The record was obtained by Willis T. Lee who, at my suggestion, visited the Denver Basin in 1915 and kindly turned his results over to me. Unfortunately the drillers did not keep the critical part of the record in writing but the results were confirmed independently by two men connected with the work. It is reported that a bed of conglomerate 50 feet thick, thought to be the Arapahoe, was encountered in the well about 350 feet below the Scranton coal and about 700 feet above a coal zone thought to mark the lower part of the Laramie formation. Because the record is from memory it should not be given too much credence, nevertheless it is of interest as supporting the evidence of the fossil leaves that the Scranton coal is of post-Laramie age.

# SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. Reminiscences.—A privately printed pamphlet of 21 pages has recently appeared, giving a memorandum of the remarks of DR. C. F. CHANDLER made at a dinner of the "Society of Gas Lighting" in New York City. As these reminiscences deal to a large extent with experiences and history concerning household illumination, beginning at a period when the candle was the principal source of artificial light, an abstract of this particularly interesting part of the address is given here.

Dr. Chandler spent his boyhood in New Bedford, where he became familiar with the whale-oil industry. At that time three or four hundred whale-ships were sent out from that place on voyages of from  $2\frac{1}{2}$  to  $3\frac{1}{2}$  years to all parts of the world. The oil of the sperm whale was used extensively for illumination at that time and sold as high as \$1.75 per gallon. The oil from the "right" whale, the one yielding "whalebone," was much cheaper, but it had a property of gumming up the lamps. Therefore, "Camphene," which was rectified spirits of turpentine, was introduced as a comparatively cheap substitute. This gave such a naturally smoky flame that it could be used only in lamps provided with chimneys. In order to modify this product so that it could be used in open wick lamps, it was mixed with a suitable proportion of alcohol to make "Burning Fluid." Both the camphene and the burning fluid were so volatile as to be dangerously inflammable, and they were the cause of many accidents, but there was no way to make these materials safe.

This was the condition of artificial illumination when Professor Chandler went to Germany to study in 1854. The next year in Berlin he saw "Coal-oil" used in lamps with chimneys. This product was manufactured from Boghead coal from Scotland by distillation. Two or three years later coal-oil factories were established in America, from Portland, Maine, to Wilmington, Delaware, in which imported Boghead mineral was used. Other materials were soon found also, such as Breckenride coal, Nova Scotia Albertite and West Virginia Grahamite, for which factories were started at or near the localities where they occurred. One of these factories named its product "Kerosene," and this name was afterwards given a much wider application. The demand for coal oil increased with great rapidity. It was furnished for about 50 cents a gallon and gave a beautiful light.

The coal-oil industry had hardly been established fully when attention was directed to "Petroleum" or "Rock Oil" which was found floating on pools of water in Western Pennsylvania and Virginia, and which had been used for some time for external application in the treatment of rheumatism. Some one in New Haven had seen a small specimen of this oil in the mineral collection of Yale College, so he became interested in it, went to Oil Creek in Pennsylvania and brought back a sample of the oil. This was examined by Professor Benjamin Silliman, the younger, who pronounced it to be a superior quality of crude oil, substantially identical with crude coal oil, or the kerosene of that time. The New Haven man, whose name is not given, organized the first Petroleum Company, and the collection of this oil for the purpose of illumination was started. Col. Drake, the superintendent of this company, was the man who first drilled a well for petroleum and he thus found oil in 1859.

Dr. Chandler gives an account of his important work in examining samples of dangerous kerosene which had been adulterated with the much cheaper naphtha. This work, and his publication of the results, brought about a proper inspection of the product, so that accidents from it became rare. He mentions the fact that as a boy he saw the first gas works built at New Bedford, but he states that illuminating gas had been in use in some of the larger cities for 25 years or more. H. L. W.

2. The Removal of Barium from Brines Used in the Manufacture of Salt.—W. W. SKINNER and W. F. BAUGHMAN have succeeded in removing all but traces of the barium in the brine used at a large salt works by the simple expedient of adding a proper amount of sodium sulphate (30 per cent in excess of the theoretical amount) in the form of "salt cake" to the brine before evaporation. It was necessary to add a little lime also to neutralize the free acid in the salt cake.

The occurrence of barium in the brines of the Ohio Valley District of West Virginia and Ohio has long been known. These brines are peculiar in being free from carbonates and sulphates. An analysis of one of them in parts per thousand is as follows: KCl = 0.61, NaCl = 63.95,  $CaCl_2 = 15.95$ ,  $SrCl_2 = 0.21$ ,  $BaCl_2 =$ 0.79,  $MgCl_2 = 5.28$ ,  $Fe(HCO_3)_2$  (?) = 0.08. The lower grades of salt produced from these brines have been found to contain as much as 5 per cent and sometimes 10, 16 and 18 per cent of barium chloride, and the poisoning of animals appears to have happened frequently by the use of such products. After the application of the new process the barium in all the grades of salt is so low that there is no danger in its use.—J. Indust. and Eng. Chem., ix, 18. H. L. W.

3. Ammonium Chloride as a Food for Yeast.—It is stated by CHARLES H. HOFFMAN that when this salt is added at the rate of  $\frac{1}{2}$  lb. to 1000 lbs. of flour in mixing dough for bread there is a saving of 30 per cent in the quantity of yeast required for baking. When a little calcium sulphate and potassium bromate are used in addition to the ammonium chloride a saving of 50 per cent in yeast results.

Upon investigating the subject carefully Dr. Hoffman has found that the ammonium chloride disappears entirely during the fermentation of the dough and that it is utilized by the yeast in forming new cells and is evidently converted by the yeast into albuminous matter. The saving in yeast is evidently due to the increased growth under the influence of a suitable food.—Jour. Ind. and Eng. Chem., ix, 148. H. L. W.

4. General Chemistry; by HAMILTON P. CADY. 12mo, pp. 522. New York, 1916 (McGraw-Hill Book Company, Inc.).— This is one of the "International Chemical Series." It is based upon the author's earlier "Inorganic Chemistry," being "something of an abridgement and much of a simplification" of the latter. It gives a very satisfactory presentation of chemical facts with a suitable amount of theory introduced in such a manner as to explain the facts as they are brought forward. Comparatively little attention is paid to the details of chemical experiments, so that it is to be presumed that the book is expected to be used in connection with another book, a guide to laboratory work.

H. L. W.

5. Generalized Relativity and Gravitation Theory.—In a number of papers published in several scientific journals during the past few years Einstein has developed a generalization of the original principle of relativity and has deduced certain results which seem to be of great importance. Since the mathematical analysis pertains to four-dimensional "space" and is extremely complex it will only be possible to give in this place a slight suggestion of these very original investigations.

The fundamental assumption consists in the "hypothesis of equivalence." Some idea of this conception may be obtained from the following considerations. Suppose an observer at rest in a gravitational field notices that all bodies fall with the same, constant acceleration. According to the non-generalized theory this state of affairs will be equivalent to the case where there is no gravitational field with the system of bodies at rest but with the observer moving in such a manner as to cause the bodies to appear to him to possess the same acceleration as they seemed to have when accelerated in the gravitational field. Because of the changes in the units of time and length in the two cases, the acceleration of the observer relative to the bodies in the second set of circumstances will not necessarily be equal numerically to the acceleration of the bodies in the first or gravitational field. Einstein's equivalence hypothesis consists in assuming that the two cases are not only equivalent for purely mechanical phenomena but that they are absolutely equivalent in all respects,electrodynamically, etc. Another noteworthy feature of Einstein's theory is that it involves only the Gaussian constant and the velocity of light in the free ether. No other quantities having physical dimensions are introduced.

Attention may now be directed to certain practical deductions from the general theory. In the first place, it can be shown that a ray of light will be deflected by a large mass just as if the luminiferous vibrations were endowed with ordinary momentum. Accordingly, when light from a star passes close to the sun and then proceeds in such a manner as to be aimed at the center of

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the earth at the instant when the light strikes the observer's eye, the star will appear to be displaced from its true position on the celestial sphere for the reason that in passing through the sun's gravitational field the ray will be bent out of the line in which it had previously been moving. The theoretical angular displacement only amounts to  $0'' \cdot 83$  which is probably too small to be observed.

A second special case relates to the solar spectrum. As a consequence of the fact that the rates at which synchronous clocks will run depends upon the potential of the gravitational field in which they are immersed, it follows that solar spectral lines should appear to an observer on the earth to be displaced toward longer wave-lengths. The magnitude of the shift is given by the approximate equation  $(v_0 - v)/v_0 = 2 \times 10^{-6}$  where  $v_0$  denotes the frequency of the light vibrations on leaving the sun, and vstands for the frequency on reaching the earth. Displacements of this magnitude and direction have been observed by L. E. Jewell and others, but, unfortunately for the present theory, it has not been possible to eliminate other causes which might have produced the effects observed ; increase of pressure, for example.

The only quantity of appreciable size for which the theory seems to account perfectly is the secular motion of Mercury's perihelion. If this be true, and not a coincidence, then Einstein has overcome a difficulty which has completely baffled all astronomers. A certain angle associated with the orbit of Mercury has the values  $\pm 118'' \cdot 00$  and  $\pm 118'' \cdot 58$  according to observation and to Einstein's theory, respectively. The agreement is perfectly satisfactory since the probable error of the experimental datum is  $\pm 0'' \cdot 43$ . On the other hand, according to Newcomb, the difference between observation and theory amounts to as much as  $\pm 8'' \cdot 48$  (instead of  $-0'' \cdot 58 \pm 0'' \cdot 43$ ) when the computations are based on the laws of Newtonian mechanics. H. S. U.

6. Ball Lightning.—The absolute reliability of the following interesting observations is vouched for by M. E. MATHIAS in a short article on the subject. On the fifteenth of last April, at about 18<sup>h</sup> 20<sup>m</sup>, a flash of lightning burned out the telegraphic apparatus associated with the observatory on the Puy de Dôme. One observer, who happened to be looking toward the south, noticed that the discharge first assumed the form of a ball of fire with a soft, delicate outline, then became spheroidal with the greatest diameter horizontal, and finally exploded, throwing out tongues of fire in all directions. At 18<sup>h</sup> 30<sup>m</sup> and 18<sup>h</sup> 50<sup>m</sup> two similar electrical discharges, which behaved in precisely the same manner as the first, were seen by all of the people at the signal station. The balls of fire made their appearance suddenly in the fog and at the same point in the air. They seemed to be very close, in fact, at the level of the second story of the dwelling house near the ruins of the temple of Mercury. The balls appeared to remain sensibly stationary for two or three seconds before bursting. Their color was primarily white with a slight

tint of mauve. The explosions sounded like the sharp crack of a whip and the associated luminosity was sufficiently intense and extended to light up the interior of the observatory. The apparent diameter was a little less than that of the moon. No other strokes of lightning occurred during the entire day.—Annales de Phys., vol. v, pp. 365, 366; May-June, 1916. H. s. U.

7. A Laboratory Course of Practical Electricity; by MAU-RICE J. ARCHBOLD. Pp. ix, 222. New York, 1916 (The Macmillan Co.).-This manual may be used in connection with any text-book and the experimental work suggested is supposed to be supplemented by lectures and demonstrations. Each page is essentially a skeleton of a laboratory report so arranged that the student has to supply the missing words in sentences, enter numerical data in ruled blank tables, and draw graphs on cross-Wiring diagrams for all of the experiments are ruled areas. given in the appendix. The number of exercises for each of the first, second, third, and fourth semesters is 27, 25, 24 and 22, respectively. To make the work practical, as many of the tests as possible are given with commercial apparatus. The experiments are carefully graded from very elementary qualitative manipulation of magnets to more advanced work, such as : "Methods of Connecting Polyphase Transformers," etc. The book is bound in the loose-leaf manner so that the instructor may change the order of the experiments. H. S. U.

8. The National Physical Laboratory. Report for the Year 1915-16. Pp. 80. Teddington, 1916 (W. F. PARROTT).—" The work of the Laboratory during the past year has been greatly affected by circumstances arising out of the war. A considerable part of the ordinary research work has been in abeyance; in its place a large number of special investigations have been undertaken for Government Departments, and the testing work for Government Departments has also very greatly increased. There has been a reduction in other test work, and the Laboratory has thus been almost entirely employed with Government work." For these reasons the report is of much less general scientific interest than usual. In the appendix is given a description of the new aeronautics buildings which were constructed in a very short time. The text is followed by large diagrams of the new structures in plan and elevation, together with photographs of the exteriors both of the buildings and of the wind-channels.

H. S. U.

## II. GEOLOGY.

1. Investigations of Gravity and Isostasy; by WILLIAM BOWIE, Chief of Division of Geodesy, U. S. Coast and Geodetic Survey. Special Publication No. 40, U. S. Coast and Geod. Surv. Pp. 196, page figs. 1-9, in pocket 10-18. Washington, 1917.— This publication extends and elaborates the lines of investigation begun in previous publications. In 1912 Bowie published the results of observations at 124 gravity stations in the United States. The present volume raises this number to 219 and adds 42 stations for southern Canada. The number of stations is thus a little more than doubled. The principal facts for 73 stations in India and 40 other stations are added, all reduced to the new method of determining the gravity anomalies. This large amount of data is subjected to analysis and several hypotheses of the nature of isostasy are tested by it.

As is familiar to those who have followed the previous publications, the hypothesis has been introduced that every topographic feature is balanced by a corresponding variation in density in a column reaching to a uniform level,-the level of complete isostatic compensation. Thus every unit column contains the same mass. Furthermore, the compensation is assumed to be uniformly distributed down to the level of complete compensation, but there to abruptly terminate. The data of geodesy shows that such a hypothesis of perfect, uniformly distributed, and local isostasy is much nearer the truth than a hypothesis of no isostasy, but it is obvious to geologists that this hypothesis must be a very much simplified and generalized picture of the truth. The new gravity stations show, as seen in fig. 11, a greater complexity of the map of lines of equal anomaly. number of new localities of high anomaly have been discovered, and, in general, where the stations are most abundant the anomaly gradients are steepest.

The question of local *versus* regional isostasy is important. The hypothesis of local isostasy satisfies the geodetic data about as well as that of regional isostasy up to some radial distance between 59 and 167 kilometers; but the geologic evidence favors regional isostasy to as great a limit as is compatible with the geodetic data and would favor a wide regional distribution for a part of it, a narrower regional distribution for another part.

The problem of the depth of compensation is also tried out by a number of solutions, with the result that Bowie states the best mean for the depth of the level of complete compensation under the hypothesis of uniform distribution to be 96 kilometers. He believes that future values derived from much more extensive data will fall between 80 and 130 kilometers. J. B.

2. The Prodromus of Nicolaus Steno's Dissertation Concerning a Solid Body Enclosed by Process of Nature Within a Solid. An English version with an introduction and explanatory notes by JOHN GARRETT WINTER, University of Michigan; with a foreword by WILLIAM H. HOBBS, University of Michigan. Pp. v, 124, pls. vii. Macmillan, 1916. This is Part II, Vol. XI. Humanistic Series, University of Michigan Studies, and is one of the "contributions to the history of Science."—Nicolaus Steno was born in Copenhagen, Jan. 10, 1638 and belongs thus to the generation which began to lay the foundations of modern science. In 1665 he was in Florence and in 1669 the Prodromus was published. It was to be the introduction to a larger work which was however never written. The work is remarkable in its record of geological observations and the sound-induction from them to principles concerning the nature of strata, fossils, crystals, and mountains. Where one solid object is contained within another, as a fossil shell, or a crystal, within a rock; how did the internal object come to exist and what was the nature of the surroundings at the time of origin? Thus the title covers the field of geology. The work antedates the real rise of geology by more than a century and is of importance to those interested in the history of science : if the time had been ripe it might well have led on to a fruitful germination. J. B.

3. Atlantic Slope Arcas; by PEARL G. SHELDON. Palæon-tographica Americana, Vol. I, No. 1, 101 pp., 16 pls. Harris Company, Ithaca, 1916.—All interested in the Tertiary Paleontology of North America have welcomed the useful and well illustrated "Bulletins of American Paleontology" which have been issued from time to time under the auspices of Professor G.D. Harris of Cornell University. The time has now come when publication in quarto form of more monographic papers may advantageously be undertaken. The editor of the Bulletins now offers the first installment of such a series under the name of "Palæontographica Americana, Vol. I, No. 1." This comprises a paper of 100 pages, with 16 plates quarto, on the Tertiary and recent species of the genus Arca from the Atlantic slope, with references to Cretaceous species and to others from the Antillean area, by Pearl G. Sheldon. This includes descriptions of five new forms. The excellent quality of the plates deserves special mention, considering the poor quality of many recent paleontological plates, especially of the European Tertiaries. It is to be hoped that the enterprise of Professor Harris will be so well sustained by those interested in this subject that the series may be continued indefinitely, as it is certain that the riches of our Tertiary horizons will afford material for many years to come.

W. H. DALL.

4. Iowa Geological Survey, Annual Report, 1914, with accompanying papers. GEORGE F. KAY, State Geologist. Pp. xxiii, 627, with 72 plates and 53 text figures, 1916.—Besides the administrative report and one on the mineral production of the state by the director of the Survey, this volume contains: (1) The iron deposits near Waukon, by J. V. Howell; (2) Pleistocene history of Iowa River valley, by M. M. Leighton; (3) Trilobites from the Maquoketa beds of Fayette County, by A. W. Slocum; (4) The origin of dolomites, by F. M. Van Tuyl (a summation of this paper appeared in this Journal for September 1916); (5) Physical features and geologic history of Des Moines valley, by J. H. Lees. C. S.

5. New York State Museum, Twelfth Report of the Director. Bull. 187, 1916, pp. 192.—In this report are set forth the activities of Director JOHN M. CLARKE of the Museum and the State Geological Survey, of the State Botanist, Entomologist and Archeologist, and of the Zoology Division. Great progress has been made in the exhibition rooms of the new Education Building, where striking installations may be seen of Iroquois wampums (here reproduced in two plates), seven life-sized groups representing the life of the Iroquois Indians (seven plates), and a testimonial case to former State Botanist Charles H. Peck, showing models of edible and poisonous fungi (four plates.) Three plates illustrate the report of progress in Paleontology, and four that in Zoology. The scientific papers accompanying the report are: (1) Landslides in unconsolidated sediments; and (2) Albany molding sand, both by D. H. Newlands; (3) On the genus Urasterella, by G. H. Hudson; and (4) Ancient water levels of the Crown Point embayment, by E. E. Barker. c. s. 6. Review of the Geology of Texas; by J. A. UDDEN, C. L.

BAKER, and EMIL BÖSE. Bull. of the Univ. of Texas, 44, 1916, pp. xi, 164, 1 pl., 10 figs.—Only 10,612 square miles out of 252,398 square miles constituting the State of Texas, are covered by detailed geologic maps. Reconnaissance maps are available for 114,066 square miles and exploratory maps for 53,735. For 87,367 square miles, or one-third of the State, no maps have been published. Likewise the detailed and reconnaissance reports on widely scattered areas, issued by various organizations, have not given a satisfactory view of the geology of the State and have been insufficient for use in comparative studies. The Review of the Geology of Texas, including a geologic map of the State, is, therefore, welcome. Under the heads Physiography, Geology, Geologic History, and Economic Mineral Products existing knowledge is classified, summarized, and briefly discussed. ' The student of Texas geology is given his bearings. Those who have had occasion to construct State geologic maps and to prepare comprehensive but condensed accounts of the geology of a large and diversified area will appreciate the time and thought involved in evaluating and correlating the work of various authors and in filling gaps in the record. The Director of the Texas Bureau of Economic Geology and Technology is to be congratulated on the successful completion of a most useful piece of work. H. E. G.

7. Annual Progress Report of the Geological Survey of Western Australia for the Year 1915; by A. GIBB MAITLAND. Geol. Survey Western Australia, 1916, pp. 44, 1 map.—Western Australia is the Nevada of the Southern Hemisphere. It owes its growth and development to its mines and receives its revenue chiefly from this source. It is but natural, therefore, that its Geological Survey should be almost wholly occupied with economic problems. During 1915 investigations were continued in the Murchison, Coolgardie, Yilgarn, and other gold fields; the building stones of the State were classified and described; limestones and foraminiferal sands were studied; possible sources of petroleum were examined and magnesite deposits were mapped.

H. E. G.

8. Economic Geology; by HEINRICH RIES, A.M., Ph.D. Fourth Edition. Rewritten, xx+856 pages, 291 figures, 75 plates. New York, 1916 (John Wiley & Sons. Price \$4.00). --Prof. Ries' new edition of his well-known text book, like its predecessors, is divided into two separate parts, "Non-metallics" and "Ore Deposits." Greater prominence is given to the former as it occupies the first part of the volume and 429 pages are devoted to it, while 329 pages are assigned to ore deposits. The book is much larger than the former editions and embraces a greater number of Canadian occurrences so that it is now essentially a text book of Economic Geology of the United States and Canada. The illustrations are profuse, and considerable discrimination has been used in their choice and arrangement. The text matter is supplemented by full statistical tables and by a complete and up to date bibliography at the end of each chapter.

The volume is essentially a compilation, but the numerous references, the complete bibliography and the illustrations taken from widely scattered sources attest to the far-reaching nature of the compilation. Personal experience of many occurrences, shown by many of the author's own photographs from scattered localities, fills in details ordinarily lacking in most compilations and the part dealing with clays is a contribution.

Part I is the most able and comprehensive treatment of nonmetallics that has yet appeared and it will serve as the standard text on that subject. In Part II the author has added much new material and made many changes in the mode of treatment and classification of the subjects.

The illustrations, tables and bibliography are commendable and the volume indicates discrimination and judgment on the part of the author in the selection of the subject matter. The book is the only one of its kind that covers the whole field of geology and will be of great value to teacher and student. On the other hand an introductory chapter, connecting together the two entirely separate parts of the book and pointing out their differences and relative importance, would enhance its value. Also, it is to be regretted that so much of the book is given over to descriptive material. This is of unquestionable value, but the volume might serve a wider field as a text if more space were devoted to the principles and theory of Economic Geology. This applies particularly to Part II. While the treatment of Part II leaves much to be desired the book as a whole is a valuable addition to the literature of economic geology and is bound to have a wide use as a text book in the United States and Canada. A. M. BATEMAN.

## III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Annual Report of the Superintendent, United States Coast and Geodetic Survey, E. LESTER JONES, to the Secretary of Commerce, W. C. REDFIELD, for the fiscal year ending June 30, 1916. Pp. 164; 53 illustrations. Washington, 1916.—This annual report recently issued gives the usual detailed statement (Part III), illustrated by many charts, of the field and office work accomplished by the Survey during the past year. Facts in

regard to the organization of the Bureau, and its immediate needs, in order that the work should go on efficiently, are discussed in Parts I and II. It is stated that important changes in the organization became effective in October, 1915, and further changes were made in July, 1916; gratifying results as regards output have already been noted. The needs of the Bureau, however, are many and important. It is now inadequately housed, in part in a building erected as a dwelling (the former home of Gen. Benjamin Butler) and in part in another structure originally built for a hotel. Considering the many lines of work carried on, not only administrative, but including a printing plant, a lithographic plant, a machine shop, etc., the conditions for effective work as well as for the safety of important documents are most unfavor-The situation now existing is presented to the public in a able. telling fashion by a series of photographs, showing how inadequately and inconveniently the charts and other materials are housed and with how great loss of economy the work must go on. Hardly less important than a new building are the needs of the Survey for expanding and perfecting its hydrographic and geodetic work. This subject is alluded to at some length in the notice of February, 1915, (see pp. 225-227).

An important memoir recently issued by The Survey is noticed on an earlier page (p. 249).

2. The Fundamentals of Psychology; by W. B. PILLSBURY Pp. ix, 562; 92 figs. New York, 1916 (The Macmillan Company).—This is a text-book, designed for relatively mature college classes, covering the range of topics usually deemed essential in a general introduction to psychology. Among such topics may be mentioned sensation, perception, attention, memory, reason, feeling and emotion, and voluntary activity. While not profound, the book will serve to put even a general reader in touch with the trend and many of the results of scientific psychological investigation. ROSWELL P. ANGIER.

3. Mechanisms of Character Formation: an Introduction to Psychoanalysis; by WILLIAM A. WHITE. Pp. 342. New York, 1916 (The Macmillan Company).—An introduction to what is commonly termed 'Freudian' psychology,—Freud, the Viennese psychiatrist, being the first to employ its unique method 'psychoanalysis.' This psychology aims to be "humanistic"; avoiding metaphysics and physiology alike, it formulates certain broad principles underlying behavior necessary to real appreciation of human beings, "especially as the priest and the physician knows them." Abnormal mental phenomena, mythology, dreams, etc. are the chief sources of material. The author presents uncritically much which requires further substantiation.

RICHARD M. ELLIOTT.

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# AMERICAN JOURNAL OF SCIENCE

# [FOURTH SERIES.]

# ART. XXIII.—Lava Flow from Mauna Loa, 1916; by T. A. JAGGAR, Jr.

In accordance with published expectations, the outbreak of Mauna Loa volcano, Hawaii, from the flank of the mountain, relieving the congested fluids within by effervescent ejection of them through gas pressure, took place May 19–31, 1916.\* The summit crater Mokuaweoweo did not appear to partake in the activity but one report from an exploring party which visited the floor of the crater in the summer of 1916 indicates that there may be some changes there. The account of the eruption here given will treat of the sequence of events at both Kilauea and Mauna Loa, 1915–16.

### Kilauea 1914–16.

The accompanying diagram (fig. 1) shows the fluctuation in level of lava in Halemaumau pit, the inner summit crater of Kilauea volcano, from the time of low level of the spring of 1914 to November 10, 1916. The black vertical lines show the height of the lava surface on the dates indicated, measured as depression below the rim of the pit in feet (left column of figures), the rim of Halemaumau standing 3700 feet (1128 m.) above mean sea-level as recorded by government bench marks. The elevations above sea-level are shown in the right hand column of figures. The periods of premonitory seismic spasms, believed to originate on Mauna Loa, are shown in the upper part of the diagram, as well as the gas and lava outbreaks of

\* This Journal, Feb., 1915, p. 167: Dec., 1915, p. 621; Annual Honolulu Chamber of Commerce, 1912, "The Cross of Hawaii," p. 12; Report Hawaiian Volcano Observatory, Jan.-Mar., 1912, Boston, p. 74; Bull. Hawn. Vol. Obs'y, vol. iii, No. 4, April, 1915, p. 39; Science Conspectus, Boston, vol. v, No. 4, 1915, p. 98.

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that volcano. In each case the local earthquake spasms occurred at the beginning of the pronounced subsidence of Kilauea lava after a temporary spurt of rising. A greater earthquake spasm of September, 1915, accompanied a more pronounced rise and fall at Kilauea.

The period September to November, 1914, exhibited high seismicity, which ceased when the summit crater flows of Mauna Loa poured forth freely in December.\* The rising of the Kilauea column spurted synchronously with the term of the Mauna Loa outbreak. Excepting for the July-September rise of 1915, the Kilauea column remained well below the 400-foot (122 m.) mark in the pit for the year February, 1915, to February, 1916, and then it climbed rapidly and a sudden spurt in May, 1916, culminated this rising spell, apparently in coördination with the new outbreak of Mauna Loa, and its swarm of earthquakes. Thereupon the lava of Kilauea sank suddenly with cataclysmal effect, accompanied by a localized carthquake spasm, and immediately recovered, rising with increased volume and rapidity until the present time (November, 1916), except for a sluggish month in September.

A general tendency to culmination at equinox and solstice is evident throughout the chart, and this habit has proved useful in guiding expectation, as for instance at the present time, when it is reasonable to look for a turning point in the great rise about December, 1916. The writer surmises, however, that a gas pressure control, with release and recovery dependent on accumulation and resistance in an adjusted conduit system, is effective in inducing rhythm in volcanic mechanism, as he pointed out for Mont Pelé in 1902, when, however, he supposed the gas to be water vapor. + The luni-solar stresses, superposed on the more dominant long-term trends inherent in the ever-rising gas and lava, probably act as trigger in opening and closing fissures, but the two curves respectively of summit culminations and sudden depressions at intervals of about eight months shown on this plat imply increasing maxima without respect to any obvious astronomic period. If this tendency led to a fourth crisis of like interval we might expect Halemaumau to overflow before February, 1917,‡ and thereafter to collapse still more profoundly than in June of 1916. But such a

\* This Journal, Feb., 1915, p. 167; Dec., 1915, p. 621; and May, 1916, p. 383.

+ Science, Nov. 28, 1902, p. 871. See also Gilbert, "Earthquake forecasts." Science, Jan. 22, 1909, p. 121. ‡ On Feb. 1, 1917, the lava was still rising and less than 50 feet (15m.)

below the rim of the pit. (Author, Feb. 2, 1917.)

Diagram showing fluctuation of level of lava in Halemaumau, in Fig. 1. relation to seismic and volcanic activities of Mauna Loa, 1914-1916.

speculation is futile without more extended records for comparison.

It is evident from this chart that the lava of Kilauea was slowly rising from April, 1914, to May, 1916, that it exhibited a spurt upward and a decline synchronous with each of the outbreaks of Mauna Loa 1914-15, November-January, and 1916, May-June, and that just at the close of the latter outbreak the Kilauea lava column sank suddenly to profound depths. It also appears that after this time the Kilauea lava column recovered with extraordinary rapidity, so that within five months it regained all that was lost by the subsidence and continued to rise still higher. In volume of lava this rising of 1916 amounted to an inflow of approximately 14,567,700 cubic meters from June 7 to November 16 inclusive (practically a cylindrical mass 335 meters in diameter, for the pit was left after the June subsidence with walls nearly vertical). This condition of verticality was quite different from the funnel shape of the vent as observed by the writer in 1909 and from 1912 to 1916.\*

## Earthquakes 1915–16.

The seismic prelude of the 1914 outburst of Mauna Loa has been described.<sup>†</sup> The seismographs of the Hawaiian Volcano Observatory registered local shocks per month in 1915 as follows:

#### 1915

Jan. 22	$_{\mathrm{shocks}}$	July	23	shocks
Feb. 9	"	Aug.	29	"
<b>Mar.</b> 22	"	Sept.	138	66
Apr. 17	"	Oct.	23	"
May 32	66	Nov.	13	"
June 30	"	Dec.	23	"

It will be seen from this table that from nine to seventeen local earthquakes are commonly recorded per month at the Whitney Laboratory,‡ that near solstice and equinox in 1915 the number tended to increase, and that the approach, culmination and recession of the autumnal equinox, allowing for a short lag, coincided with an extraordinary swarm of local quakings which led us to watch Mauna Loa attentively. At the same time the lava of Halemaumau sank suddenly. The phase intervals of the seismograms indicated origins up to sixty miles (97 km.), and while some of the shocks were of

\* Report Hawaiian Volcano Observatory, Jan.-Mar., 1912. Boston. Figures 13, 25, 27.

† This Journal, Dec., 1915, p. 623; Bull. Seis. Soc. Amer., Mar., 1915, p. 39.

‡ This Journal, Dec., 1915, p. 623.



FIG. 2. Diagram showing by height of vertical lines approximate number of local earthquakes per day registered at Hawaiian Volcano Observatory from April to July, 1916. The May crisis corresponds with Mauna Loa eruption, that in June with Halemaumau subsidence.

Fig. 2.

much nearer origin and felt sharply three miles (5 km.) northeast of Kilauea crater, the larger number were propagated from origins as far as the Mauna Loa rifts.

This September crisis of 1915 deserves close scrutiny in view of the double Mauna Loa-Kilauea culmination, accompanied with earthquakes and intense volcanic vibration, which happened eight months later. A similar seismic spasm, premonitory to, and two months before, the 1914 outbreak, occurred in September, 1914, when twenty-nine shocks were felt at Kapapala on the southeast flank of Mauna Loa from September 27 to September 28 and the seismologist of the Observatory reported\* that "without question this forty-eight hours . . . was a period more active seismically than any interval of like duration since the establishment of this station." A similar but milder seismic spasm had occurred during the early days of July, 1914 (fig. 1). Coördinately with each of these premonitory seismic events of 1914 there was a spurt of rather gradual rising of Kilauea lava followed by relatively sudden subsidence. The earthquakes, however, showed origins more distant than Halemaumau and were believed to arise on the Mauna Loa rifts.

The 1915 spasm as instrumentally recorded at the Observatory was described as follows by H. O. Wood, seismologist: "In the following six days (after September 16, 1915) sixteen well-marked local earthquakes were registered. None of these were felt close by the Observatory, but several, one in particular, were felt at Hilo, Kapapala and on the Hamakua coast.

"Most of these, while distinctly of local origin, were from more distant sources than the average of local shocks. Besides these there were thirteen, more or less, seismic disturbances grading in character and energy from well-marked earthquake wavegroups to those usually considered as volcanic-vibration wave groups. All these were of very small amplitude; and there is no genetic distinction between an earthquake record and a volcanic-vibration record. The former is a group of earthwaves with a distinct indication of fore-phases. Though Mauna Loa shows no sign from the Observatory, the possibility that these disturbances point to renewed action there cannot be overlooked.

"The week ending with September 29, 1915, has been marked by extraordinary local seismic activity—though none of the earthquakes registered have been felt at the Observatory or at the Volcano House. However, within three miles (5 km.) in the direction of Hilo several have been felt, particularly on September 26, some quite sharply.

> \* Bull. Hawaiian Volc. Obs'y, Nov., 1914, p. 134. † Bull. Hawaiian Volc. Obs'y, Sept., 1915, pp. 100 and 103.

"Disturbances were registered during the twenty-four hour periods, ending in the forenoon of the dates specified, as follows:

September 23, three well-marked shocks and about nine other disturbances; September 24, one well-marked shock and about five others; September 25, two well-marked shocks and one other; September 26, the day of the crisis, forty-four wellmarked shocks, thirty-seven definite shocks of lesser amplitude and eighty-three other wave-groups, some of which almost surely were minor earthquakes; September 27, ten wellmarked shocks and twelve others, more or less; September 28, ten well-marked shocks and three others; and September 29, one well-marked shock and eight other disturbances. The total for the week, therefore, is 108 earthquakes about half of which were of very small amplitude and none of large amplitude, and 121 other definite wave-groups, many of which probably were minute earthquakes and many, doubtless, only groups of volcanic vibrations."

It will be seen from this description that the total of all local seismic disturbances instrumentally recorded at Kilauea, greater and smaller, for the fortnight ending September 29, 1915, was 258. The 138 for the month in the foregoing table refers only to positive earthquakes.

The earthquakes of the nine days September 17 to 25 were especially strongly felt in the Mauna Loa axis (districts Hilo, Hamakua and Kau), while those from September 26 to 29 were sharply felt in the Kilauea axis (district Puna). The Weather Bureau reports\* that eight shocks, September 17, 18, 19 and 25, 1915, were reported from Kohala, Hamakua and Hilo districts, especially severe the 19th and 25th at Ookala and Honomu. These districts lie on the north side of Mauna Kea in the line of the long axis of Mauna Loa which extended would divide the island of Hawaii into almost equal halves. In southern Hawaii no earthquakes were reported from Weather Bureau stations for September, and none whatever for the date of the instrumental crisis September 26.

Thus it would appear that the actual equinox period September 19-25, 1915, was marked by a few strongly felt earthquakes in the Mauna Loa axis; that this was followed by a spasm of trembling partly felt on Kilauea mountain, very intense on September 26 and declining thereafter, and exhibiting earthquake origins locally remote from Halemaumau; and that a great crisis of subsiding lava in the Halemaumau pit took place at the average rate of sixteen feet per day during the six days September 22-28, with a sudden acceleration in the subsidence September 25-26 (fig. 1). In view of the record of a year before, September-November, 1914, and the

\*Climatolog. Data, Hawaii Section, Sept., 1915, Honolulu.

similar seismo-volcanic crisis first on Mauna Loa and then on Kilauea in May-June, 1916, it seems probable that the September disturbances of 1915 indicated a spasm of rising lavafoam splitting its way upward in the edifice of Mauna Loa, attaining release of gas pressure in some unobserved irruption subterranean or submarine, and so temporarily impoverishing Kilauea as to induce subsidence in its lesser edifice. Even an outward eruption of fume from the Mauna Loa rifts enduring several hours might take place at any time in the year during the long cloudy spells, and pass entirely unperceived except as a seismic event. Complete observation of Mauna Loa will remain impossible until there are permanent observers housed above the cloud zone.

In 1916 the earthquake frequency increased by leaps and bounds with the outbreak of Mauna Loa and during the subsidence cataclysm of Halemaumau. The numbers in the following table for 1916 are only approximate as the seismograms have not yet been measured:

#### 1916.

Jan.	16 shocks before Jan. 15.	June	. 418	shocks
Feb.	) Incompletely recorded because of	July	17	"
Mar.	$\int$ storm damage to laboratory.	Aug.	13	66
Apr.	14 shocks.	Sept.	15	"
May	454 "	Oct.	23	"

That there was seismic activity coördinate with the volcanic events cannot be questioned (fig. 2). Whether the deeper earthquake rift movements were cause or effect may well be considered a subject of controversy. There is no reasonable doubt that the epicentral tract of the earthquakes of May 19-28, 1916, lay along the southern rift zone of Mauna Loa in the district of Kau. (See map of Hawaii, this Journal, Dec. 1915, p. 622;) nor that the earthquakes of June 5-7, 1916, centered about Halemaumau.

In proof of these places being the respective seismic centers may be cited the fact that the first series was felt principally at Hilea and Papa, on opposite sides of the place of lava outflow and that the second series was felt most strongly at Kilauea. The Weather Bureau reports<sup>\*</sup> that felt earthquakes on the island of Hawaii for 1916 were as follows:

#### January 1916.

6 earthquakes in north Hawaii.

In south Hawaii :--

Jan. 8, 5:20 P. M., Hilea (SE. base Mauna Loa) 10, 5:20 P. M., Glenwood (NE. slope Kilauea) 21, 4:20 P. M., Pahala (SE. base Mauna Loa) 21, 5:00 P. M., Hilea

\*Climatolog. Data, Hawaii Section, Jan.-July, 1916, Honolulu, U. S. W. B.

#### February 1916.

No earthquakes reported.

March 1916.

2 earthquakes in north Hawaii. In south Hawaii :---Mar. 27, 6:00 P. M., Hilea

April 1916.

4 earthquakes in north Hawaii. (1 heavy, 28th) In south Hawaii :--Арг. 28, 7:30 A. м., Glenwood " 66 " Hilea " 66 "

Kealakekua (W. base Mauna Loa) Holualoa " " " Holualoa

#### May 1916.

No earthquakes reported from north Hawaii. In south Hawaii :---May 20, numerous earthquakes in Hilea.

66

#### June 1916.

2 earthquakes in north Hawaii. In south Hawaii :---

21,

.

June 12, Hilea (severe) 66 Glenwood

"

Hilo

24, Hilea (severe)

#### July 1916.

2 earthquakes in north Hawaii.

In south Hawaii :---

July 2, 5:25 A. M., Glenwood 11, 10:00 р. м., Hilea (severe) Glenwood Pahala 12,7:55 A. M., Glenwood 21,

The absence of complete records for May is covered in the Weather Bureau published data by a blanket statement of unusual volcanic activity. There are unfortunately no Weather Bureau stations on the southwest slope of Mauna Loa. The earthquakes from May 20 to 30 were generally felt in Kona aud Kau. The earthquake of June 12 was felt generally over the island of Hawaii just three weeks after the Mauna Loa outbreak as was the earthquake of April 28, three weeks before the outbreak. It will be observed that Hilea, which bore the brunt of seismic activity of the eruption, also reported

more earthquakes throughout the seven months than any other station and greater severity in the shocks felt during and after the lava flows.

Mrs. Z. V. de la Nux, living at Hilea, was so impressed with earthquake swarms of Saturday and Sunday, May 20 and 21, that she noted the times of the stronger shocks in the afternoon and evening of both days as follows :

May 20	, 1916.	May 21, 1916.
11:55	А. М.	2:45 р. м.
1:35	P. M. (strong)	3:40 ''
$1:\!40$	" " "	4:10 "
$2:\!25$	"	4:15 "
2:30	66	4:23 "
3:07	"	4:24 "
5:17	"	4:26 "
5:18	"	4:30 "
7:05	"	5:28 "
7:10	"	5:33 "
$7:\!28$	" (strong)	5:40 "
8:00	"	5:53 "
8:08	"	6:10 "
8:20	"	
8:22	"	
8:23	" "	
8:40	"	
9:09	"	
9:23	"	
9:28	"	
9:32	"	

One Maeda, a Japanese living in the Mohokea hills (a large ancient crater) five miles (8 km.) nearer the lava source than Hilea, felt more and stronger earthquakes than the inhabitants of Hilea. He reported thirty strong shocks in three hours on the evening of May 20. On the other hand, neither Waiohinu nor Pahala, respectively eight and six miles from Hilea, on either side of it, and both on the Mauna Loa flank, felt any such number of shocks as were reported from Hilea. Waiohinu, an equal distance from the lava source with Hilea, reported on the evening of May 20 "one or two shocks in the last two days." An overseer in the upper Waiohinu sugar fields, however, reported several earthquakes felt in the open on the afternoon of May 20. Pahala for May 20 reported "an earthquake this morning." The middle Kona district on the west flank of Mauna Loa reported two earthquakes on the morning of the 20th. It was evident, therefore, that the position of Hilea on a line at right angles to the lava rift opposite the point of emission, was peculiarly sensitive to the jarring of

the outbreak and that the felt earthquakes did not travel far from the source at the time of actual rapid rise of lava near the surface.

Cursory inspection of the seismograms of the Mauna Loa eruption period of 1916 shows

- May 19, morning, continuous trembling.
  - 19-20, trembling followed by a shock.
  - 20-21, trembling followed by several shocks.
  - 21-22, some trembling, but increase of definite shocks.
  - 22-23, many distinct shocks of large amplitude.
  - 23-31, earthquakes continued, generally decreasing in amplitude, except for occasional ones of very large amplitude. One of these appears May 25-26 and another May 30-31.

June 1-3, Four ordinary earthquakes.

The larger amplitude shocks of the closing days of the eruption were felt especially strongly on the Mauna Loa slopes. The writer felt a sharp shock at Waiohinu about 1:50 A. M., May 27. Mr. Wood was on the mountain at an old cone east of the lava source on May 30, when\* "at about 8:45 P. M., a short sharp earthquake occurred, plainly felt by all three of us sitting or reclining on the cinders in the reëntrant of the cone. This shock was felt sharply at Waiohinu and at Kapapala. At Hilea it was felt as the strongest shock of the entire series connected with this eruption. Within less than a minute after the shock there occurred a spasm of greatly increased action at the southern active lava vent, with the jetting of lumps of lava and a great increase in the flow. This quickly declined to normal."

This observation is of interest in showing the immediate kinship of the lava-gushing and the earthquakes. The above cited sequence in the seismograms shows that the earthquakes waxed from a continuous jarring to large numbers of moderate shocks in four days, and thereafter for eight days there was fairly regular decrease in numbers of shocks and increase in their occasional intensity. The approximate numbers of earthquakes per day are shown diagrammatically in fig. 2; the column of figures on the right of diagram signifies numbers of earthquakes and larger wave groups; the length of the vertical line corresponds to number of such shocks counted on the seismograms for each twenty-four hour period following the morning of the date indicated.

The swarm of local earthquakes which accompanied the sudden drainage of the lava from Halemaumau, June 4 to 7, 1916, increased in number to about double the maximum registered

\*Bull. Hawaiian Volc. Obs'y, June, 1916, p. 54.

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during the May crisis in a similar period of four days from June 3 to 6 and declined more abruptly, the greatest number of shocks being recorded and also felt during the twenty-four hour period following the morning of June 5. This happened simultaneously with the most rapid fall of the lava. The sequence is shown in fig. 2, and the following notes were made by the writer from casual inspection of the seismograms:

- June 1-2, two shocks.
  - 2-3, two shocks.
  - 3-4, eight very small shocks.
  - 4-5, 69 shocks of various amplitudes.
  - 5-6, about 217 shocks ; but from noon to 6 p. m. June 5 increasingly, a steady trembling followed by steady decline.
  - 6-7, 43 definite shocks, one of large amplitude but not larger than some of June 5.
  - 7-8, 25 definite shocks, some rather strong.
  - 8-9, 12 very weak shocks.
  - 9-10, 9 very small shocks and one very strong one.
  - 10–11, 13 feeble shocks.
  - 11-12, 4 shocks, one a considerable earthquake followed by continuous trembling for three hours.

This second seismic spasm was described by the seismologist\* as comprised wholly of local shocks of feeble character felt near Kilauea crater but attracting no attention at Hilo or Pahala. None was stronger than III of the Rossi-Forel scale. They proceeded from origins nearer to the Observatory than the shocks of the May spasm. Volcanic vibration exhibited larger amplitude than usual during the week of this June crisis and the tilting of the ground as registered seismometrically changed from northeastward to southwestward about the time of the great subsidence.

# Explosion of May 19, 1916.

The first recorded symptoms of actual outbreak on Mauna Loa in 1916 were earthquakes recorded in a swarm by the seismographs during the very early morning hours of May 19, and felt, in part, as smart shocks at the southern end of the island of Hawaii. Glow and fume, also, above the mountain were reported seen before daybreak from a vessel. Nothing was seen from the vicinity of the Observatory until 7 A. M., when a white cumulus rose above the profile of Mauna Loa south of the summit region and developed two pronounced jets of fume and a vortex ring. At 8 A. M. the two jets were united into one and the column was 20,000 feet (6100 m.) high above its base (fig. 3). The higher fume jet bore approximately S.

\* Bull. Hawn. Volc. Obs'y, June, 1916, p. 49.

FIG. 3.



FIG. 3. Fume jet over southwest rift of Mauna Loa. 8 A. M., May 19, 1916. Looking S. 84°W., taken from Volcano Observatory at Kilauea crater by H. O. Wood.

 $82^{\circ} 30'$  W., and the lower one approximately S.  $85^{\circ} 30'$  W., from the Observatory, indicating an explosion about the 11,000-foot (3360 m.) contour of Mauna Loa along a N.E.–S.W. rift over a distance approximately one and a half miles long (2.4 km.) and a few miles to the southwest of the crater Mokuaweoweo. This preliminary explosion of vapor reached its maximum force in a little over an hour, and by 8:15 A. M. was declining so that by 10 A. M. the stem of the column had disappeared. The fume made a milky bluish cirrus which spread over the sky and was visible above the lower rain cumulus until nightfall, developing a ripple pattern. The color was quite distinct from that of ordinary clouds and showed iridescence in places.

Some lava was ejected from this high vent according to the reports of cattlemen, and a line of whitish discoloration along the high rift at the site of this outbreak was seen and photographed from a distance of about ten miles (16 km.) south by an Observatory party in July. This was probably a spatter of pumiceous lava adjacent to the fissure.

A little fume was seen at sundown May 19 and 21 in thin wisps near the place of first outbreak. Miss Paris in upper Kaawaloa, the middle Kona district, reported seeing in the morning of May 20, a "pillar of smoke" high up the southern Mauna Loa slope. Local earthquakes diminished on the 19th after the first storm of vibrations, increased on the 20th in frequency and amplitude, and thereafter were registered by hundreds as recorded above.

# Lava Outflow May 21, 1916.

At about 11 P. M. May 21, liquid basaltic lava spouted up in fountains along the main southern fissure system of Mauna Loa north of the well-known cone called Puu o Keokeo in the middle of the southern lobe of the mountain at an elevation higher than 6600 feet (2000 m.) above sea-level. As is usual with Hawaiian lava, the outwelling was quiet and produced no sufficient noise or quaking to awaken inhabitants of the coastwise plantations nine to fifteen miles (15 to 24 km.) away. The glow on the sky, however, became very brilliant and was first seen from the Observatory in a direction S. 66° W.

During the night, the writer accompanied by Mr. H. O. Wood, seismologist, motored from Kilauea by the government road to Kau-Kona boundary making a partial circuit of the center of outflow east, south and southwest at a distance from sixteen to eleven miles (26 to 17 km.) of Puu o Keokeo. A column of fume illumined red from below was seen at apparently about the same distance inland everywhere from Waiohinu westward looking north across the lava flows of 1868, 1887 and 1907. A brilliant radiance extended southeast from the fume column showing that the first extension of the lava from the vent was eastward, all being dark to the west of it. It was a clear, calm night, and there was not the slightest noise or perceptible quaking of the ground. We were obliged to awaken the residents of Hutchinson Plantation and Waiohinu who were unaware of the eruption although the sky above them was brilliant with a ruddy glare.

At 2 A. M. May 22, W. Vredenburg, manager of Kahuku Ranch, rode inland between the 1868 and 1887 flows and after passing the koa forest, came to the open country of the upland and saw two flows in rapid motion headed respectively southeast and south-southeast at a distance approximately ten miles (16 km.) north of the road.

At daylight May 22 looking northwest from the Kahuku Ranch gate, we saw the main fume column extending itself in a series of puffs developing to the right or northward. This may have been the beginning of the second flow which poured westward during the next twelve hours. This western, or Kona flow, passed through the land called Honomalino, a cattle ranch, and its progress southwestward was mostly accomplished during this day, for no glow in that direction was seen before daylight, whereas on the following night most of the illumination was on that side.

### Distribution of 1916 Lava.

To make clear the general arrangement of these flows of 1916, there is here reproduced (fig. 4) a tracing from a rough sketch map made by a government surveyor of the Territory of Hawaii after the eruption showing known trigonometric stations. As shown on Baldwin's map of Hawaii,\* the 1907 lava flow originated in a fissure extending some miles above Puu o Keokeo, but the main outpouring of that year was from an opening below Puu o Keokeo, which perhaps remained open after the upper fissure had closed so that it came to be considered the 1907 source. Fig. 4 shows only this lower 1907 The 1916 lava welled up cracks extending three and orifice. a half miles (5.6 km.), about N. 10° E. from Puu o Keokeo, the zone of outpouring being about thirty feet (9 m.) wide, and bending more to the northeast above. There is more lava to the north and east than the map shows. The elevation of this source rift lies from 6500 to 7500 feet (2000 to 2300 m.) above sea-level. Along it about ten new cones were developed in 1916 of lava and vari-colored cinders, and the upper mile (1.6 km.) is solfataric with much sulphur deposit and no lava except as spatter. The lava flow eastward in Kahuku poured from cones for about one mile north of Puu o Keekee, and

\* Loc. cit., p. 622.

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the flow westward from cones still farther north, the line of cones being nearly straight (fig. 5).

Comparing the map of Hawaii (this Journal, Dec., 1915), it will be seen that the new flows straddled the northward extension of the 1907 flow, coming out of the same general zone of cracks, and forked southeast and southwest in the same fashion as the 1907 flow had done, but from a higher point on the mountain, and with a more extensive spread of the lava to



FIG. 4.

FIG. 4. Sketch map 1916 lava flows, showing general arrangement fissure eruption north from Puu o Keokeo. Map furnished by courtesy Territorial Surveyor of Hawaii.

the east. This was due to the presence of a flattening of the mountain surface near Puu o Keokeo and it was probably this flattening and the expenditure of the flood in two branches thus early which partly saved the ranches and prevented the flow from reaching the government road. There is great need of a good topographic map of Mauna Loa for the benefit of ranches during such a crisis. The flood of lava which spread eastward during the first night was the widest and probably the thickest portion of the 1916 basalt and this area has tongues eastward not shown on the map. An Observatory party skirted the edge of this eastern flow on May 30 and "encountered many thin narrow tongues (from five to eight or ten feet (from 1.5 to 3 m.) in depth and from fifty to two hundred yards (46 to 180 m.) in width) radiating to the southeast and east. These departed from the main stream at higher and higher points. Wherever junctions were seen, the departures of these minor branches appeared capricious—i. e. no evidences of local damning or pooling were seen. Though much thinner and less massive than the main stream, these were still fuming, and in varying degrees the air above them

Fi	G.	- 5.



FIG. 5. Line of heapings at fissure-source, 1916; lava flows looking north from Puu o Keokeo. Eastward flow in foreground. Photo. Miss Tulloch, May 26, 1916.

was in a state of shimmer from heat. The emanation of the fumes, however, furnished a more reliable indication of their course than the heat-disturbed air above them."\*

### Journal of the Eruption May 22.31, 1916.

The following narrative is quoted from the writer's account prepared on June 1:†

"During the day, May 22, the accumulated lavas of the upland were discharging southwestward from a vent about two miles (3.2 km.) above Puu o Keokeo. As no glow was seen west of the

\* Bull. Hawaiian Volc. Obs'y, vol. iv, No. 6, p. 56, June, 1916. † Bull. Hawaiian Volc. Obs'y, vol. iv, No. 6, pp. 40-43, June, 1916.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 256.—April, 1917. 19 vent before 6 A. M., this southwest flow across Honomalino Ranch must have progressed at least six miles (9.6 km.) in twelve hours, for at 6 P. M. it was within three miles (4.8 km.) of the road at Honomalino. The settlement here lies in a valley and the flow was headed directly for the houses. The timber could be seen burning from the road and the flowing lava, advancing down a ten degree slope, from the housetops. Detonations from exploding gas, and the crash of falling trees, could be heard. The homes were temporarily evacuated but fortunately the flow stopped at this point, its front resting on a hillside forested with lehua, kukui and guava. This flow was rugged aa eight to twelve feet (3 to 4 m.) in thickness and a quarter of a mile (400 m.) wide along its lower course.

At eight o'clock on this night, Monday, May 22, the fiery radiance above the fountain head and the flows probably reached its greatest brilliancy. Unlike the night before, the glow was now all to the west of the column of fountain fumes which shot up in purling volutes on the right spreading to the west in a high cloudy haze, which was lighted from below a bright red from the glowing river of melt in Honomalino. On the left a great purplish swirl of smoke from the burning forest rose and curled over to the east. There was darkness over the Kahuku flow, showing that for the time the lavas on that side were sluggish and congealing.

During the night May 22-23 there was revival in Kahuku. Messrs. Waldron and Hardy found the front of the first flow nearly motionless at altitude 5,500 feet (1700 m.) by aneroid. At 1 A. M. May 23, an arm of this flow more southerly in trend developed near the source and for two hours advanced brilliantly. Then it became sluggish, cooled down and stopped. About daylight the western glow and the fountaining at the source had both diminished.

On May 23 motion within the Honomalino flow diminished rapidly. In the morning flowing lava could be seen and trees were still being overturned. At 3 P. M. high ohia trees were still standing in the midst of the flow, their trunks blazing, a few blocks were tumbling at the front but no pasty lava was to be seen. The side of the flow resembled a heap of burning anthracite coal, with flames playing through the incandescent blocks, and the only odors were a strong smell of burnt charcoal and occasional coal-gas (fig. 6).

At 7 P. M. the glow seen from the south indicated distinctly a revival of the southeast flow toward Kahuku. All was dark west of the fume column. There was a tapering line of reflected light on the clouds trending south-southeast, and in the same direction along the ground below could be seen a low straight-topped film of smoke, highest near the source and lowest at the lava front. Over this smoke could be seen the radiant glow from the lava.

May 24. On this date the writer inspected the Kahaku flow eight miles (12.8 km.) from the road and in the region between the

1868 and the 1887 flows. At about seven miles (11.3 km.) there is a broad rolling paddock with sparse koa. Above this is a steeper slope of koa forest, down which the ancient aa flow, Pele o Iki, had cut a swath. Above this forest is an extensive bushy upland consisting of old pahoehoe and aa which stretch out as far as the eye can reach toward distant cones and on the west to the rugged ridges of the 1887 flow.

On reaching the upper edge of the koa slope, it was found that the fronts of the new flow had moved down more than a mile



FIG. 6.

Fig. 6. Front of Honomalino lava flow in forest, May 23, 1916. Photo. Colville.

(1.6 km.) since the previous morning and were now close to the forest. On riding up the west side of the flow, which was in process of overriding Pele o Iki, we came to the moving lava advancing in billows and cascades of red hot viscous liquid and overflowing the already cooled as surface of the previous day. The moving liquid lay in streams from 100 to 300 feet (30 to 90 m.) in width and one of these only 100 yards (91 m.) from us was coursing down the main lobe of the previous day, driving in front of it a fan-shaped pool of dark red color with a sugary surface which advanced at the rate of perhaps a half a mile (800 m.) per hour. The cascades above carried huge rafts and bowlders of a ten to thirty feet (3 to 10 m.) in diameter, and these blocks moved along majestically in a procession, about as fast as a man might walk.

The advancing flood became deflected to the west and tumbled over the bank of congealed lava into the vegetation at our feet not fifty yards (46 m.) away. The liquid would develop a cindery surface and then congeal into what appeared to be a glowing mass The only odor was of the carbon gases and these were of coals. strong and oppressive, particularly as we were directly to leeward and a fresh breeze was blowing from the northeast. The heat was intense, and occasionally fierce small whirlwinds developed at the edge of the hot flood and moved along the border with a whistling noise, carrying up clouds of grit and smoke. Out in the molten river gigantic bubbles would occasionally burst with a thud but there were no fountains as in Halemaumau. Cascade beyond cascade could be seen up stream vanishing into the hot vibrant fume of the distance and I was much impressed by the piling-up effect of this motion, the advance being always by overflow. This is in marked contrast to the usual mechanism of pahoehoe flow where the new floods push out from beneath in tongues which break through the skin, or else a crust breaks up and founders in the rising melt. No crusts whatever were seen forming on this aa. There were moving blocks and there was the red hot flood. When it cooled, it appeared to cool as a unit and the new floods overflowed it. There were one or two patches of roundish shape in the chilled part of the flow which resembled pahoehoe. These were probably blocks transported from far above where near the vent the flow actually was pahoehoe.

The front of the overriding flow was advancing in the direction  $S.15^{\circ}$  E. The under-flow was in two lobes, one leaf-shaped and headed in this direction and one more to the east pushing forward very slowly at a rate estimated sixty feet (18 m.) per hour.

Between 2 P. M. and 7 P. M., according to Messrs. Bonesteel and Moses, the fan-like advance pool which we had seen overran the leaf-shaped lobe and coursed down the koa slope carrying the forest before it, following the western margin of Pele o Iki. This became the main Kahuku front and flowed a mile farther, stopping on the paddock about seven miles (11 km.) from the road. The flood would surround the trees, burn them and uproot them, and in some cases the koas were seen to be carried along upright like blazing torches before they toppled over and were engulfed. At the front the flow was only a few hundred feet wide.

An interesting mechanism which occurred whenever the flow poured over old cavernous pahoehoe was furnished by gas explosions in caves. This was probably coal gas mixed with air. Detonations were frequently heard, and the writer saw the dust from one of these explosions a few feet away, puff up through cracks above a cavern. The old rock was very hot, and it was evident that some of the hot gases and perhaps the new lava had penetrated a subterranean tube. Mr. L. A. Thurston in the same region on the following day found several of these places where the whole roof of the cavern had blown off and large blocks of rock were strewn about several feet from the orifice. The noise of the lava itself in motion was not great. It was a splashing sound, and where the pasty lava dripped the quickly cooled droplets fell with a tinkle. The bubbles bursting made thudding noises, but there was no sustained explosive fountaining such as the writer had imagined. In general the advancing floods were unexpectedly noiseless. The horses advanced fearlessly to within two hundred feet of where the liquid lava to windward was actually cascading on to the grass and bushes, and showed as complete indifference as they would to a camp fire. In the forest, of course, there were the noises of falling timber and crackling flames.

The various estimates of rate of motion of lava flows which different observers reported of these flows were based usually on observed progress of the runways compared to a man's pace. But the runways are no measure of the movement of the lobe as a whole, nor is the movement of a lobe a measure of the advance of the whole arm of lava which may be slowly pushing down a grade. The flows progress apparently by impulses of overflooding into hollows, the central vent above feeding a great pooled area. Somewhere the margin of this area finds outlets. From what the writer saw he would judge five miles (8 km.) an hour to be a fast rate for the runsh of the runways, and half a mile (800 m.) an hour for average general progress of a flow as a whole during its most rapid advance on a steep slope. This progress appears to be not gradual, but in spasms, with intervals of many hours of stagnation.

At midnight May 24, the profile north from the Kahuku gate showed a column of dark smoke thought to be burning forest, bright flames at two points shooting up on its right, and strong radiance both east and west of the smoke column. The smoke and flames were at the front of the Kahuku flow, and so nearer the observer, while the radiance was from the floods of molten stuff in the distance.

R. McWayne about this time reported for the head of the Honomalmo flow a cone about the 7000 foot (2300 m.) level ejecting with a roar high lava fountains and blocks of rock. There were two main vents in action, both above Puu o Keokeo and in a line with it, the higher feeding several tongues in motion toward Kona, the lower supplying the Kahuku flows.

Vredenburg left the Kahuku flow at 2 A. M. May 25. The main lobe had then advanced three quarters of a mile in twelve hours, and the eastern lobe had pushed forward somewhat along the east margin of Pele o Iki. The main front was stagnant and three hundred feet (92 m.) in width, widening above. The main direction was about S.15° E.

During this day the main flow advanced a quarter of a mile (400 m.) farther, there was some activity and burning forest on the front of the east lobe, and to the westward glowing lava could be seen in motion overriding the flows already cooled.

At 11 P. M. May 25 the mountain profile showed a red general glow behind a screen of cloud, with rapid rising white cumulus over the fountain head.

May 26. A second visit to the Honomalino flow on this day showed that it had cooled off remarkably. Only a few glowing and flaming cavities a few inches across could be found. The surface aa was cold. One could walk out over the middle of the flow. Nearly all the imprisoned timber had fallen. There was little smoke, but a hot refraction haze over the profile of aa showed that all was glowing inside, and this was evident when one looked into the deep cavities. Rare small explosions were heard. Many leaves on the fallen trees in the flow were still partially green. There was no channel discernible in the middle of this arm. The slope of the ground was carefully measured and found to be ten degrees.

L. A. Thurston's party visited the Kahuku flows. Motion was seen in a stream carrying a procession of large blocks within a branch flow extending south-southwest from the upper part of the main flow. Rapid flow was seen in overriding layers of the main arm upstream. Vredenburg made his way on foot around the foot of the west branch, which he found nearly stagnant at the front and climbed Puu o Keokeo, a cone about 200 feet (61 m.) high. From there looking up the line of cones northward he saw a line of fuming vents, two nearer ones vomiting lava. The first was a throbbing pit seventy-five yards (68 m.) away sending a stream twelve feet (4 m.) wide towards Kahuku (fig. 5). The second, much farther away, was a cone with a red stream flowing down its Kona flank. The thunderous noise under foot and a whiff of overpowering sulphurous gas drove him back along the line of white stained cracks which extends from Puu o Keokeo to the source of the 1887 flow. The flows of 1916 at the source are a rough pahoehoe.

May 27. Messrs. Farrell, Bryan, Forbes and Barnes visited the source region from Papa. Mr. Farrell describes a line of fuming cracks as far as the eye could see up Mauna Loa northnortheast. A few miles northeast was a cone that appeared to be the first source of this lava eruption.\* From this a fresh flow had poured southward to a second nearer cone which was spouting lava in jets every few seconds. This flowed down in a northern branch of the Kona flow toward Papa, and was a very rough glistening sponge-like black pahoehoe. Sulphur smell was noticed and the noise was a heavy roar attributed to the thudding fall of the fountain material. Lava could be seen in motion toward Kahuku from the vent to the south. Some Pele's hair was seen. There was no trembling of the ground observed.

The mountain profile from the south at 9 P. M. on May 27 showed marked dwindling of size of fume column and of glow. The fountain fume rose in small, rapid, bright jets and a band of slight radiance extended a short distance east from it; then came a wide zone of darkness and finally a slight whitish glare, probably a forest blaze at the extreme east limit of the lava. From the Volcano Observatory at Kilauea only a faint radiance was seen.

At 8 A. M. May 28, Vredenburg was at the vents and saw sluggish pahoehoe emerging from the Kahuku vent, and occasional spasmodic spouting from the northern cone. He could see no lava flowing towards Kona. No movement was seen in the Kahuku flows.

May 30 and 31 H. O. Wood and D. Lycurgus made the circuit of the Kahuku flows on the south, east and north. The fountaining at the sources was ceasing, and motion in the flows had stopped."

### Activity at the Source.

A. Farrell describes a visit to the still active cones from the Kona side,\* May 27, 1916. The ascent was in the forenoon from Papa to the 7000-foot (2300 m.) level. "For miles before we reached the spatter-cone we heard a confused but continuous roar directly ahead of us. . . . We saw ahead the final line of old lava ridges, which looked down on the fresh black flows. From behind these ridges came the bombardment of the fountains, and the fire of mounting jets appeared under the smoke cloud which rose over our heads."

On reaching the last ridge glistening black pahoehoe in confusion was seen, glowing with red fire here and there in mounds, overhung on the south by a curtain of heat waves. A spatter-cone was belching a few hundred yards away, its walls split by a great rent north and south. Its interior glowed and two jets were rising from it. One was of great volume, seemingly four or five times the size of an average Kilauea fountain, and spurting high into the air an intensely red incandescent fluid as a single jet. The jet split and branched into filagree, falling as black rocks "in sharp outline against the flaming new-born fluid." Probably the cone marked "7050 ft." was the one referred to (fig. 4).

There was no roar of explosion whatever, only the clatter of falling slag striking as it fell. This larger jet was on the west side of the cone. The smaller one was more to the north, throwing small bits of slag twice as high as the larger fountain, which as they descended showed the effect of the trade wind, for all that fell on the outside steep slopes of the cone fell upon the leeward side. The cone was slightly higher on the leeward (west) side. (See fig. 5. The heapings on the left are the leeward accumulations. The cone seen by Mr. Farrell was probably the larger smoking peak in the distance.)

\* Pacific Commercial Advertiser, Honolulu, June 4, 1916, pp. 7 and 10.

"These lava bits seemed to freeze tightly to the mass of the cone when they fell outside." At this time the number of fragments that overtopped the walls in both jets was very small compared with the quantity that seemed to descend perpendicularly back into the liquid lava.

The action of the fountains was spasmodic in the extreme. "It appeared that we had reached the cone as it was attaining a maximum. Some jets rose in a futile manner, as though the heart action were dying away, but another would spurt to the former height. Two hours after we arrived at the cone the fountaining appeared to be almost done; but within a few minutes it resumed more violently than ever; the roar was more overwhelming and the smoke bank soared higher and in a livid sheet tinged with crimson."

Climbing an old cone, Mr. Farrell saw the white streak far up the mountain which had been the source of the explosion of May 19, and as he watched it on the afternoon of May 27 he observed white vapor arising in two cylindrical pillars which joined a cloud bank hovering above. This vapor increased "filling the rent from rim to rim," but it nowhere rose far from the ground except at the site of the two high columns.

Mr. Farrell noted a number of tongues to the main lava flood on the Kona side. The upper portion of the flows showed little motion above. "Once or twice the black wall of the river shelled off, and gleaming red showed forth for a minute before the surface cooled again." At the same time men farther down the mountain saw this stream moving rapidly as aa, suggesting that in the pahoehoe part of the flow above the liquid moved in tunnels, whereas the aa moves in overriding surface sheets.

Mr. Farrell found filamentous lava glass, "Pele's hair," scattered in wisps on the surface of the old lava hundreds of yards to leeward of the fountains. A conspicuous whitish sulphur bank was seen along the northern part of the rift giving off strong sulphurous fumes. On the cone occupied the magnetic needle of a hand compass was erratic.

Mr. Farrell assumed in his account that the source rift opened first in the northernmost cone seen. This assumption is not justified by the facts. Dr. A. L. Day and Mr. H. O. Wood explored the source region at the end of June<sup>\*</sup> and found much crystalline sulphur and other solfataric staining along the cracks of the rift zone for a mile above the line of the main flow source, the latter line extending two and onehalf miles (4 km.) above Puu o Keokeo. The solfataric cracks extended to an old cone three and one-half miles (5.4 km.)

\* Oral communication.

north of Puu o Keokeo, showed only a little lava sputter of 1916 origin, and ended abruptly at this cone. About ten miles (16 km.) to the northeast across the gently swelling desert and some 4000 feet (1219 m.) higher, could be seen the white rent in the basalt carapace of Mauna Loa whence had issued the fume explosion of May 19. If we examine the map and photograph of the source region (figs. 4 and 5) in relation to the order of events cited in the foregoing Journal of the eruption we find the following :

- (1) The largest cluster of new cones, the first and eastward outbreak of lava, the most voluminous and most repeated and eastward flowing, were all from the southern third of the active 1916 rift and immediately north of Puu o Keokeo.
- (2) The second outbreak of lava, making the southwest Honomalino flow of less volume than the Kahuku flow southeast, and of less endurance, came from the middle third of the active rift and farther north than No. 1 above.
- (3) During the closing stages of the eruption May 30-31 Messrs. Wood\* and Lycurgus reported that conspicuous activity of the dying cones was seen in sputtering vents of the *northern* part of the line of still glowing heaps of lava and cinder which marked the rift line. This and the solfataric character of the northern third of the active belt, sulphur deposits being distinctive of waning eruptivity, would imply that the third stage of activity on the source rift north of Puu o Keokeo was from the northern third of the 1916 fissure.

It will be remembered that on the early morning of May 22 we saw new fume columns developing northward in a series of jets like a moving locomotive, as we looked from Kahuku gate toward the eruptive center. During the preceding night the southeast flow was in action. The following day and night produced most of the western flow. The remainder of the journal accentuates eastward flow on the nights of May 22, 23, 24, 25 and 27, and for the morning of May 28 describes slow eastward flow from the large southern cone and sputter from the northern one.

All of these facts appear to mean that the lava outbreak May 21 near Puu o Keokeo did not split its way down the mountain from the high gas vent of two days before, but welled up independently at the Puu o Keokeo center, and then split its way northward, the maximum outflow of the rift being from near this center and eastward, the secondary western flow emerging from the same fissure a mile and a half (2.4 km.) to the north, and the final solfataric action of the

\* Bull. Hawaiian Volc. Obs'y, June, 1916.

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# 280 Jaggar-Lava Flow from Mauna Loa, 1916.

eruption taking place still farther north where the sulphurbearing gas could make its deposit along a crack not clogged by freshly congealed magma.

## Pahoehoe and Aa Lava.

The moving basaltic lava of the 1916 outflow was aa, or block lava, away from the vents but in the lava stream courses close to the rift source the surface had the ropy and mem-



FIG. 7. Detail of aa lava, Honomalino flow, showing tendency of surface rock to separate into endlessly divisible fragments. Flames in crevices when picture was taken, May 23, 1916. Photo. Colville.

braneous character of a coarsely vesicular pahoehoe. The transition to block lava took place along the course of the flows within a few hundred yards of the source. There was gaseous explosion ejecting pumiceous fragments at the cones until the end of the eruption, for much of the lava is there buried under such light fragments.

The aa of Kahuku which the writer saw in rapid motion on May 24 consolidated into finely vesicular fragments of light weight, but that of Honomalino was largely coarse, heavy and lithoidal (fig. 7). The specimens of pahoehoe collected near the source during activity were fresh black glistening vitreous basalt of a very foamy or sponge-like consistency. The aa, on

FIG. 7.

the other hand, wherever the writer saw it, was always strongly oxidized and tarnished to various colors from the time of its first consolidation. This appeared inevitable from the manner of its shrinkage into almost endlessly divisible blocks as it cooled with flames playing through the interstices (fig. 7), the whole process appearing to be a consolidation throughout the mass, intimately bound up with gas action, in contrast to the skinning and crusting over with a definite dermal layer which is the distinguishing feature of pahoehoe. This outer layer appears to confine the melt by forming a relatively non-conducting envelope and the consolidation is gradual from without inwards, the magma being compelled to stretch, crack, break through or push from under the outer membrane, which in turn confines the heat and preserves an inner filament in a liquid condition.

The stages of consolidation of aa as described in these flows by different writers it is of some interest to compare. The present writer's observations on May 24 of liquid aa in rapid motion are quoted above in the journal. In that same Kahuku district two nights earlier Mr. Thornton Hardy saw a flow rapidly cool down and he has kindly furnished me with the following description:

"The flow Mr. Waldron and I had under observation was the toe of the Kahuku flow, which we reached at dusk on the evening of May 22. When we first saw it the point was descending rather steeply into a gully leading down into the koa forest just below. Shrubs, bushes and stunted trees stood in its path, and these, from time to time, it battered down and buried with small avalanches of loose slabs, or grubbed up and pushed ahead of it, flaming brightly. The movement was very slow, only a few feet an hour, and later became almost imperceptible. From the first, it was to be measured only by its advance on some fixed landmark, such as a doomed tree.

Our first intimation of proximity was the great shimmering billows of heat we saw rising ahead of us, as far upward as the eye could reach, drifting down the wind and troubling the dying light of day. Next, we heard the crunching, crackling, tumbling, crashing noise of the march itself. At that point, the tiptoe of the column, much restricted from its width above, was perhaps fifty feet (15 m.) across, and, sloping steeply backward, thirty feet (9 m.) in depth. There was no sound of gushing or hissing, though here and there, at wide intervals, jets of gas burned with a silent blue flame, barely luminous : and there was almost no odor. What little there was smelt like the fume of an anthracite fire. The surface of this massive wedge—for such it seemed, rather than a river, a flow, or any of the other conventional epithets applied—was incredibly rough and rugged in texture and dull black in color. More than anything else it resembled a glacial

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moraine of half-burnt coke; but where fresh coke is a hard, bright, silver grey, the cooling lava was the sheer negation of color. Coal black, soot black, charcoal black, all connote shades or qualifications which the lava did not have. It was as lackluster as soot, but without the same soft depths of obscurity; it was as friable as charcoal, but without the shining grain; it was as hard and brittle as coke, but without the tough cohesiveness and definite structure; nowhere had it a suspicion of the iridescence seen in coal.

Fractures and fissures showed the interior mass to be glowing hot, but the brightest surfaces, seen at midnight, never approached the sparkling incandescence of a blacksmith's welding heat, to say nothing of the intense radiance of molten iron. The shades toned down from a cherry red, where freshly exposed, to dull maroon, fading imperceptibly into black.

The mechanism of the onward creep was complex and curious. As the foremost faces of the coming cliff cooled dead black, apparently the contraction tended to split off fragments from the hot masses behind. A narrow vertical fissure would open behind an outcropping, deepen gradually and widen at the top until, pushed outward from behind, a section of the face would tilt forward until it lost its balance, or its adhesion at the base was overcome, and go crashing down the declivity. These fragments might be tens of tons (milliers) in weight or no bigger than a coal hod. By watching the growth of the fissures, one could predict the next fall ten or fifteen minutes in advance.

Wherever the cleavage took place, the newly exposed surface glowed a bright cherry-red, and at first, after each fracture, we looked closely for jets of molten lava from the core within, or at least for some appearance of tumescence such as one would expect to denote the urge of liquid pressure behind, but at no time was there the slightest suggestion of viscous or even malleable consistency. On the contrary, the fractures were always sharp, hard and clean. Usually they were succeeded at intervals of a minute or more by small rapid avalanches of glowing dust, pulverized so fine by the stresses of contraction and rupture that they trickled with the smooth swiftness of rivulets of fire, but the likeness was never deceiving for more than a moment: they fell with a crystalline, tinkling sound, like a cascade of shivered glass. Whatever note might for a passage of time be in the ascendant, this tinkling accompaniment of fairy bells never was absent and, in moments of comparative quiet, it was the dominant characteristic of the orchestration.

As the larger fragments were nudged forward down the slope, they formed, as it were, a revetment fringing the base of the levee behind them, so that the flow—I revert to the inadequate accepted term—was constantly obliged in its descent to climb up over its own disjecta membra. It did not fumble them along before it; it buried and surmounted them. Though the appearance was that of a moraine, the action, as I thought I understood it, was quite different. I fancied if one could have examined the flooring underneath, one would have found none of the deepscored surfaces left by the march of the glaciers. In the faint light of the stars and the reflected glow from the clouds overhead, there was no discoverable movement of the mass, as a mass. The forefront of it, always preserving its appearance of solidity but always changing and always renewed from the rear, stumbled on blindly downhill. Thirty feet behind the line of recurring fractures, a cross check on fixed objects revealed no motion discernible to the unaided eye during a period which saw the toe of the flow advance perceptibly.

Twelve hours after our first sight of the Kahuku flow it had become virtually stationary. The tinkling, crumbling clatter of tiny fragments was still audible, but the movement of masses had ceased."

On May 23 in the morning the Honomalino flow at its front had cooled to a degree similar to the one described by Mr. Hardy and was described as moving very slowly, making loud explosive noises supposed to be due to the action of hot lava on vegetation, and cracking open at its front so as to reveal cherry red mobile lava in a semi-solid condition. By the afternoon of that day there was hardly any motion and the lava front resembled a heap of blackened cinders with bluish flame through them.

### Close of the Eruption of Mauna Loa.

There is no evidence that the Mauna Loa eruption of 1916 came to an end suddenly. As in other volcanic eruptions it began by an escape of gas and probably very light lava foam from a high orifice. This was followed by a more voluminous but still frothy magma from fissures 4000 feet (1200 m.) lower, this fluid poured right and left from six to eight miles (10 to 13 km.) in both directions and gas appears everywhere to have been the dominant uplifting and propelling agent causing high jets that built pumice and lava cones along the fissure, permeating the magma to produce extreme vesicularity, flaming, subdivision into aa fragments, intense oxidation and strong exhalation of carbon and sulphur gases, the latter chiefly at the During the closing days of the eruption all of these vents. gas phenomena ceased gradually from the fronts of the longest flows back to the rift source. The last activity appears to have been gas and pumiceous lava spurting in the cones, sluggish pahoehoe near them and the deposition of sulphur and sulphates along the upper cracks.

The period May 31 to June 5 was not recorded by direct observation of the region of outflow on Mauna Loa, so that it is entirely possible that the last-named date may have been a time of rapid sinking-back of the lava in the fissures. On that day Kilauea suffered sudden and cataclysmal subsidence.

## The Great Subsidence in Halemaumau.

In the Kilauea fire pit during the month preceding the outbreak of Mauna Loa there was an elliptical lava lake which on April 30 measured 775 feet (236 m.) long east-west by 665 feet (203 m.) wide north-south. This lake was confined by an annular bench of overflow the outer periphery of which was an oval 1110 feet (338.5 m.) long by 1000 feet (305 m.) wide. There were two islands in the lake, respectively 400 feet (122 m.) and 250 feet (76 m.) long and 55 feet (17 m.) and 41 feet (12.7 m.) high. These islands had gradually developed during the spring from tilted bench crags on the border of a less symmetrical lava pool which had risen and surrounded them. The depression of the lake on April 30 below the rim of Halemaumau pit was 321 feet (98 m.). Occasionally overflowing the benches, the lake rose slowly in May so that the depression was approximately as follows:

April 30	321	feet	(98	m.)
May 17	300	6:	(91.7	m.)
Мау 19, 8 р. м.	295	66	(90	m.)
May 20, noon	290	"	(88.4	m.)
May 21	285	66	(86.9)	m.)
May 23	270	66	(82.3	m.)
May 24	265	66	(80.9	m.)

Analysis of this rise reveals the remarkable fact that from May 1 to the morning of May 19 the average rate of rising was less than one foot per day, whereas beginning suddenly on the evening of May 19, the rising increased to a daily average of six feet per day for the five days May 19-24. The morning of May 19 witnessed the high explosive outburst of Mauna Loa, and May 24 represented about the culmination of the period of lava outflow on Mauna Loa.

On May 24, 1916, the Kilauea lava column reached a turning point and thereafter for eleven days to June 4, it sank, with average subsidence of  $3\cdot3$  feet (1 m.) per day. The measured depression below the 3700-foot (1125 m.) contour, the rim of Halemaumau, including the great collapse of June 5-6 and the recovery later, are shown, graphically on fig. 1, and in the following table:

May 25	270 feet ( 82.3 m	.)
May 26	273 " ( 83·1 m	i.)
May 27	278 " ( 84·9 m	i.)
May 28	270 " ( 82·3 m	i.)
May 29	280 " ( 85•5 m	.)

May 30	283 feet	( 86·3 m.)
May 31	286 "	( 87·3 m.)
June 2	295 "	( 89·9 m.)
June 3	293 "	(89·3 m.)
June 4	302 "	(92·1 m.)
June 5, 2:30 P.M.	549 "	(167·4 m.)
June 6, noon,	673 "	(205.1  m.)
June 7-22	rising	
June 23	592 "	(180 <sup>.</sup> 3 m.)

After May 30 large blocks of the inner bench of overflow began to crack and occasionally were engulfed in the lava pool. After several days of remarkably quiet action in the lake with thick blankets of skin on the magma and sluggish fountaining, there began on the evening of June 4 turbulent effervescence of large gas fountains, increased rapidity of convectional surface streaming and the tumbling of avalanches.

The seismographs indicated a growing swarm of narrowly localized earthquakes and during the following twenty-four hours, night and day, these were frequently perceptible both at the Observatory and at Halemaumau as small earthquakes or as prolonged trembling sufficient to rattle windows. They were not accompanied with seismic noises.

June 5, 1916, was a day forever memorable in the annals of Kilauea volcano, like July 11, 1894, when there had been a similar subsidence of 220 feet (67.1 m.) in twenty-three hours.<sup>\*</sup> By actual survey the lava lake, which was 340 feet (103.7 m.) below the rim of the pit at 8:30 A. M., June 5, 1916, sank 200 feet (61 m.) in seven hours, or about 30 feet (9 m.) an hour; and during the following twenty-one hours the lava subsided another 133 feet (41 m.) The rate of drainage must have been very similar to that described for 1894 by L. A. Thurston<sup>†</sup> who wrote at that time that the column fell steadily at the rate of about twenty feet (6 m.) an hour from 10 A. M. to 8 P. M.

The effects in both cases were the same, crashing avalanches and spectacular avalanche clouds of dust, seething lava foam, benches falling inward bodily (fig. 8) and disclosing red-hot parting planes, incandescent debris slopes and in the closing stages of the cataclysm, pahoehoe lava springs welling out from wall fissures which made fiery cascades down the inner slopes to the remnant pool beneath.<sup>‡</sup>

The islands in the 1916 event sank bodily with the lake as though the solidified saucer, of which they appeared to be pro-

\* W. T. Brigham, Memoirs B. P. Bishop Museum, No. 2, vol. iv, Honolulu. p. 187. †Loc. cit.

Described more fully, Bull. Hawaiian Volc. Obs'y, June, 1916, p. 47.

truding parts, itself subsided through withdrawal of support beneath. 'They never appeared to be floating. Shoals were disclosed (fig. 9) when the lake had gone down not more than thirty feet (9 m.) and the pool became converted into a torrent pouring eastward toward drainage conduits which seemed to be of limited size in the floor of the sinking saucer. Tumbles of talus from the benches into the lake were not deeply engulfed, but protruded above the shallow pool. It is difficult,

FIG. 8.



FIG. 8. East inner wall of Halemaumau, 10:30 A. M., June 5, 1916, during the sudden subsidence. Benches falling, incandescent talus, lava lake on left. Depression 400 feet (122 m.). Photo. Jaggar.

however, to imagine what supported the saucer and what was withdrawn when the saucer sank. The subject of the crosssection of Halemaumau deep down is a matter for special discussion.

The withdrawal was so extensive that the old walls outside of the recent inner benches of overflow were undermined and crumbled inward, especially below. The upper rim of the pit remained unchanged. Throughout the day the writer was able to work with transit and camera on the rim without inconvenience except for occasional whirlwind blasts when it was necessary to lie down. The earthquakings were insignificant and there was little smoke or fume. The solid rock built up of lava flows which bounded the inner pit with funnel slopes was so affected by withdrawal of support beneath that a terrific spalling inward of this rock sent up red avalanche clouds, upset all the higher remnants of recent benches and changed the shape of Halemaumau from a funnel to a cylinder with vertical and, in some cases, overhanging walls.

Two days later this cylinder was 700 feet (214 m.) deep with



FIG. 9. Lava pool converted to torrent, island remnants and shoals, Halemaumau, June 5, 1916, 10:30 A. M., after 60 feet (18 m.) of rapid subsidence, looking N.E. Matches fig. 8 on the left. Photo. Jaggar.

a large crusted lava pool surrounded by talus in its bottom. After June 9 rapid recovery took place and for twenty-three weeks the lava rose at a rate averaging 3.34 feet (1.01 m.) per day and the rise continues at the time of writing so that on November 16, 1916, the depression of the surface was only 161 feet (49 m.) below the rim of the pit (fig. 1).

# Conclusions.

The outflow of lava in 1916 from Mauna Loa brings to a close the eruptive period of that volcano 1914–16.\* The \*Bull. Hawaiian Volc. Obs'y, April, 1915.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 256.—APRIL, 1917.

diagram, fig. 1, summarizes the relations of the outbreaks to local seismicity and to the fluctuations of Kilauea lava. Contemplation of the Kilauea curve leaves little doubt, to the writer's thinking, that the Mauna Loa and Kilauea lava columns are connected, and that the connection is that of correlated gas vents and not that of hydrostatic siphon tubes. The Kilauea spurts appear to be due to gas pressure accumulation probably in Mauna Loa chambers, relieved by gas discharge, along with seismic jarring, at intervals, so as to induce Kilauea subsidence. The gas discharge in the larger unpluggings of the Mauna Loa rift carries magma foam with it, inducing central and summit eruption at the beginning of the eruptive period, and lateral fissure eruption at the end. Floods of highly vesicular olivine basalt accompanied both initial and final eruptions, and high fume jets initiated both outpourings. Kilauea as a decadent volcano of older origin, acting as a gas pressure-gauge adjacent to and partially buried by the young and vigorous Mauna Loa,\* becomes much more intelligible than the steaming Kilauea of nineteenth-century geology. We have to thank Albert Brun for inaugurating, by controversy as well as by contribution,<sup>†</sup> the new conception of volcanoes as gas-engines and not as steam-engines.

Hawaiian Volcano Observatory, Nov. 25, 1916.

\* Cross of Hawaii, by T. A. Jaggar, Annual Honolulu Chamber of Commerce, 1912.

<sup>†</sup> A. Brun, Recherches sur l'exhalaison volcanique, Paris, Hermann, 1911. R. A. Daly, The nature of volcanic action, Proc. Amer. Acad. Arts and Sci., vol. xlvii, No. 3, June 1911.

Sci., vol. xlvii, No. 3, June 1911. F. A. Perret, Volcanic vortex rings, etc., this Journal, Nov. 1912, p. 405; The Ascent of lava, this Journal, Dec. 1913, p. 605; Volcanic Research at Kilauea in the summer of 1911, this Journal, xxxv, 139, 273, 337, 469, 611; xxxvi, 151.

A. L. Day and E. S. Shepherd, Water and volcanic activity, Bull. Geol. Soc. Amer., vol. xxiv, pp. 17-27, Dec. 1913.

# ART. XXIV.—The Formation of Salt Crystals from a Hot Saturated Solution; by E. TATUM LONG.

IN 1909 Professor G. D. Harris propounded the theory that the "Domes" of Louisiana and Texas are due to the force exerted by growing crystals at some great depth where a saturated hot solution from below became cooled and thus caused a precipitation of the salt.

In the June number of this Journal of last year Mr. Stephen Taber published an article on "The Growth of Crystals Under External Pressure." While the latter's experiments were in progress other investigations were started with the object of demonstrating from the viewpoint of geology and physical-chemistry that a saturated hot solution of sodium chloride when cooled, would deposit salt, and that this released salt would form crystals which in growing would exert an appreciable force and which would continue to grow in spite of resistance.

Mr. Taber's object was "determining whether it is possible for growing crystals to exert a linear pressure and if so, the conditions under which the pressure is developed." Though the purpose of the two investigations was thus somewhat different, one fact at least seems to have been demonstrated in common.

In Mr. Taber's article, "The Growth of Crystals Under External Pressure," he constantly lays stress upon the necessity that the surface where growth is to take place be in contact with a supersaturated solution. In the experiment here described, another salt was used from those employed by Mr. Taber, but the same fact was again demonstrated. The crystals ceased to grow as soon as the supersaturated solution was withdrawn from their surface. Furthermore the rate of growth was largely governed by the amount of flow and hence the quantity of salt released for crystallization.

An apparatus (fig. 1) was set up with a reservoir A placed considerably above the point where crystallization was to take place, C. This reservoir contained cold water and a good deal more common table salt than the water could take into solution. A was connected with B, a second reservoir, also with salt in excess, by a long glass tube with rubber connections to short glass tubes, placed in the rubber stoppers in the side necks of the two receivers. On the lower connection a stopcock was placed so as to regulate the flow of the cold brine into B. A Bunsen burner was placed under B and a thermometer, T, was run through the top stopper well down into the



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hot brine. During the first step of the experiment, a second glass tube was run through the stopper (X) in the right hand side neck of B without rubber tube connection, at the outer end of which, however, there was a connection on which another stopcock was placed. During the second step, instead of the glass tube, a common rubber finger was used. It was punctured at the tip and a small glass tube inserted, while the open end was stretched over the same rubber stopper, X.

The most effective temperature to bring about deposition from the hot brine was found to be between 70° and 75° C. Below that, there was not enough NaCl absorbed for an appreciable deposition, and above 75° recrystallization went on in B. As enough hydrostatic pressure could not be obtained by raising A so that the passage through the stopper at X could be kept open, it had to be frequently cleared by a steel rod with a right-angle turn run through the top neck of B. This stopper was also removed to replenish the supply of salt, but otherwise B was kept air-tight to prevent crystallization by evaporation.

After five or six days the hot brine became sufficiently saturated to begin the formation of crystals at C, the first point where crystallization took place, and therefore the point where it was always farthest advanced. At the end of a few weeks the crystals had grown so that they completely filled the tube and stopped the flow entirely. Figure 2 shows the conditions at this stage of the experiment. The hydrostatic pressure was increased but no seepage could be forced through. This run was repeated several times under slightly different conditions, but the result was always the same even though the time varied somewhat.

The second step was then started : to make the crystals grow against pressure, in this case a rubber finger. This was so successful that after a month, one crystal expanded the rubber wall of its prison so far as to puncture it. The tiny hole was cemented over and effectually closed, but in a few days another crystal went through at a different point, this time making a much larger hole.

On page 550 of Mr. Taber's article he says, "The tendency to form crystals is much stronger in some substances than in others, but it is never so strong as to cause growth on a face which is not in contact with a supersaturated solution, and even if a growing surface is in contact with a supersaturated solution, the relative rate of growth is chiefly controlled by the rapidity with which the material for growth is made available."

The results of the two series of experiments thus independently worked out would therefore seem to establish without question, not only that a hot saturated brine will deposit salt when cooled, but that the developing crystals in growing exert a lateral pressure sufficient to permit continued growth even against opposing external forces.

Some of the stages of growth of the crystals in this experiment are given in figs. 3-6. Fig. 3 shows the collapsed finger

FIG. 3.





FIG. 5.



FIG. 6.



with only the liquid running through. Later the crystals began to expand the rubber, and at the end of the first run, the connection with the stopper sprang a leak; fig. 4 shows the condition of the second run, after the first puncture and before the second one, which ended the experiment. Fig. 5 is an enlargement of 3, and 6 an enlargement of 4.

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# ART. XXV.—An Upper Cretaceous Fulgur;\* by BRUCE WADE.

THE family Fulguridæ was proposed by Grabau and Shimer+ in 1909. It includes a well-defined group of pyriform gastropods that are very common in the Tertiary and Recent of North America. The group was first recognized by Fischer: in 1887 and given the rank of subfamily under the Turbinellidæ, and its unity was again pointed out by Cossmann§ in 1901. Since the assigning of the group to the rank of family in 1909 the name Fulguridæ has been used by some paleontologists to include Tudicla, Pyropsis, Perissolax, Busycon, Strepsidura, Levifusus and Pyrifusus. Of these genera Pyropsis, Pyrifusus and Perissolax are especially profuse in the Upper Cretaceous of North America. Tudicla, Levifusus and Strepsidura are most abundant in the Eocene. Busycon, commonly known as Fulgur, and sometimes Sycotypus in part, is very abundant in the later Tertiary and Recent.

The Fulgurs are especially interesting on account of their limited geographic range which is restricted to the eastern United States. This distribution is explained by the fact that the animal is deprived of an active free-swimming larval stage by the loss of the velum before the young emerge from the egg-capsule. The geological range of Fulgurs is also of The most common and important Pliocene to Recent interest. Fulgurs are: Busycon carica and Busycon canaliculatum. Among the forms ranging from Miocene to Recent Busycon perversum is important. Busycon excavatum is found from the Miocene to Pliocene. Busycon pyriformis, Busycon incile and Busycon coronatum are limited to the Miocene. The above-named species are less than half the number of known forms, but include the more important that are wellestablished. Busycon (spiniger var.?) tampaense Dall, Busycon spiniger var. nodulatum Conrad and Busycon stellatum Dall are common in the Orthaulax puqnax zone of the socalled Oligocene of Florida.

The present knowledge of the Fulgers older than the Oligocene seems to be in a chaotic state. There has been a confusion of both species and genera of the fulguroid forms in the Grabau has questioned the existence of any Fulgurs Eocene.

<sup>\*</sup>Published with the permission of Dr. A. H. Purdue, State Geologist of Tennessee.

<sup>Grabau and Shimer, North American Index fossils, vol. i, pp. 764-772.
Fischer, P., Manuel de Conchyliologie, Paris, 1887, p. 618.
§Cossmann, M., Essais de Paleoconchologie Comparee, Paris, 1901, Liv.</sup> 

iv, p. 61. || Grabau, A. W., American Naturalist, vol. xxxvii, pp. 515–539, 1903.

older than the Oligocene. Dall,\* however, points out that the genus had assumed its essential shell features before the close of the Eocene and that the group took its rise within the Eocene. The fulguroids are abundant in the Eocene and are represented by a number of forms whose generic relationships have not been well-established and have been variously assigned. The more important of these are "Busycon spiniger" Conrad, Fulgur triserialis Whitfield, Fulgur? dallianum Harris, Levifusus dalei Harris, Levifusus Blakei Conrad, Levifusus trabeatus Conrad, Bulbifusus inornatus Conrad, etc. Which of these are true Busycons has not been established. The Eccene Fulgurs have small, thin shells and less bulbous protoconchs in contrast with the ponderous conchs which constitute one of the most conspicuous elements of the later Tertiary. This has led to the conclusion that the Eocene species were the most primitive forms and that the genus evolved in that period. However, the recent discovery, in the Upper Cretaceous of McNairy County, Tennessee, of a typical Busycon or Fulgur would seem to show that the genus was welldifferentiated long before Eccene time. Further collecting and study of well-preserved Cretaceous and Eocene material may throw much light on the relations of this most interesting family of North American late Mesozoic and Tertiary gastropods.

There appear to be two species of Busycon in the Upper Cretaceous of Tennessee, the larger and more perfect of which forms the basis of the present note. For the sake of completeness the generic synonymy is given followed by a description of the new form.

## Family BUSYCONIDÆ

#### Genus Busycon Bolten.

Busycon Bolten, Mus. Boltenianum, p. 149, 1798, First species. Fulgur carica Montfort.

Fulgur Montfort, Conch., vol. ii, p. 503, and figure, 1810. Type, F. carica var. eleceans Montfort.

Sycopsis Conrad, Amer. Jour. Conch., vol. iii, p. 184, 1867.

Sycopsis (Browne) Gill, ibid., vol. iii, p. 147, 1867.

Fulgur Fischer, Manuel de Conchyliologie, Paris, p. 620, 1887.

Fulgur Dall, Trans. Wagner Free Inst. Sci., Philadelphia, vol. iii, pt. 1, pp. 109-118, 1890.

Fulgur Cossmann, M., Essais de Paleoconchologie Comparee, Paris, pp. 76-77, 1901.

Fulgur and Sycotypus Grabau and Shimer, Index Fossils of North America, vol. i, pp. 767-770, 1903.

Busycon Dall, Fauna of the Orthaulax pugnax zone, Bull. 90, U. S. Nat. Mus., p. 66, 1915.

\* Dall, W. H., Trans. Wagner Free Inst. Sci., Philadelphia, vol. iii, pt. 1, p. 109, 1890.

## B. Wade-Upper Cretaceous Fulgur.

This genus was assigned to the subfamily Fulgurinæ in the Turbinellidæ by Fischer in 1887. In 1890 Dall gave a discussion of the known species at that time and assigned the genus to the family Fasciolariidæ. In 1901 Cossmann published probably the most careful generic description to be found in the literature on the genus Busycon and assigned it to the subfamily Fulgurinæ. In 1903 Grabau and Shimer very fittingly applied the family name Fulguridæ. In 1915 Dall called attention to the ruling of the International Committee on





Nomenclature and revived the old Bolten name Busycon, but referred the genus to the family Buccinidæ. The present paper extends the range of the genus by including a description of an Upper Cretaceous species, and emphasizes the desirability of recognizing the family rank of the Fulguridæ for the fulguroid group. In accordance with the accepted rules of nomenclature this should be the family Busyconidæ, as Busycon has replaced Fulgur as the type genus.

The new species described below differs from its congeners sufficiently to form the type of a new subgenus for which the name Protobusycon is proposed.

## Busycon (Protobusycon) cretaceum, new species.

Description.-Shell rather small for the genus; outline typically fulguroid; spire low, less than one-fourth the entire length of the shell; earlier volutions broadly rounded, later whorls broadly and somewhat obliquely shouldered,-the periphery falling about two-thirds of the distance from the posterior to the anterior sutures; apex obtuse; protoconch broken away in the type,-the scar large; the remaining four in number, increasing rapidly in size to a much inflated body; external sculpture inconspicuous and rather irregular; axial sculpture restricted to a series of low, sub-spinose protuberances crowning the shoulder keel, ten in number upon the last whorl of the spire, horizontally elongated and irregular in size and spacing upon the final half turn of the ultima; a second obscure keel outlining the base of the body, obsolete toward the aperture,—the keel beset with four, or possibly five, rudimentary spines; incrementals vigorous and crowded toward the aperture, especially upon the shoulder; spiral sculpture obscure and irregular,-the line approximately ten in number on the medial portion of the body of the type, tending to alternate in size, minutely crenulated by the incrementals; surface of spire so badly decorticated that the character of the finer sculpture can not be determined; line of demarkation between the base of the body and the pillar outlined by a shallow sulcus; incrementals very sharply folded along the sulcus, the fold directed toward the aperture, and terminating as a slight projection at the margin of the labrum; posterior portion of whorl closely appressed; suture inconspicuous; aperture pyriform, feebly sulcate at the posterior commissure, terminating anteriorly in a long, open canal; outer lip broadly arcuate, notched at the shoulder, the incrementals produced into a series of varix-like spines; labrum feebly insinuated also at the base of the body, directly in front of the basal sulcus; inner margin of the aperture quite strongly excavated; parietal wall widely and heavily glazed; columella smooth, sinuous; anterior canal broad, slightly recurved, probably feebly emarginate at the anterior extremity.

Dimensions.—Altitude,  $63 \cdot 2^{\text{mm}}$ ; length of aperture including canal,  $50^{\text{mm}}$ ; maximum diameter,  $35 \cdot 2^{\text{mm}}$ .

This very interesting species is represented in the Coon Creek collection by the single specimen figured which, aside from the loss of the protoconch, is well-preserved. In shape and elevation of the body, angle of the shoulder, sub-spinose angulation of the posterior portion of the body and in the general aspect, it is curiously similar to *Fulgur carica* (Gmelin) so abundant in the recent faunas. The impressed line at the base of the body does not appear on any of the later Tertiary and Recent representatives of the genus and may possibly be explained as an inherited character from a more primitive type with an abruptly constricted body whorl such as that of *Pyropsis* and *Tudicla*. Much more probably, however, the basal sulcus and marginal notch are in some way analogous to the more or less well-defined band and marginal notch used by many of the recent groups, notably in *Strombus*, for the extrusion of the eye-stalks. Although the sulcus is peculiar to *Protobusycon*, the abrupt basal constriction is shared by some of the Eocene members of the group, and by *Busycon stellatum*\* Dall of the Florida Oligocene.

Occurrence.—RIPLEY FORMATION: Dave Weeks Place, on Coon Creek, McNairy County, Tennessee. (Collected by the writer.)

Geological Laboratory, The Johns Hopkins University.

\*Dall, W. H., Molluscan Fauna of the Orthaulax Pugnax zone, U. S. Nat. Mus. Bull. 90, p. 67, pl. 10, figs. 7, 9, 1915.

# ART. XXVI.—A Middle Eocene Member of the "Sea Drift"; by Edward W. Berry.

STUDIES made during the past few years have brought to light extensive fossil floras in southeastern North America which range in age from the lower Eocene to the Pliocene. Practically all of these are coastal floras and the bulk of the plants discovered belong to the strand flora and comprise many plants whose fruits or seeds are normal constituents of the sea drift and are distributed mainly by ocean currents. Among these are such striking forms as the Nipa palm, Dodonæa, Sapindus, Sophora, Rhizophora, Conocarpus, Avicennia, etc. These Tertiary floras, partially published,\* indicate progressively warmer climates commencing with the lower Eocene and culminating in the lower Oligocene, at which latter time tropical climates prevailed throughout this region.

Some years ago I received from Mr. Otto Veatch a striking seed collected by him from the middle Eocene of western Georgia. This has remained undescribed until now, but as it represents such a well-defined type of seed of the tropical or sub-tropical sea drift and a type not heretofore represented in the fossil state by seeds, it seems worthy of a brief note. It is referred to the genus Carapa of the family Meliaceæ and may be characterized as follows:

#### Carapa xylocarpoides sp. nov.

Seed of large size, somewhat trapezoidal or pyramidal in outline, tapering toward the hilum, rounded distad. Length about  $3 \cdot 5^{\text{cm}}$ , maximum width about  $3 \cdot 5^{\text{cm}}$ , thickness about  $6^{\text{mm}}$ . The lateral margins are rounded. The distal margins tend to be somewhat angular and there is a more or less pronounced angular ridge on the proximal face of the seed. The outline and the degree of rounding or angulation and the variability are the results of mutual pressure of the seeds of a head, and the range of variation among existing forms is considerable. The texture is ligneous and the seeds obviously formed part of the middle Eocene sea drift and are contained in marine sediments.

This striking form is unquestionably referable to the modern genus *Carapa* Aublet or to the allied genus *Xylocarpus* König and Jussieu, the latter often made to include two existing oriental species frequently referred to Carapa, especially in the older literature. The differences between the two genera are

\*Berry, E. W., Lower Eccene Floras of Southeastern North America, U. S. Geol. Survey, Prof. Paper 91, 1916.









those of floral structure, degree of buoyancy of the seeds, and manner of dehiscence of the fruit, characters upon which the fossil sheds but little light. The seed coat of Carapa is woody while that of Xylocarpus is corky and consequently more buoyant and better adapted for dispersal by ocean currents. In this feature the fossil seed seems more like those of Xylocarpus. In form Xylocarpus seeds are somewhat more regularly pyramidal than those of Carapa and in this respect also the fossil is more like Xylocarpus, especially the oriental mangrove *Xylocarpus obovatus*, a seed of which is shown in fig. 1b.

However, in considering an American Tertiary form and recalling that Carapa is much the better known generic term even for the oriental mangrove and other modern species of both Carapa and Xylocarpus, and that Carapa is represented by foliage in the lower Eocene (Wilcox) flora of this general region,<sup>\*</sup> it seems advisable to adopt the generic term Carapa for the fossil, since it can hardly be more closely related to the oriental mangrove *Xylocarpus obovata* Blume or the oriental beach plant *Xylocarpus moluccensis* Lamarck than to the half dozen existing species of the American and west African tropics. The absence of the more or less massive seeds of the various existing species in our larger herbaria is my excuse for not making more detailed comparisons between them and the present fossil form.

The locality where the fossil was collected is  $2\frac{1}{2}$  miles east of Fort Gaines, Clay County, Georgia, and it came from the marine clays of the middle Eocene (Claiborne). The fossil is shown natural size in fig. 1*a* and a somewhat larger seed of the oriental *Xylocarpus obovata* is shown in fig. 1*b*.

Johns Hopkins University, Baltimore.

\*Berry, op. cit., p. 253, pl. 55, fig, 4.

# ART. XXVII.—Correlation of the Mississippian of Ohio and Pennsylvania; by WALTER A. VERWIEBE, Ohio State University, Columbus, Ohio.

EVER since the time when it became possible to discuss geologic systems in this country in formational detail, the problem of the correlation of Devonian and Carboniferous formations in northeastern Ohio and northwestern Pennsylvania loomed large in geologic literature. It was not a simple matter to trace the Devonian formations of New York into northwestern Pennsylvania, nor was it an easy task to define the continuation of the lower Carboniferous formations of eastern Pennsylvania, in western Pennsylvania. Both of these problems, however, have been solved to a satisfactory degree.

In the west the excellent work of Orton, Newberry, and Prosser soon brought order out of the profusion of shales and sandstones which compose the Devonian and lower Carboniferous of Ohio. By some strange coincidence, however, the line dividing this state from Pennsylvania seemed also to form an insuperable barrier between the formations in both. Many of our most capable stratigraphers have attempted to correlate the Devonian in these two areas, but it must be confessed, with unsatisfactory results.

The writer does not presume to think that he has found the key to this riddle, but after spending two seasons in the field he has reason to hope that some of his findings may contribute a little in that direction. The area covered in this survey extends approximately from the Cuyahoga River in Ohio to the Allegheny River in Pennsylvania and from Lake Erie south to the parallel of 41° north latitude. It thus includes roughly the northeastern part of Ohio and the northwestern part of Pennsylvania. In a former article published in this magazine\* the correlation of the Berea formation was treated in some detail as the basal member of the Mississippian. In this article the remaining formations will be taken up.

## Formations involved in this discussion.

Sharon conglomerate: This is the basal formation of the Pottsville series of the Pennsylvanian system. It was used merely as a key horizon and was not studied to any further extent in connection with this work.

## Mississippian formations of Pennsylvania.

Shenango Shale: This formation was named by I. C. White. It is recognizable as a stratigraphic unit only over a limited extent of territory since it merges imperceptibly with the

\* This Journal, vol. xlii, pp. 43 to 58, July, 1916.

Shenango sandstone toward the east and is largely absent because of erosion toward the west. It is generally a bluish gray, argillaceous shale though locally also very sandy. Its maximum thickness is perhaps 50 feet, but, on account of the unconformity at the top, usually less than this is found.

Shenango Sandstone: As a key horizon to the stratigraphy of western Pennsylvania this is a most important formation. It received its name from the Shenango River of Crawford



FIG. 1. Sections showing the character and thickness of the Shenango formation. The map on p. 312 (fig. 6) inserted shows location of sections.

and Mercer counties. In lithologic character it is unique. Always coarse and quartzitic, it is marked as well by the great amount of iron present in concretionary form, in secretions, and in veinlets. The solution and redeposition of this substance has given it a deep brown color throughout, but especially on exposed surfaces. In thickness it is very uniform, ranging gradually from 15 feet in the west to about 40 feet in the east. Farther east and south of the region studied it merges more and more closely with the overlying shale and has been named as a unit the Burgoon formation.\*

In fig. 1 are platted sections to show the nature and thick-

\* Butts, Chas., U. S. G. S. Folio No. 115, p. 5.

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# Mississippian of Ohio and Pennsylvania.

ness of the Shenango sandstone and the Shenango shale overlying it. Since the top of the latter is the locus of an unconformity, the thickness is variable. A feature well brought out, however, is the gradual thickening of the sandstone at the expense of the shale as they are traced eastward. Toward the west both shale and sandstone are cut out by the unconformity, but reappear in the longitude of Cleveland as the uppermost part of the Royalton formation. The formation representing the Shenango shale and sandstone in central Ohio is the Logan.



FIG. 2. Sections showing the Meadville and Sharpsville formations.

Meadville formation: The county seat of Crawford County, Pa., is Meadville. It suggested the name of this formation to Dr. White. Consisting essentially of bluish gray sandy shales, it would appear at first not to be of any great value for the stratigraphic geologist. However, two layers at definite horizons are of such striking lithology that they serve as excellent guides. They are essentially limestones, but because of their high silica content are very hard and compact and possess a conchoidal mode of fracture. Pieces of these layers can therefore readily be recognized in streams even though the parent rock may be covered.

In fig. 2 sections have been platted showing the character and thickness of this formation together with the Sharpsville

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below. The two limestones are somewhat exaggerated in order to make them more prominent. They are usually six inches to two feet thick but may be less and are sometimes absent. A third limestone of exactly the same nature as the Meadville limestones is found about the middle of the Sharpsville. It will be noted that along the state line between Ohio and Pennsylvania the Meadville already begins to show a considerable proportion of thin sandstones. These increase in number toward the east. But toward the west the opposite takes place and the Royalton formation, which represents it toward its upper part, has only a small percentage of sandstone layers.

Sharpsville formation: This formation was named after the village of that name which lies a few miles north of Sharon on the Shenango River. It consists largely of sandstone, though shale layers may occur; furthermore muddy sediment is so thoroughly mixed with the sand grains that the sandstone is very impure. Frequently the formation is divided into two subequal parts by a limestone layer like those in the Meadville formation, which is on the average one foot in thickness.

In tracing the formation toward the east it was found more and more difficult to separate it from the Orangeville below. Toward the west it becomes more shaly and finally also loses its identity in the Cuyahoga terrane. It is distinctly recognizable as far west as the Warren (Ohio) region, but becomes indefinite beyond that.

Orangeville formation: Lying just beyond the border of Pennsylvania in Trumbull County, Ohio is Orangeville. Here a series of soft, argillaceous, bluish gray shales are exposed to which I. C. White gave the name Orangeville. They are interbedded to a slight extent with thin sandstones. Iron is present in the form of marcasite concretions and the solution of these causes the formation to present a rather rusty outcrop. When followed toward the east the sandy layers become more abundant and in the region of the Allegheny River form the largest part of the formation. Toward the west the opposite holds true, also the layers toward the base become more carbonaceous, blacker, tougher, and more fissile. This phase in its typical development is called the Sunbury shale. Whenever the Orangeville is encountered it is found to contain an abundant though not varied fauna which consists of the following species:

> Lingula melie, Hall Lingula membranacea, Winchell Discina newberryi, Hall Discina pleurites, Meek

Fig. 3 shows that the thickness increases noticeably from east to west, also that the formation has a definite sandstone horizon toward the west which separates the Brecksville from the Sunbury shale. This is the Aurora sandstone.

Berea formation: This formation is considered by far the most important of the Mississippian formations in the territory surveyed. In Pennsylvania it is subdivided into the Cussewago sandstone, Cussewago shale and Corry sandstone, of



FIG. 3. Sections showing the Orangeville formation.

which the first two are unimportant because they are only local in extent. The Berea is to a large extent the key horizon to the stratigraphy not only of the district under discussion but also of the region to the south. Therefore much time and care were spent in tracing it accurately. All described exposures were visited and many new sections involving its nature or position were made. A careful search for fossils was also instituted, but none were found. I. C. White, who has perhaps done more detailed work in this region than any other geologist, mentions finding fossils only at two localities.\* One is at Corry, where, he states, the formation contains a "few ill-preserved fossils." The other is "east of the county line (Craw-

\* Second Geol. Surv. Pa., vol. Q<sup>4</sup>, p. 92.

ford), in Warren County on the road to Enterprise," where "it is finely exposed and very fossiliferous near its base." This last-named place was visited by the writer and it was found that the exposure showed not the Corry sandstone, but a sandstone located stratigraphically about 180 feet lower, the first Venango sandstone. In the volume mentioned above White has described numerous sections involving the Corry sandstone, but nowhere does he mention the occurrence of fossils, although that is his custom in the case of other formations. It appears, therefore, that the Corry must be considered essentially an unfossiliferous sandstone.

This conclusion does not seem to be in harmony with the findings of Dr. Girty. In a paper recently published,\* he aims to show that the Bedford formation of Ohio is Devonian in age. The Bedford is admittedly found beneath the Berea and in order to strengthen the case the fauna of the latter is adduced and an attempt made to show that it is Carboniferous. Inasmuch as the Berea is practically barren in Ohio, its correlate the Corry is analyzed faunally. No sections are given and the only clue to guide the reader in deciding where the fossils were found is the following statement : "The 'Corry' horizon carrying the fauna can be traced eastward to Cobham's hill just east of Warren, where it comes in immediately above what has been called the 'sub-Olean conglomerate' (Knapp formation), in the short interval which separates that formation from the Ölean conglomerate." This locality (Cobham's hill) was visited by the writer, and it was found that the fossiliferous horizon corresponds stratigraphically to the Venango first This can be traced very easily along the Allegheny sandstone. River toward the south in the numerous rock cuts along the railroad, and is found to underlie the Berea or Corry by an interval of about 180 feet. It is very easy to see, however, how these two sandstones might be confused. Both are very similar lithologically and both are overlain by bluish shales, the Orangeville and the Riceville respectively. One important guide to their separation is a layer of very calcareous sandstone at the very base of the Corry. This resembles the Meadville limestone in every detail, breaks with a conchoidal fracture, and is usually very hard and covered with a ferruginous crust. In addition the base of the Orangeville is generally quite fossiliferous, the characteristic genera being Lingula and Discina. This is not true of the Riceville formation above the first Venango sandstone.

If it should be found that a confusion of sandstones has occurred here then a peculiar anomalous situation arises. Since the Venango sandstone lies considerably below the Corry, the

\* Ann. N. Y. Acad. Sci., vol. xxii, p. 295-319, Nov., 1912.

equivalent of the Berea, then it must also lie stratigraphically beneath the Bedford. Thus we should have a formation carrying fossils which show a distinct affinity with Carboniferous species below another, the fauna of which is distinctively Devonian. To escape from the enigma three possibilities suggest themselves; either the Bedford must be considered as Carboniferous in age or the 'Corry' as Devonian, or, the fauna of one or the other is not sufficiently conclusive.



FIG. 4.

FIG. 4. Sections showing the Cuyahoga formation.

#### Mississippian formations of Ohio.

Royalton formation:—This formation was named by Dr. Prosser from Royalton township in Cuyahoga County, Ohio.\* It consists largely of shales both arenaceous and argillaceous, which are generally bluish or bluish-gray in color. Interbedded are thin, impure sandstones many of which are full of *Spirophyton* markings. It includes the Sharpsville and Meadville formations of Pennsylvania and is equivalent to the upper part of the Cuyahoga of central Ohio. Also it is quite probable that it includes the Shenango of Pennsylvania and the Logan of central Ohio. However, since the unconformity between the Mississippian and Pennsylvanian has cut down lower in northern Ohio than in central Ohio, it is only in favored spots that we may expect to find the Royalton thick enough to include the stratigraphic horizon of the Logan.

\* Geol. Sur. Ohio, Bull. 15, p. 493, 1912.

Such a locality as this is found two miles east of Strongsville, Ohio, along Willow brook. This section is No. 107 in fig. 5 and shows 172 feet of Royalton exposed with about 60 feet covered, a total of 232 feet.

Brecksville:—This name was applied by Prosser to the upper and largest part of the terrane which is equivalent to the Orangeville of Pennsylvania. The other members are the Aurora sandstone and Sunbury shale. The formation consists



FIG. 5. Sections showing the variation in the Mississippian from west to east.

of shale generally dark in color and prevailingly argillaceous. In thickness it varies from about 70 to 115 feet.

Aurora sandstone :--- This is a rather local member of the Orangeville terrane in Ohio. It was named from Aurora creek in the northwestern part of Portage County, Ohio.\* Here it is a blue, fine-grained sandstone six feet thick with some thin shale partings. Elsewhere it is frequently a single unit and of considerable value as a stratigraphic horizon. It is clearly recognizable as far east as Warren, Ohio, but beyond that it soon loses its identity.

Sunbury shale:—This is a familiar term to a stratigraphic geologist. The name was first applied by Prof. Hicks (1878) and has since been discussed a good deal in connection with

\* Geol. Sur. Ohio, Bull. 15, p. 211, 1912.

Ohio geology. The black, rather tough, strongly laminated shales to which it is applied are, though thin, a well marked lithologic unit. When traced from Ohio into Pennsylvania this formation loses its distinctive character and becomes an inseparable portion of the Orangeville shale. The black color is noticeable as far east as the longitude of Linesville in Crawford County, but the hard compact texture is perceptible somewhat farther east. The fauna is also characteristic and is the same as that of the Orangeville formation.

#### Mississippian as a whole.

The correlation of the formations enumerated has been given in connection with each. In conclusion a few words may be added regarding the Mississippian as a whole. Figure 5 shows a number of typical sections across the region under discussion which will indicate the variation in thickness and character from west to east. The first section (107) has a considerable portion covered. As explained elsewhere, this interval most probably consists of Royalton shales. The great irregularity in thickness is explained largely by the unconformity between the Mississippian and Pennsylvanian systems, still there is evidence of considerable thinning toward the east. In sections 31, 47, and 74 the Sharon comes to rest upon formations below the Shenango sandstone or its equivalent, whereas this as well as the overlying shale forms part of the sections farther east. Another prominent feature is the tendency to increasing coarseness toward the east. All formations show this, so that the whole system changes from a shaly aspect in the west to a sandstone and conglomerate facies in the east (along the Allegheny River). Still farther east the whole series becomes the The following table gives a summary of Pocono formation. the formations and their correlation in different areas:

Pennsylvania		Ohio	)	
	east	west	$\operatorname{north}$	central
ĺ	Mauch Chunk		•	
Mississippian	Greenbrier		`	
	(Burgoon)	Shenango shale Shenango sandstone Meadville Sharpsville	$\mathbf{R}$ oyalton	- Logan
	Pocono	Orangeville	Brecksville Aurora Sunbury	> Cuyahoga Sunbury
		Corry sandstone Cussewago shale & sandstone	Berea	Berea

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## Unconformity between Devonian and Mississippian.

It will be noted that in the above table the Berea has been considered the basal formation of the Mississippian system. A good deal has been written to determine the proper place to put the dividing line between the Devonian and Mississippian and a few words of discussion on this subject may therefore not seem out of place. In the article by Dr. Girty discussed above some excellent reasons are given for drawing the line at the base of the Berea. The fact that the Berea inaugurates a new series of rocks as a basal conglomerate (though it is most commonly a coarse sandstone), secondly the fact that the underlying rocks are extensively eroded giving rise to a disconformity, are strong arguments in favor of this view. The importance of this disconformity is not admitted by all geologists. Professor Cushing, for instance, holds that it is merely contemporaneous erosion. In a paper published in the Bulletin of the Geological Society of America\* he states certain conditions which should be present in order to indicate a gap of sufficient length of time to entitle the break to be considered of diastrophic importance. The first is that oscillation upon which an unconformity depends must be accompanied by some warping. He finds that nowhere does the Berea rest upon any formation but the Bedford (ranging in thickness from 50 to 100 feet) and assumes that therefore no warping has taken place. This reasoning is no doubt very good. Still, would it not be perfectly possible that a negative movement of the strand line involving a narrow strip of continent, say one hundred miles wide and extending roughly east and west, might be caused by a slight lowering of the sea level ? Assuming that the shore line during the Bedford age lay to the north approximately within the present confines of Lake Erie and that the shales and sandstones of that age were being accumulated in a shallow sea gently sloping toward the south, does it seem unreasonable to suppose that the strand line shifted slowly south until it reached approximately the latitude of central Ohio? Such a shifting would explain very nicely the fact that the Bedford shale increases in thickness toward the south and that the sandstones are present in the south and missing toward the The Berea formation then represents the coarse phase north. of deposition which should accompany a sea transgressing the region again toward the north. And again we should expect that the Berea would show a less thickness in central Ohio and a greater thickness in northern Ohio, which an analysis of the facts proves to be true. If we accept this condition of affairs

\* Vol. xxvi, p. 205-216, June 15, 1915. Diastrophic Importance of the Unconformity at the Base of the Berea Grit in Ohio. it will not be necessary to have any warping in the region affected by the unconformity.

On the other hand, it has not yet been proved that the Berea nowhere cuts down below the Bedford. In fact Mr. Burrows\* cites one example in Lorain County, where a channel 175 feet wide and extending down considerably into the Cleveland shale (which underlies the Bedford) was carved in the interval between Bedford and Berea times. It is quite likely that further search will reveal others that penetrate beneath the Bedford.

Even if we disregard this evidence, however, and look at the matter from another angle, we may say that the sub-Carboniferous period witnessed the inception of the epeirogenic movements which culminated in the formation of the coal-swamps of the upper Carboniferous in eastern United States. The Laurentian shield has always been a positive segment of the continent and it does not seem improbable that one of its preliminary movements brought a section three hundred miles wide into relief without appreciable warping. Furthermore, the coal measures offer abundant testimony of periods of emergence of slight relief, so that we may assume that northern Ohio also emerged but slightly and that therefore the agents of erosion consumed a great deal of time in cutting through the sandstones of the Bedford and into the red, blue, and black shales beneath.

Another bit of evidence from another direction may not seem amiss. Sufficient well records are now available to enable one to trace the Berea from its outcrop in central and southern Ohio across the eastern part of the state well into Pennsylvania. In a similar way the writer has traced the Corry into southern Pennsylvania from its outcrop in northwestern Pennsylvania.<sup>†</sup> By this method it will be found to correlate pretty definitely with the base of the Pocono. Since this formation is universally admitted to represent the base of the Mississippian in the east, it should indicate that its correlate, the Berea, also occupies the same horizon.

It must be admitted that the problem of finding the dividing line in Ohio is a difficult one and that the evidence at present available is insufficient to warrant a clear-cut conclusion; still, the writer is of the opinion that further evidence will place it at the base of the Berea.

#### Summary.

The correlation of the Devonian and Mississippian formations in northwestern Pennsylvania and northeastern Ohio is a

\* Burroughs, W. G., Berea Sandstone in Eroded Cleveland Shale, Jour. of Geol., vol. xxii, p. 766, 1914.

† This Journal, vol. xlii, p. 51, 1916.

# W. A. Verwiebe—Correlation of the

problem which has not been satisfactorily solved up to the present. In this paper an attempt is made to correlate the Mississippian formations in these two areas, preliminary to a discussion of the Devonian. Also an effort is made to defend the proposition that the Berea is the basal formation of the Mississippian.

#### New Sections bearing on this Discussion.

The following hitherto unpublished sections were made by the writer in the territory under discussion, and, since they



FIG. 6.

FIG. 6. Map showing the location of sections platted in figs. 1 to 5.

throw new light on the stratigraphy are deemed worthy of publication:

1a.	Sharon	Section.
	NO LECTE O LE	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

	1 110	kness
No.	F	eet.
6.	Sharon :Sandstone, coarse, friable, white quartz grains,	
	but weathering buff; pebbles scattered throughout in	
	lenses	18
<b>5</b> .	Shenango:-Sandstone, grayish white, rather loose tex-	
	tured, numerous iron spots	10
4.	Shale, bluish, largely argillaceous, with many sandstone	
	layers, some of which are buff colored.	40
3.	Sandstone, white, quartzitic, turns reddish brown on	
	weathering	10
2.	Covered to quarry of Sharon Clay Products Company	25
1.	Meadville:-Sandstone and shale, mostly hard, sandy	
	and blue in color	34

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This section was secured partly in the quarry of the Sharon Clay Products Co., and partly in an abandoned quarry just above. Both are located about one mile west of Sharon.

#### 3a. Buchanan Ravine,

No		niiess
20	Meadville Shale bluich availlaceous : some sandstones	eet.
<i>L</i> .	interhedded	Q
28	Mend unner Limestone Hard blue silicoous limerock	0
20.	in four lavers fossils abundant also nabbles	13
27	Meadville lower Shale bluish arcillagoous some sand-	- 4
~	stong	15
26	Shale and sandstones	15
25	Sandstone laver	10
24	Shale and sandstones	$10^{2}$
23	Mead middle Limestone Same as No 28 · 2 layers	10
22	Sharnsville Sandstone flaggy brownish in color	19
21	Sandstone fine-grained bluish grey micaceous	12
20	Mead lower Limestone Same as No 28 · 2 lavers	2
19.	Sharpsville Lower. Sandstone, massive laver	1
18.	Sandstone, thin layers from a fraction of an inch to 6	-
10.	or 7 inches thick, even-bedded	20
17.	Orangeville. Shale, blue and grey, soft, argillaceous.	
	weathers to a rusty color	8
16.	Sandstone, dull chocolate color	3
15.	Shale, as above, but more sandy	$\overline{7}$
14.	Shale, as above, fossiliferous	19
13.	Covered	11
12.	Shale, same as No. 17, interbedded with thin, hard	
	micaceous sandstones, fossils	23
11.	Sandstone, dull brownish grey, with black carbonaceous	
	streaks	$\frac{3}{4}$
10.	Sandstone, hard, blue, calcareous and ferruginous; con-	_
	tains a great amount of marcasite	1/2
9.	Shale, blue, weathers rusty on outcrop	$5\frac{3}{4}$
8.	Sandstone, dull gray, fine-grained	$2\frac{1}{2}$
7.	Shale, blue, argillaceous	$1\frac{3}{4}$
6.	Sandstone, blue, rather fine-grained	1
5.	Covered	11
4.	Corry. Sandstone, coarse, rather friable, massive, fer-	
	ruginous, as shown by deep crust of weathering	$\frac{3}{4}$
3.	Covered	12
2.	Same as No. 4	1
1.	Cussewago. Shale, blue, argillaceous ; thin sandstones,	
	many tossils	25

This section was secured a few miles south of Meadville on the farm of Mr. David Buchanan. It is just opposite the small station of Buchanan on the Erie R. R. The section is a

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valuable one, inasmuch as it shows the formations from the upper Meadville down through the Corry and well into the Cussewago, in great detail. The Corry is here shown to have a thickness of 13 feet and 8 inches and the Orangeville of 81 feet and 10 inches, while the Sharpsville is 55 feet 11 inches and the lower Meadville 40 feet and 8 inches thick.

#### 6a. Shaws School House Section.

No.	Fe	et.
15.	Shenango Sandstone. White quartz rock, weathering	
	buff and brown, massive layers, iron concretions	11
14.	Meadville upper. Largely thin sandstones with some	
	argillaceous shales interbedded	80
13.	Mead. upper Limestone. Blue, siliceous, conchoidal	$\frac{3}{4}$
12.	Mead. lower. Shale, bluish, with numerous sandy layers	26
11.	Sharpsville upper. Sandstone, brownish gray, irregu-	
	lar layers	25
10.	Mead. lower Limestone. Fine development, breaks up	- 1
	into several layers; much iron, concretionary	$1\frac{1}{4}$
9.	Sharpsville lower. Sandstone, irregular layers, dull	
0	chocolate color, flaggy	22
8.	Limestone	4
1.	Covered	51
6.	Sandstone, very thin, bluish grey, separated by a few	1 = 3
F	Organowille Shale withow ananacooner upper part is	194
э.	bluich block in color and more availlaceous; middle	
	largely eccupied by this conditions	94
Δ	Shale blue arcillacoous: thin sandstone	24 951
ત્ર. ૨	Covered	202 18
9. 9	Sandstone ash gray hard fine-grained	3
1	Shale typical rusty outcrop	4
-L +	Share, cyproat, range outbrop	-

This section was measured in the ravine which passes the Shaws schoolhouse. Shaws is a small station on the Erie railroad about eight miles south of Meadville, Pennsylvania.

#### 18a. Torpedo Section.

Thickness Feet.

25

Thickness

No.

12. Conoquenessing. Sandstone, very massive, but poorly cemented and friable; composed of white quartz grains which weather buff on exposure. Scattered through the mass are seams and lenses of small pebbles, especially near the bottom; many seams of iron or rather bands of quartz highly charged with iron also occur. Interesting are the clay dikes, some twenty feet high, which fill the joint planes in the rock.

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		OK HUSE
N0.		Feet
11.	Sharon. Shale, black, fissile, tough, somewhat argilla- ceous in spots, carbonaceous and ferruginous. This seems to be disconformable under the Conoquenes-	
	sing	15
10.	Covered (section continued on road to south)	54
9.	Sandstone, hard, close grained, pebbles	3
8.	Covered	43
7.	Shenango. Sandstone, shaly, drab; some clay shale	24
6.	Sandstone, white quartz rock, weathering deep to buff	
	and brown, massive, ferriferous	12
5.	Covered, with occasional shale or sandstone	270
4.	Venango. Shale, blue, and thin sandstone	12
3.	Sandstone, single layer, weather flaggy, fossils	35
2.	Shale	1
1.	Covered to railroad level	17

The above succession of rocks may be seen by following the road from the works of the Warren Silica Co. up to the quarries from which the raw material is secured. Torpedo is a station on the D. A. V. & P. R. R. between Titusville and Warren in Warren County, Pa.

## 23a. Hyde Run Section.

No	. F	eet.
15.	Meadville. Sandstone, rather coarse, brown color;	
	layers are fairly massive	18
14.	Mead, upper Limestone. Bluish, siliceous, conchoidal	11
13.	Shale and thin sandstone, partly covered	$52^{-}$
12.	Mead. lower Limestone. Same as above	34
11.	Sharpsville. Shale and thin sandstone, bluish grey and	-
	brown	$2\frac{1}{2}$
10.	Covered	$30^{-1}$
9.	Orangeville. Shale, bluish and drab, soft, argillaceous,	
	much stained by iron	45
8.	Corry. Sandstone, thin-bedded toward top, shaly in	
	center and massive below (lowest layer is 21 inches	
	thick); color is buff throughout and the rock is of fine	
	texture	14
7.	Cussewago. Shale, blue, argillaceous	1
6.	Cussewago Limestone. Very typical, a blue siliceous	-
	limerock which also carries much iron. On weather-	
	ing the lime is dissolved, leaving behind a crust of	
	deeply stained ferruginous sand. Here the limestone	
	occurs in two layers.	$1\frac{3}{4}$
5.	Shale, soft, argillaceous, bluish; lithologically very	-
	much like the Orangeville	4분
4.	Covered	$42^{-1}$
3.	Riceville. Shale and thin sandstone	8
2.	Sandstone, thin-bedded and shalv	12
7	Covered to Thompson's Run	

Thickness

Thickness

# W. A. Verwiebe-Correlation of the

A few miles northwest of Titusville is the village of Hydetown, through which flows Thompson's Run. A branch of this run just above the village is called Hyde Run. Along this creek the section was seen.

#### 24a. Run on Simmons Farm.

Thickness Feet.

	· · · · · · · · · · · · · · · · · · ·	
8.	Shenango. Sandstone, medium to coarse grain, brown	15
7.	Shale and thin layers of sandstone	13
6.	Covered	33
5.	Meadville. Sandstone, brownish, flaggy, rather coarse	5
4.	Shale and sandstone in thin layers, largely covered	110
3.	Orangeville. Shale, blue, argillaceous	2
2.	Covered	68
1.	Corry. Sandstone, massive, buff, hard, close grained.	
	Middle section shaly and upper part less massive	
	than the lower	15

In the section above it is more than likely that the Meadville formation begins with No. 5. In that case the Shenango sandstone is concealed in the 33-foot interval (No. 6). The general topography of the stream also seems to bear this out. The part of the section including No. 2 to 5 was obtained by following the road leading to Thompson's Mills. The Corry may be seen directly below the bridge over Thompson's Run, about one-half mile below Kerr's Mills, which is a few miles north of Titusville in Crawford County, Pa.

#### 25a. Wolfkill Hollow Section.

No	. The	ekness eet.
24.	Shenango Sandstone. Massive, white quartz sand,	
	coarse and rather friable, iron concretions	1
23.	Meadville. Sandstone, weathered to a deep brown	
	color, layers fairly massive	40
22.	Mead. upper Limestone. Blue, hard, conchoidal frac-	
	ture, ferruginous crust of decayed rock	11
21.	Sandstone, coarse, brownish	4
20.	Shale, thin, even-bedded, gray, sandy	4
19.	Sandstone, irregular laver, coarse, greenish	$\frac{1}{2}$
18.	Shale, same as No. 20	11
17.	Sandstone, layers up to 3 in. thick	2
16.	Shale and sandstone, partly covered	23
15.	Mead, lower Limestone. Like No. 22	$\frac{1}{2}$
14.	Sharpsville. Shale, bluish gray, weathering to deep	2
	brown, thin, sandstones interbedded	10
13.	Covered	25
19	Orangenille Shale soft drah	85

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No

<ol> <li>Sandstone, massive, close-grained, buff</li> <li>Shale, soft, drab, fossils</li> <li>Sandstone, like No. 11</li> <li>Sandstone, irregular, flaggy, some shale</li> <li>Corry. (?) Covered</li> </ol>	Thickness Feet.
<ol> <li>Shale, soft, drab, fossils</li> <li>Sandstone, like No. 11</li> <li>Sandstone, irregular, flaggy, some shale</li> <li>Corry. (?) Covered</li> </ol>	· <u>3</u>
<ol> <li>9. Sandstone, like No. 11</li> <li>8. Sandstone, irregular, flaggy, some shale</li> <li>7. Corry. (?) Covered</li> </ol>	3
8. Sandstone, irregular, flaggy, some shale	
7. Corry. (?) Covered	9_
C Saudatana huff not magaine this larger	45
6. Sandstone, buil, not massive, thin layers	5
5. Shale and sandstone, bluish grey	2
4. Limestone, blue, fairly hard	$-\frac{1}{4}$
3. Shale and sandstones, bluish, fossils	8^^
2. Covered	12
1. Shale and sandstones to railroad tracks	8

Wolfkill Hollow is a deep ravine with all the earmarks of an interglacial valley. It empties into Oil Creek just below the station called Miller Farm, on the Pennsylvania railroad between Titusville and Oil City, Pa. The section shows that in this region the upper Meadville is a coarse, brown sandstone and so similar to the Shenango sandstone that it becomes difficult to separate them. The Corry, unfortunately, is not exposed, but is quite probably concealed in the covered interval No. 7.

26a. Sprott Ravine Section.

No.	. F	'eet.
15.	Shenango Sandstone. Coarse white quartz rock, massive, layers up to three feet thick; on weathering	14
7.4	It turns a light buff	14
14.	Shale, once, arginaceous	2
10. 10	Sandstone, like No. 15	24
12.	color, layers are thin, mostly less than 3": the rock is	
	of medium grain and micaceous	13
11.	Sandstone like No. 12 but more massive	$25\frac{1}{2}$
10.	Mead. upper Limestone. Blue, hard, in two layers,	
	edges rounded as usual	1 1 1 1
9.	Sandstone, as above, but more flaggy	$6\frac{1}{2}$
8.	Shale, blue, argillaceous	1
7.	Sharpsville. Shale and thin sandstones, mostly	
	covered	22
6.	Mead. lower Limestone. Same as limestone above	12
5.	Covered to outcrop at junction with Hammond Run.	88
4.	Orangeville. Sandstone, buff color, hard but rather	
	flaggy	3
3.	Shale, blue and drab, sandy	$2\frac{3}{4}$
2.	Sandstone, one massive layer, buff color	11
1.	Shale, chocolate color, largely argillaceous	4

This section was made in a small ravine crossing the road just above the farmhouse of W. H. Sprott, two miles southeast

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Thickness

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of Titusville and leading into Hammond Run below. It also shows the character of the upper Meadville in excellent fashion. But for the presence of the upper limestone it might well be mistaken for the Shenango sandstone.

#### 29a. Markley Quarry Section.

Thickness

No	. I	Feet.
10.	Shenango Shale. Shale, bluish grey, somewhat argilla-	9
9.	Sandstone, brownish	길
8.	Shale, sandy	1 =
7.	Sandstone, coarse, ferruginous, whitish grev	34
6.	Shale, blue, clayey	$5\frac{3}{4}$
5.	Shenango Sandstone. Sandstone, somewhat flaggy,	-
	more massive toward the top, whitish grey, mica-	
	ceous	26
4.	Same, single layer	91
3.	Covered	146
2.	Corry. Sandstone, white quartz rock weathering to	
	buff, massive, layers irregular	4
1.	Riceville. Shale, bluish grey, partly argillaceous with	
	interbedded sandstones to R. R. level	38

Just south of Titusville, Pa., is the abandoned quarry of O. W. Markley. It was worked for the sandstone of the Shenango formation. The section then continues down to the Pennsylvania railroad tracks nearby. The importance of this section is that it shows in great detail the character of the Shenango shale and underlying sandstone. A study of it will show that the term Shenango Shale is a misnomer, since it consists largely of sandstone and that the term Shenango should cover both phases in other parts of the district as well as this.

## List of Sections used in Figures 1-5.

The following sections are taken from Bull. 15 of the Geol. Survey of Ohio: No. 16, page 72; No. 31, p. 143; 38, p. 158; 47, p. 194; 74, p. 316; 79, p. 336; 82, p. 353; 86, p. 363; 89, p. 380; 90, p. 382; 92, p. 399; 107, p. 489.

The following were published in vol. xliii of this Journal, July, 1916: No. 13a on page 56; 21a, p. 56; 22a, p. 57.

The following may be found in vol. Q4, Second Pa. Geol. Survey, 1881: 6w, p. 194; 8w, p. 182; 11w, p. 139; 12w, p. 173.

No. 2B was taken from the general section published on page 193 of the Report of the Top. and Geol. Surv. Comm. of Pa. for 1906-1908.

The following will be found published in this article: 1*a*, p. 312; 3*a*, p. 313; 6*a*, p. 314; 18*a*, p. 314; 24*a*, p. 316; 25*a*, p. 316; 29*a*, above.

# ART. XXVIII.—A New Labyrinthodont from the Triassic of Pennsylvania; by W. J. SINCLAIR.

REMAINS of vertebrates from the rocks of the Newark group are so rare that every additional specimen obtained from them cannot fail to be of interest. The material which forms the subject of the following note was collected by Professor Gilbert Van Ingen and the writer from the locally basal beds of the Norristown shale at Holicong, Bucks County, Pennsylvania. It comprises the front part of the left half of the lower jaw of a large Stegocephalian, No. 12302 Princeton University Geological Museum, comparable in size with Mastodonsaurus, and apparently pertaining to an undescribed genus and species for which the name Calamops paludosus is proposed. Two large pieces, evidently belonging to the back of the jaw, do not make contact with the tooth-bearing portion of the ramus and have been omitted in the drawing (fig. 1). They are somewhat fragmentary and so heavily covered with matrix that little or nothing can be made of them.

The jaw was found in a red shale abounding in impressions of large horse-tail rushes which are observable on the surface of the hard siliceous capsule investing the bone (whence *Calamops*, "reed-face"). This capsule is of variable thickness up to half an inch or so, is apparently siliceous, of radiate structure, and is applied so closely to the outer surface of the bone, and has become so much a part of it, that its removal has proved impracticable, especially as the bone-substance is quite soft and spongy, owing to partial solution.

The portion of the jaw preserved is straight lengthwise, except toward the forward end where it curves inward toward the symphysis. Here the matrix is broken off and bone tissue exposed below the base of one, or perhaps two teeth. The upper margin of the ramus carries a series of seventeen large teeth without sockets. Perhaps an additional small tooth or two occurs in front of the first large tooth in the series. The matrix has been chipped off the tips of several of the teeth giving some rather imperfect cross sections. These have been supplemented by a thin section of the penultimate tooth, cut transversely. Apparently the teeth are without enamel, with smooth or but slightly grooved crowns, circular in cross section at the base and, in the case of some of them, with the crown slightly flattened laterally toward the tip, with acute anterior and posterior edges. In thin section, cut transversely to the crown, radial prolongations of the pulp cavity are seen toward which numerous fine dentine tubules seem to converge from

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the outer wall of the tooth. Labyrinthine infoldings of cement have not been made out. The radiating pulp canals are especially well shown on the tenth tooth in series, counting forward from the back of the jaw, where an attempt at removing the exceedingly hard matrix resulted in chipping off the outer wall and exposing the ends of the pulp canals which appear as a series of vertical grooves. The anterior teeth are somewhat variable in height, but none seem to be specially enlarged unless the tooth supported on the base exposed at the broken symphysial margin might have been so. The last three teeth are much shorter than the rest. Although their tips are broken off, their bases are considerably higher than those of the teeth in front owing to a sudden increase in depth of the jaw. Externally, the teeth anterior to these three are supported by a flange from the jaw, only their tips projecting above it.

Owing to the thick capsule of hard material adhering to the bone, none of the jaw elements can be made out, which renders difficult a comparison with forms hitherto known. On the outer side of the jaw, the matrix has an irregular hummocky surface suggestive of pittings in the bone. The latter is flat behind and slightly convex in front in vertical section. Internally and toward the back of the jaw, a wedge-shaped depression is inclosed between a strongly convex ridge above and a lower ridge below. This depression fades out anteriorly until below the eleventh tooth, counting forward from behind, the jaw is strongly convex in vertical section. Its lower margin is broadly concave upward, increasing in curvature toward the symphysis.

Calamops is larger than any labyrinthodont hitherto described from the Newark group and is the largest amphibian thus far reported from the Triassic of North America. The fragment figured has an extreme length, measured in a straight line, of 446 millimeters; at its narrowest part below the fourteenth tooth, counting forward from the last, the depth of the jaw is 55 millimeters; measured vertically below the base of the last tooth it is 118 millimeters. Owing to the heavy coating of matrix, not even approximate figures for the thickness can be given. The longest tooth rises 43 millimeters above the inner, upper margin of the jaw and is about 16 millimeters in diameter anteroposteriorly at the base.

Princeton University, Department of Geology, January 1917. 321

ART. XXIX.—On the Calcium Phosphate in Meteoric Stones; by GEORGE P. MERRILL, Head Curator, Department of Geology, United States National Museum.

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UNDER the caption On the monticellite-like mineral in meteorites, I have elsewhere\* described a previously unrecognized form of calcium phosphate occurring among the silicate constituents of stony meteorites. Examination of a large number of thin sections of other stones than those there mentioned has shown the occurrence of this mineral to be so widespread as to warrant a brief note devoted exclusively to it.

The first noted occurrence of a mineral phosphate in a meteorite was that of C. U. Shepard, who in his description of the Richmond, Virginia, stone mentions the occurrence of a minute, but macroscopically visible, yellow mineral, particles of which reacted for phosphorus and calcium and which he interpreted as indicative of the mineral apatite. In this he was essentially right, but singularly enough the discovery remained unverified almost to the present time (see my paper), nor was apatite again reported until Berwerth+ found it among the silicate constituents of the Kodaikanal iron, and Tschermak<sup>‡</sup> in the stone of Angra dos Reis. Singularly enough, too, the phosphorus reported in chemical analyses of meteorites is in the majority of cases relegated to the metallic constituent, a matter to which attention was called in my paper on the minor constituents of meteorites published by the National Academy of Sciences.§ The cause of this is not difficult to determine, as noted in the following descriptions, in which I have repeated, in part, matter given in previous papers, adding the results of more recent observations, particularly in slides of the New Concord and Waconda stones.

The New Concord stone, a veined intermediate chondrite according to Brezina's classification, fell in 1860. It has been the subject of much study, and need be referred to here only in connection with its mineral and chemical composition. Dr. Smith's analyses showed the stone to consist of 10.7 per cent nickel-iron and 89.37 per cent "earthy mineral," the nickeliron yielding 0.012 per cent of phosphorus, but no mention is made of this same constituent in the "earthy" portion. An examination of the stone in thin sections, a method not available in Smith's time, reveals the presence of numerous areas of the phosphatic mineral 1 have elsewhere described and pro-

\* Proc. Nat. Acad. Sci., vol. i, p. 302, 1915.

† Min. Petr. Mitt., vol. xxv, p. 188, 1906. ‡ Ibid. xxviii, 110, 1909. § Memoirs, vol. xiv, p. 27, 1916. In the 42 selected analyses there tabu-lated, the phosphorus is given as P in 24 cases and as  $P_2O_5$  in the remaining 14. This Journal, vol. xxxi, 1861.

visionally referred to francolite. Three of these occurrences in a single slide (No. 62–a) are figured herewith, the actual diameters being from 0.5 to  $1.5^{\text{mm}}$ . The mineral is in all cases colorless, without crystal outline (its form being controlled by that of the interstices in which it occurs), no definite cleavage, a complete lack of pleochroism, polarizing if at all only in light and dark colors, sometimes almost completely isotropic, and giving at best poor interference figures indicative of its biaxial nature. The isotropic sections are so colorless and lacking relief that on hasty inspection such might be mistaken for holes in the slide, a glass, or even

the problematic maskelynite. Once seen, however, they are readily recognizable. In the three forms here figured the position of maximum extinction is shown by the small black cross. In the case of the larger form, the black brushes of the hyperbola emanating from a point outside the field of view, indicative of its biaxial character, are readily obtained. The phosphatic nature of the mineral has been determined beyond question by the usual microchemical method. An attempt at a quantitative determination was made, but with unsatisfactory results.

Studies of thin sections of the Waconda, Kansas, stone, a redescription of which is in process of preparation, reveal the presence of the phosphate even where it can not be determined microscopically. It

was found that when the surface of an uncovered slide was treated for but a few minutes with a dilute acid the solution obtained would react for both calcium and phosphorus, and the slide when again placed under the microscope be found to contain numerous minute and irregular cavities left by the dissolving away of the mineral. A quantitative analysis shows the presence of 0.26% P<sub>2</sub>O<sub>5</sub> in the stony portion, or 0.23% in the bulk or mass analysis.

Unmistakable evidences of the presence of the phosphate I have thus far found in the stones of Alfianello, Bath (South Dakota), Bluff, Dhurmsala, Estherville, Farmington, Felix, Homestead, Indarch, Knyahinya, Mocs, Plainview, Pultusk, Quenggouk, Rich Mountain, and Waconda.



These results agree in all respects with those given in my previous paper, and show with seeming conclusiveness that a calcium phosphate is a very general if not universal constituent of meteoric stones, and that, further, it differs from normal apatite in its optical and other physical characteristics, which may be summed up as below, a repetition in part of what I have previously stated :

Occurrence sporadic, without crystal form, very brittle, colorless; cleavage for the most part lacking though sometimes imperfect and interrupted, showing angles of 60° and 120°; optically biaxial and positive (?), birefringence weak, less than 0.005, refractive indices  $a=1.623\pm0.002$  and  $\gamma=1.627\pm0.005$ ; no pleochroism and often undulatory extinction, polarizing in light and dark colors, sometimes almost isotropic; easily soluble in cold dilute nitric acid and less so in hydrochloric, giving solutions reacting for calcium and phosphorus. The mineral is further distinguished from normal apatite in that it is a product of the last rather than the first stages of consolidation.\* Just what meaning and how much importance is to be attached to this different habit of the phosphate in the history of a meteorite it is yet too early to say. Obviously it bespeaks conditions governing crystallization unlike those which prevailed during the consolidation of terrestrial rocks.

For the present it would seem best to designate this member of the apatite group by the name *francolite*, with which it most nearly agrees,<sup>†</sup> as was done in the paper mentioned above. It may be added that its common presence in optically recognizable quantities suggests the advisability of exercising greater care in the determination of phosphorus and calcium in chemical analyses of meteoric stones.

\*In his description of the meteorite of Angra dos Reis, Tschermak mentions the occurrence of abundant small colorless granules, without cleavage, weakly doubly refracting, *uniaxial* and *negative*. These he identified as apatite, a conclusion borne out by the chemical composition of the silicate portion of the stone. The mineral I have described, which apparently is quite similar, is, however, biaxial. The possibility of the apparent biaxial interference figures being those of a uniaxial mineral cut parallel with an optic axis was considered, but deemed wholly improbable from the fact that in not one of the many sections examined was I able to find a uniaxial figure. It seems improbable that among so large a number should not be found at least one, did such exist.

<sup>†</sup> See Schaller, Bull. 509, U. S. Geol. Surv., p. 91, 1912.

# ART. XXX.—Crystals of Pyromorphite; by EARL V. SHANNON.

## 1. Pyromorphite from the Caledonia Mine, Coeur d'Alene District, Idaho.

CERTAIN specimens showing hexagonal crystals of some secondary lead mineral were collected by the author in February, 1915, in the Caledonia Mine-near Wardner, Idaho. Recent study has shown this mineral to be pyromorphite but, although the crystals are quite simple and show no new forms, the habit and mode of occurrence are somewhat unusual.

Occurrence.—The Caledonia vein consists in its unaltered portion of a rather large body of pure, fine-grained, argentiferous galena with smaller amounts of chalcopyrite and tetrahedrite. From the surface downward for some 800 feet the vein maintains a rather high dip, but on the 900-foot level it flattens out into an almost horizontal position and forms a 'blanket' ore-body of considerable size and richness. Below this level the vein is traceable as a gouge-filled fissure which has not been shown to contain any commercial ore. The inclosing rock consists of a much crushed white quartzite belonging to the Burke division of the Belt Series of sediments of Algonkian age. No igneous rocks are known from the vicinity. The zones of oxidation and secondary enrichment were well defined in the portion of the vein above the 700-foot level. In the oxidized ore, pyromorphite, of the pale green color common in the Coeur d'Alene District, occurred in crystal masses of extraordinary size and beauty, associated with cerussite, massicot, bindheimite, and native silver. The material here described is totally unlike the green pyromorphite in appearance and was not noted in the oxidized nor in the secondary sulphide ore. The crystals commonly occur deposited in cracks in masses of unaltered galena or in the wall-rock adjacent to such masses of galena, from the 500-foot to the 900-foot level. There is no other secondary lead mineral associated with the pyromorphite which has here apparently formed directly from the galena without the intermediate compounds, anglesite and cerussite.

Pyromorphite in this district is a characteristic mineral in the extreme upper portion of the oxidized zone. Ordinary green pyromorphite has not been found here at a greater depth than 300 feet below the surface. No specimen is known, from the district, showing green pyromorphite associated with galena. It is of importance to note that the mineral described below occurs in some abundance in the lowest ore opened, 900 feet, vertically, below the surface. Description.—The mineral occurs commonly in crusts of minute crystals coating cracks in galena or as larger individuals in cracks in quartzite. The color ranges from faintly pink to colorless in the smallest crystals to quite deep grayish violet in some of the larger ones. In size they range from microscopic to an occasional length of  $1.5^{\text{cm}}$ , the larger being those in the wall-rocks. Those over  $5^{\text{mm}}$  in length are commonly nearly opaque with curved prism faces and brush-like terminations. The luster in the smaller crystals is adamantine while that of the larger opaque crystals is resinous. Quite commonly the crystals are attached by a prism face and are then doubly terminated, the form being essentially like the accompanying figure 1 with the length several times the diameter. At times



these small prisms greatly resemble quartz crystals, the resemblance being heightened by an unequal development of the pyramid faces which gives them a rhombic aspect. As no suitable material was at hand when it was decided to describe the occurrence, a specimen of the type material was borrowed from Col. W. A. Roebling. The crystals measured were taken from this specimen. While promising in appearance these crystals are somewhat dull and give very poor signals. The forms noted were the pyramid x (1011) and the prism m (1010). No other planes have been observed. The best crystal, measured on the reflecting goniometer, gave the value  $x \wedge x''' =$  $80^{\circ}50'$ . This is sufficiently close to the calculated angle ( $80^{\circ}44'$ ) to identify the form.

The presence of lead, chlorine, and phosphoric acid were proven by qualitative methods, as were the absence of vanadium, calcium and arsenic. Col. Roebling reports that a preliminary analysis on insufficient material gave approximately lead 75 per cent and chlorine 3 per cent. The composition thus corresponds to ordinary pyromorphite.

# 2. Pyromorphite from Broken Hill, New South Wales.

For purposes of comparison Col. Roebling very kindly loaned the author a recently acquired specimen of pyromorphite from Broken Hill. The specimen consists of an irregular mass of iron oxides completely encrusted with glittering microscopic crystals of gray pyromorphite. Measurement on the reflecting goniometer showed that the dominant forms present were the prism  $\alpha$  (1120) and the pyramid s (1121) of the second order and the prism m (1010) of the first order with a small base and an occasional pyramid of the first order. The habit is thus quite unlike the Idaho material. Figure 2 shows the appearance of these crystals.

# SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. The Penfield Test for Carbon.—W. G. MINTER and F. L. HAIGH have made an interesting examination of the delicacy of this method which was originally devised for testing for carbon and carbonates in minerals. They observe that the method does not appear to be in the literature of analytical chemistry. It is novel only in the very delicate way in which the late Professor S. L. Penfield applied well-known reactions. He fused the substance to be tested with lead chromate in a small horizontal hard glass tube, closed at the heated end, and containing near the open end a small drop of barium hydroxide solution. The appearance of a film of barium carbonate indicates the presence of carbon in the substance. If no film is seen when the fusion is effected, the open end of the tube may be closed with the finger to keep out carbon dioxide from the air and the tube may be removed from the flame so that the result may be more carefully observed.

The method has been used by Professor Mixter in the Sheffield Chemical Laboratory for a number of years, especially for testing metals for carbon. It is so delicate that lead chromate which has been exposed to the air in preparation will react for carbon, but the reagent may be freed from carbon by heating it below its sintering point in an atmosphere of oxygen. Special precautions are necessary also to clean thoroughly the glass tubes used for the experiments, and to protect them from dust. In order to determine the delicacy of the method a mixture of very finely powdered silicon carbide ("carborundum") and aluminium oxide, prepared by igniting the hydroxide in oxygen, was made, containing 9.990 g. of alumina and 0.01 g. of the carbide. The mixture was heated for an hour in oxygen to burn out all carbon compounds except silicon carbide, and it was carefully protected from atmospheric dust.

Experiments were then made by fusing varying quantities of the mixture with lead chromate in sealed tubes containing in each case a drop of saturated barium hydroxide solution in a small depression blown near the open end, and provided at this end with an attached protective tube containing solid potassium hydroxide. The following results were obtained with different weights of the mixture :

100 mg. gave an abundant white film.

20 mg. gave a distinct white film.

14 mg. gave a slight but distinct white film.

10 mg. gave a very faint white film.

8 mg. gave a doubtful result.

4 mg. gave absolutely no result.

1.5 mg. gave absolutely no result.

Ten milligrams of the mixture was the smallest amount that gave an unquestionable reaction. This corresponds to 0.01 mg. of silicon carbide containing 0.003 mg. of carbon. Undoubtedly smaller amounts of carbon may be detected by using a minute drop of solution of barium hydroxide and observing the result with a microscope. In doubtful cases a blank test should be made for comparison.—Jour. Amer. Chem. Soc., xxxix, 374.

H. L. W.

2. A New Volumetric Method for the Determination of Cobalt.—W. D. ENGLE and R. G. GUSTAVSON have devised a method for the determination of cobalt when nickel is present, which according to their test-analyses gives excellent results. Metals of the copper and iron groups as well as manganese must be first removed by the usual methods, and while zinc, the alkali, and the alkali-earth metals may be present, the solution must contain nothing that will liberate iodine in acid solution.

To about  $100^{cc}$  of the solution containing about  $5^{cc}$  of dilute sulphuric acid in excess, 1 or 2 g. of solid sodium perborate are added, and after this has dissolved an excess of sodium hydroxide is added and the liquid is boiled for 10 minutes. The mixture is then cooled to room temperature, and after 1 g. of potassium iodide has been added it is acidified with dilute sulphuric acid, and finally after the precipitate has dissolved the free iodine is titrated with sodium thiosulphate solution with starch as an indicator. The thiosulphate solution may be standardized by means of a pure cobalt compound or by means of potassium dichromate. In the latter case, as the cobalt is oxidized to the trivalent condition, one dichromate is equivalent to six cobalts.— *Jour. Indust. and Eng. Chem.*, viii, No. 10. H. L. W.
3. On the Determination of Molybdenum by Potassium Iodate. - GEORGE S. JAMIESON of the Sheffield Scientific School has applied the general method of titration of L. W. Andrews to the determination of molybdenum. He recommends that the solution of a molybdate strongly acidified with hydrochloric acid, and heated to about 50° C., should be passed slowly through a rather long and warm "Jones reductor" of granulated and amalgamated zinc, the outlet of which leads to the bottom of a glassstoppered bottle placed in cold water and containing iodine monochloride in hydrochloric acid, as well as a little chloroform for use as an indicator. Under these conditions the molybdic acid is reduced to  $Mo_{2}O_{3}$  in the reductor and is readily oxidized to  $Mo_{2}O_{5}$ by the iodine monochloride with the liberation of iodine. The liquid is then titrated, in the presence of at least 10 per cent of actual hydrochloric acid, with a standard solution of potassium iodate until the chloroform loses its color. A good end-reaction was obtained at this point, but it was observed that the oxidation goes further to  $MoO_3$  in the course of about 2 days. The test analyses show good results, but they all deal with small quantities of molybdenum, the largest of which is 0.0627 g. It would be interesting to know if the process can be easily applied to the ammonium phosphomolybdate precipitate.-Jour. Amer. Chem. Soc., xxxix, 246. H. L. W.

4. The Fixation of Nitrogen.—JOHN E. BUCHER has made the observation that a process depending upon the formation of potassium cyanide by the action of atmospheric nitrogen upon a heated mixture of carbon, potassium carbonate and finely divided metallic iron, described as long ago as 1839 by Lewis Thompson, is the basis of a practically important method for the fixation of nitrogen. It appears that numerous attempts to utilize the method or to confirm its application in those early times failed to be successful on account of omitting the use of the finely divided iron which acts as a catalyzer and is of the greatest importance.

The author has found that at moderate temperatures of  $920^{\circ}$  C., or lower it is possible to obtain large yields of sodium cyanide from mixtures of sodium carbonate, carbon and finely divided iron upon passing nitrogen gas. It is even possible to start with oxide of iron in the place of the metal and to use producer gas under proper conditions in place of pure atmospheric nitrogen. The author's description of his many experiments with their results leads to the opinion that the process is a promising one for commercial application. An interesting experiment was the distillation of the sodium cyanide from the mass in which it was formed by heating *in vacuo.—Jour. Indust. and Eng. Chem.*, ix, 233. H. L. W.

5. The Volatilization of Potash from Cement Materials.—In connection with the possibility of volatilizing potash from silicates during the process of manufacturing Portland cement and the collection of the volatilized material by means of the electrical precipitation of the dust from the furnace gases, E.

ANDERSON and R. J. NESTELL have made a long series of experiments with a number of actual cement materials. They have found that it is possible to volatilize all the potash from cement material provided the temperature, time, and volume of gases are sufficient. The lower point of temperature for this volatilization is 1100° C., and the rate increases rapidly with the temperature. The presence of chlorides, particularly calcium chloride, increases the rapidity, while sulphates decrease it. Sodium is driven off nearly as easily as the potassium. No conclusions are given as to the applicability of this operation as a practical source of potassium salts.—Jour. Indust. and Eng. Chem., ix, 253.

H. L. W. Dispersion and the Size of Molecules of Hydrogen, 6. Oxygen, and Nitrogen.-From theoretical considerations, it has been recently shown by L. SILBERSTEIN that the molecular refractivity N of an isotropic substance the molecules of which consist of two equal atoms may be expressed by the formula  $N = (2/3) N_0 [2 + (1 - \sigma N_0)^{-1}]$ .  $N_0$  denotes the *atomic* refractivity, and  $\sigma = a/(2\pi R^3)$ ; where  $a = 3m_{\rm H}/1.008 = 4.88 \times 10^{-24}$ gram, and R symbolizes the mutual distance of the "centers" of the two atoms composing each molecule, that is, of the positions of equilibrium of the dispersive particles within their atoms. This formula reduces to the usual relation  $N = 2N_0$  when R is so large as to make  $\sigma N_0$  negligible as compared with unity, and it owes its generality to the fact that in its derivation the mutual influence of the atoms in one molecule was taken into account. When  $\lambda_0/\lambda$  is small enough to admit of the omission of terms involving the fourth and higher powers of this ratio the equations of refractivity reduce to the very simple form  $N = b + g/\lambda^2$  and  $N_0 = b_0 + g_0/\lambda^2$ .  $\lambda$  and  $\lambda_0$  denote respectively the wave-length of an incident radiation in the visible spectrum and the free wave-length in the extreme ultra-violet characteristic of each atom when undisturbed by its neighbors.  $b_0$  and  $g_0$  are explicit functions of certain properties of the atoms, such as  $\lambda_{o}, \sigma$ , the mass m of a dispersive particle, and the charge e of such a particle. b and g, which are called respectively the "refractioncoefficient" and the "dispersion-coefficient," are amenable to direct experimental determination. Under the conditions of approximation considered, b and g are dependent upon  $b_0$ ,  $g_0$  and R (through  $\sigma$ ) in the following manner:  $b = (2/3) b_0 [2 + (1 - \sigma b_0)^{-1}]$ and  $g = (2/3) g_0 [2 + (1 - \sigma b_0)^{-2}]$ . The denominator  $1 - \sigma b_0$ being a fraction, the dispersion will show a greater departure from additivity than the refraction, which is a well-known feature of this class of phenomena.

The problem before us may now be stated: "Given the molecular refractivity N of the diatomic substance, that is, given its coefficients b, g, find the atomic coefficients  $b_0, g_0$ , and therefore the atomic refractivity  $N_0$ , and also the interatomic distance Rinvolved in  $\sigma$ ." Obviously, another relation between  $b_0$  and  $g_0$  is necessary for the solution of the last two equations. Silberstein makes the very plausible assumption that  $b_0^2/g_0 = \kappa \epsilon$  where  $\epsilon$  is the electronic value of  $b_0^2/g_0$  ( $\epsilon = 183 \times 10^8$  cm/gram) and  $\kappa$  is the smallest integer compatible with the physical conditions. This may be interpreted as meaning that an atomic resonator consists of  $\kappa$  electrons or that each atom contains  $\kappa$  dispersive electrons.

The practical application of the preceding theoretical outline to the case of hydrogen will now be considered. The indices of refraction for the radiations  $H_a$ , D,  $H_\beta$ , and  $H_\gamma$ , for hydrogen at 0° C. and 76<sup>cm</sup> pressure, are 1.0001387, 1.0001392, 1.0001406, and 1:0001412. Hence, the well-known formula  $N = (\mu^2 - 1)$  $(\mu^2 + 2)^{-1} Md^{-1}$  gives 2.074, 2.082, 2.103, and 2.112 for the corresponding molecular refractivities. (Molecular weight of  $H_2$  is M = 2.016, density  $= d = 8.9873 \times 10^{-5} \text{ grm/cm}^3$ .) These values of N satisfy the equation  $N = 2.0445 + 1.279 \times 10^{-10}/\lambda^2$  very satisfactorily ( $\lambda$  in cm.). Hence b = 2.0445,  $g = 1.279 \times 10^{-10}$ . It is also found that  $\kappa = 1$ , so that "we shall attribute one dispersive electron to each hydrogen atom." The equation  $b_0^2/g_0 = 183 \times 10^8$  when combined with the two equations connecting b and g with  $b_0$ ,  $g_0$ , and  $\sigma$  leads directly to  $\sigma b_0 = 0.4932$ ,  $b_0 = 0.7719, g_0 = 0.3255 \times 10^{-10}$  c.g.s. units. Accordingly the atomic refractivity of hydrogen is expressed by  $N_0 = 0.7719 + 0.326 \times 10^{-10}/\lambda^2$ . The "free" wave-length  $\lambda_0$  of a hydrogen atom = 649.4 A. The central distance between two atoms in a hydrogen molecule =  $R = 1.067 \times 10^{-8}$  cm. For oxygen  $\kappa = 2$ ,  $\lambda_0 = 622.6 A$ , and  $R = 1.265 \times 10^{-8}$  cm. For nitrogen  $\kappa = 3$ ,  $\lambda_0 = 570.5 A$ , and  $R = 1.493 \times 10^{-8}$  cm. In conclusion, attention should be called to the facts that (i)  $\kappa$  agrees with the valency of the elements, (ii)  $\lambda_0$  falls near the limit of Lyman's extension of the Schumann region so-called, and (iii) the values of R agree more closely with the molecular semidiameters derived from data on viscosity than these data agree with the radii obtained from other consequences of the kinetic theory of gases, such as Boyle's law, heat conduction, and diffusion. In fact, the viscosity values of  $\hat{R}$  are given respectively as  $1.024 \times 10^{-8}$ ,  $1.405 \times 10^{-8}$ , and  $1.448 \times 10^{-8}$  for hydrogen, oxygen, and nitrogen. - Phil. Mag., xxxiii, p. 215, February, 1917. H. S. U.

7. Lubrication of Resistance-Box Plugs.—In making accurate comparisons of electrical resistances, by the aid of plug or dial boxes, it is important to have the surfaces of contact of the plugs and lugs maintain sensibly constant resistances. The fact that a satisfactory approximation to this condition may be made by lubricating box-plugs and switches has been known for at least fourteen years, since it has been the custom at the National Physical Laboratory (England) to use petroleum or paraffin for this purpose during the interval of time specified. Since, however, the scheme does not seem to be generally known and as quantitative data are apparently lacking, it may not be superfluous to call attention to some of the results recently obtained and published by J. J. MANLEY.

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A certain box, fitted with 9 plugs, was tested 10 times, by Carey Foster's method, under each of the following conditions, the plugs being removed between the tests: (a) plugs in a bath of Geryk pump oil, (b) plugs smeared with Geryk pump oil, (c) plugs smeared with medicinal paraffin oil, (d) plugs smeared with "pure" vaseline, and (e) plugs and lugs clean and unlubricated. The mean contact resistances were found to be respectively 0.00135, 0.00118, 0.00124, 0.00116, and 0.00119 ohms. The corresponding extreme variations from these means are given as  $\pm 20, \pm 18.6, \pm 19.3, \pm 8.6, \text{ and } \pm 72.2 \text{ per cent.}$ Similar results were obtained with three other boxes having 17 plugs each, and with a box of 4 dials. The conclusions are that the usual process of cleaning the surfaces of contact with emerypaper or otherwise and using the plugs dry is very unsatisfactory, and that the scheme of smearing the plugs with pure vaseline is the most convenient and reliable procedure to follow.—Phil. Mag., xxxiii, p. 211, February, 1917. H. S. U.

8. Unipolar Induction.—The work of E. H. KENNARD should be added to the list of investigations which have dealt with the vexed problem of unipolar induction and its bearing on the moving-line hypothesis, on the existence and state of the luminiferous ether, etc. For lack of space, a description of the apparatus used and an outline of the associated theory will be omitted. By rotating a cylindrical condenser inside a magnetized coaxial solenoid it was found that the condenser became charged in accordance with the theory of Lorentz. Rotation of the solenoid alone had no effect, as had previously been observed by Barnett. The author also says: "The disproof of the moving-line theory is thus completed ; electromagnetic induction depends in part upon absolute rotation in the mechanical sense. Analysis in terms of electrons seems to make necessary the existence of a stationary aether in order to explain the observed effect; so that the phenomenon seems to present difficulties for those relativists who reject the aether."

The following by-product of the work merits attention for pedagogical reasons. Some text-books state that the effect of rotating the armature of a dynamo is the same as that of rotating the field magnets in the opposite direction. This statement must be understood to refer to the *total* electromotive force produced. On the other hand, the electromotive force in the first case is developed almost entirely in the longitudinal parts of the drum winding, while in the second case a large fraction of it is produced in the radial parts, and the distribution of electrification on the armature will be different in the two cases.—*Phil. Mag.*, xxxiii, p. 179, February, 1917. H. S. U.

9. Model Drawing; by C. OCTAVIUS WRIGHT and W. ARTHUR RUDD. Pp. xviii, 246; 300 figures. Cambridge, 1916 (University Press and G. P. Putnam's Sons).—The authors have found that students become much more proficient in the art of model drawing when the usual apparatus of simple geometrical models is supplemented by numerous practical exercises selected from typical architectural forms than when the subject is presented in a stereotyped Euclidean manner. Accordingly, although the volume is not intended to be an architectural textbook, it contains an undercurrent of suggestion of the historical development of architecture which should add interest to the theory of correct drawing, appeal to the esthetic sense, and act as an incentive to original work.

The text is divided into two parts, the first of which deals primarily with geometrical constructions (4 chapters) and the second (4 chapters) pertains mainly to drawing in perspective. The following salient features also deserve notice. No measuring points are employed. "The authors believe that the perspective treatment of the circle is quite new, and they have found that pupils can use the method with ease and advantage." Comparisons of representations on changing picture planes are given, and their relative advantages are discussed. Frequent opportunities are afforded for sketching from memory, and free use of tracing-paper in observation work and of clay in modelling is indicated. The line diagrams and other illustrations are excellent, the pages make a pleasing impression on the eye, and the subject is presented in a very attractive manner. H. S. U.

10. The Teaching of Arithmetic; by PAUL KLAPPER. Pp. vii, 387; 51 figures. New York, 1916 (D. Appleton and Co.).-This volume is an outgrowth of a course of lectures given to teachers in the elementary schools. The book is not a text on the subject of arithmetic, but it is a manual of method of teaching arithmetic. The early chapters are devoted to a critical study of the values of arithmetic, of the principles governing the organization of the course of study, and of the pyschology underlying sound methods in arithmetic. The later chapters set forth methods rather than the method of teaching each of the important branches of The index is preceded by two appendixes, arithmetic. of which the first is a classified list of the titles of reference books on the subject, and the second contains standard tests for classes of different grades. Although the text refers primarily to arithmetic it merits the attention of all teachers of elementary subjects because the underlying principles are of general applicability and since the material is presented in a very clear and thorough manner. H. S. U.

# II. GEOLOGY AND MINERALOGY.

1. American Fossil Cycads, Volume II, Taxonomy; by G. R. WIELAND. Issued by the Carnegie Institution of Washington as Publication 34, Volume II, on July 28, 1916.—In this, Professor Wieland's second, volume on American Fossil Cycads, are embodied the results of his labors for the last ten years, reports of which have appeared from time to time chiefly in this Journal. Like its sister volume, the present one is splendidly and generously illustrated and its beautiful quarto pages are a delight.

Taxonomy is the special subject treated, and though Wieland recognizes the flimsy basis\* of external morphology upon which Cycadeoid species have been created, yet he does not quarrel with the "cast-makers" of species but considers it "of the greatest importance to present structural details as rapidly as those can be assembled, and with as little specific rearrangement as possible." So thoroughly has he presented these details, that considerable headway has been made in the reduction of species, possibly also in the reduction of genera. For example, Wieland has shown that the score or so of species of Cycadella can probably all be included in four, and that even the genus Cycadellat can well be merged into Cycadeoidea. Though Wieland has no quarrel with the makers of species, yet he has one complaint which must appeal to every scientist as a very valid one. In some cases "type specimens" are hoarded intact in museums and only their external appearance is known, it being considered a sort of sacrilege to have their structure determined by sectioning! This most unenlightened view of the purpose of a museum retards scientific advance. It is a new phase of the old struggle between the systematist and the modern botanist, in which the hand of the strateographic geologist can be clearly discerned. In the end such museums will suffer by their narrow policy, for as time goes on, and the structure in related species become known, the value of the type ones will become less and less. The National Museum at Washington and some European museums have set a good example, and it will no doubt not be long until their lead will be followed. Wieland further considers that extensive field work, opening up of quarries like those for Dinosaurs, affords the only means for an adequate study of fossil plants.

Aside from the taxonomic results of his work the chief points of interest lie in the elaboration of the woody-structure of the stem and in connection with the fruiting habit and the character of the staminate disk.

A most remarkable new species (*C. dartoni*) which bore 500-600 well-preserved fruiting strobili, one in practically each leaf axil, and all uniformly mature, illustrates the occurrence of a culminating fruiting period (monocarpy) in the Cycadeoidea. Wieland had found traces of such a condition, but in this case the evidence is practically conclusive. The similar habit in the

\* "It is no exaggeration to say that most Cycadeoid species have been based on the characters which are the most liable to individual variation in life, the least diagnostic of species, and the least susceptible to constancy of preservation" (Vol. II, p. 15).

 $\dagger$  "But while it should by no means be considered that this new genus is finally and absolutely overthrown, it is, definitely speaking, necessary to recognize the fact that up to the present hour no features have been found in the case of any single specimen referred to *Cycadella* which are not found duplicated over and over in characteristic Cycadeoideas " (Vol. II, p. 106). bamboo is well known to the gardeners of Devon and Cornwall, where, after seven years of vigorous growth, the bamboo produces fruit, afterwards dying and having to be replaced. It is interesting also to note the accumulating evidence in the Cycadeoid forms of the dioecious and the moneocious conditions, in addition to hermaphrodism.

Many features of the staminate disk have been worked out in detail, notably in C. collosalis, and comparisons instituted with other forms. Perhaps the most novel and stimulating of these has to do with the relative value of the synangial and disk hypothesis of the origin of the integument, the latter view of which would bring the Cycadeoids into line with the Pteridosperms. It is an interesting attempt to explain the structure of the members of a phylum belonging to an older geological epoch by derivation from that of those from more recent formations. The extension of Wieland's disk theory to the living Cycads leads to the reversal of the accepted view as to their inter-relationships, in that the Cycas-type of megasporophyll has to be regarded as more specialized than that of the Zamieae. Wieland further uses his staminate disk hypothesis to bring the origin of the protective covering of the angiosperm ovule (the carpel) into line with that of the integument of the gymnosperm, the former being considered as a further stage in the progressive sterilization of parts which marked the origin of the ovule. Whether or not one agrees with those who see so much of a "proangiosperm" character in the Cycadeoidea it is certainly indisputable that the discovery of the peculiar structure of these forms has had more of an unexpected and revolutionary character in it than has the discovery of any recent group of fossil plants. Dr. Wieland is to be heartily congratulated on the admirable contribution which his two volumes on American Fossil Cycads make to fossil botany. R. B. THOMSON.

2. New Zealand Geological Survey; P. G. MORGAN, Director. Tenth Annual Report, 1916. Pp. 31, 2 maps.-The work of the New Zealand Geological Survey for the year 1915-16 included the following field studies: 1. The volcanic region of Mount Egmont, where the strata range from Miocene to Recent. 2. The Gisborne and Whatatutu areas of Cretaceous and Tertiary strata previously described as complexly folded but interpreted by J. Henderson and M. Ongley as much disturbed by faulting along an east-west belt. In this region "the indications of petroleum are favorable," and oil has been struck in wells in "moving faultpug." 3. The Tuapeka district, where an areal survey has been completed by Dr. P. Marshall. 4. The Oamaru district surveyed by Professor Park. Paleontologic work includes studies of Tertiary Mollusca by H. Suter (in press) and of Mesozoic fossils by C. T. Trechman. Preliminary reports on the geology of the Kaipara district and on water supply for Kaikoura have been prepared.

One of the most widely discussed and important geologic prob-AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 256—APRIL, 1917.

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lems of New Zealand is the stratigraphic relation of the Cretaceous to the Tertiary and of the various Tertiary formations to each other. Unconformities between Cretaceous and Tertiary, between Early Tertiary and Miocene, and between Miocene and Pliocene have been strongly affirmed and strongly denied. Marshall has advanced the extreme view that physical conformity characterizes the entire Cretaceous-Tertiary sequence of New Zealand. New studies bearing on this problem have been made by the Director of the Survey. A clear angular unconformity between Miocene and probable Cretaceous rocks was noted on Komiti Peninsula and an unconformity between Miocene and Early Tertiary or Cretaceous at Kaipara Flats (North Island). Field studies in Marlborough and North Canterbury, with special reference to unconformities post-dating the Amuri limestone, recognized as "Upper Cretaceous (Danian) or very early Tertiary," resulted in the recognition of a new stratigraphic hiatus. At Kaikoura the Amuri limestone is separated from the overlying Tertiary sediments (Weka Pass beds) by a water-worn surface on which lies a thin layer of conglomerate composed of fragments of phosphatized limestone with glauconite and green-At Amuri Bluffs, Weka Pass, and at Waikari, the same sand. features were noted. The suggestion is offered that the presence of an unconformity at a given horizon in one locality is not inconsistent with its absence elsewhere and that it is unnecessary to assume that any of the stratigraphic breaks so far recognized are co-extensive with the area of New Zealand. Mr. Morgan reaches a conclusion in harmony with the belief previously expressed by McKay that the Great Marlborough Conglomerate (Pliocene?) is unconformable with the Grey Marl (Early Tertiary?), thus dissenting from the view of C. A. Cotton (Journal of Geology, Volume XXII, 1914, pp. 346-363). H. E. G.

3. The Gold Belt South of Southern Cross; by T. BLATCH-FORD. With Petrological Notes, by R. A. FARQUHARSON, and Minerological Contributions, by É. S. SIMPSON and A. J. ROBERT-Western Australia Geological Survey. Bulletin 63, 1915. SON. Pp. 186, 19 pls., 31 figs., including 4 geological maps.—Bedrock in the vicinity of Southern Cross consists of highly metamorphosed sediments, probably Pre-Cambrian in age, intruded by granite and by masses of basic igneous rock. The granite is the dominant type; it occupies 85 per cent of the field and extends widely beyond, covering many thousands of square miles; its age is unknown. At the contact of igneous and metamorphosed sediments, ironstone lodes, exposed by erosion, stand as ridges. The outcrop of these lodes is goethite and ferruginous oxide of manganese; below the zone of weathering the ore is iron carbonate, magnetite, and especially pyrrhotite. One solid mass of pyrrhotite at Mount Caudan measured 70 feet from wall to wall. These ironstone lodes, also amphibolites and ancient sediments, are auriferous; the granites and associated pegmatites and the superficial deposits are not gold-bearing. H. E. G.

4. The Relationship of the Tetracoralla to the Hexacoralla; by W. I. ROBINSON. Trans. Connecticut Acad. Arts and Sci., vol. xxi, 1917, pp. 145-200, pl. I, text figs. 1-7.—The conclusions of the author in this interesting morphologic paper are : "The Tetracoralla are a natural group differing in a definite structural phenomenon from all Mesozoic and later forms in which the ontogeny of the skeleton is known. . . There are no known Hexacoralla in the Paleozoic. . While the writer does not pretend to have settled the question of the origin of the Hexacoralla, it is hoped that the evidence here presented will be conclusive in showing that there are no known Paleozoic Hexacoralla, and that the data furnished by this study of Paleozoic forms favor the theory of direct descent of modern hexacorals from tetracorals."

"The Cyathophyllidæ and Zaphrentidæ approached Mesozoic time as strong stocks capable of important structural variation. A marked tendency among Carboniferous forms is the widespread development of columellas. Even the conservative genus Zaphrentis was subject to this change. The columella is a far more prominent feature of the Hexacoralla than it is of the Tetracoralla. A correlative tendency is toward an increase in the number of septa and a consequent approach to radial symmetry." (150, 153.) C. s.

5. A new genus and species of the Thecidiinae, Geol. Mag., dec. VI, vol. ii, 1915, pp. 461-464, text fig. 1; The genera of Recent and Tertiary rhynchonellids, ibid., pp. 387-392, text figs. 1, 2; Additions to the knowledge of the Recent and Tertiary Brachiopoda of New Zealand and Australia, Trans. New Zealand Inst., vol. xlviii, 1915, 1916, pp. 41-47, pl. 1. By J. ALLAN THOMSON. —This author is studying the Cenozoic and Recent molluscs and brachiopods of the New Zealand region in a thorough and modern manner. In these papers on living and fossil brachiopods he defines the following new genera : Thecidellina, Ætheia, Liothyrella, Neorhynchia, and Murravia.

6. The Tertiary formations of western Washington; by CHARLES E. WEAVER. Wash. Geol. Survey, Bull. 13, 1916, pp. 327, pls. 30 (including 7 maps in pocket).—This industrious author here brings together all that he and others know of the topography and drainage, the pre-Tertiary formations, and, in the main, the stratigraphy of the Cenozoic formations of western Washington. C. S.

7. Paleontologic contributions from the New York State Museum; by RUDOLF RUEDEMANN. New York State Mus., Bull. 189, 1916, pp. 225, pls. 36, text figs. 46.—This book is replete with much that is new and of considerable importance to all paleontologists. Favosites turbinatus is shown to be operculate; Plumalina is not a plant but an alcyonarian like the gorgonians; the problematic Paropsonema whose structure so many of us have tried to guess is here shown to be probably related to Porpita and thus to be a siphonophore; of asterids twenty-two species are described and the new genera Clarkeaster, Lepidasterina, Klasmura, and Argentinaster; Serpulites is shown to be related to Conularia and both, along with Sphenothallus, Enchostoma and Torrellella, are thought to be tube-inhabiting annelids; Spathiocaris and the Discinocarina are probably aptychi; the new species, Pseudoniscus clarkei, is described; there is a note on the habitat of eurypterids and a very valuable description of median eyes in trilobites; and finally we learn that Trinucleus has free cheeks and is therefore an opisthoparian. c. s.

8. The Great Eruption of Sakura-jima in 1914; by B. Koto. Jour. Coll. Sci. Imp. Univ. Tokyo, vol. xxxviii, 1916. Art. 3, pp. 1-237, pls. i- xxiii, and map.-This account gives an excellent description of this great eruption, which was unusual, not only by reason of its magnitude, but from the lateral eruptions accompanying it, which poured large volumes of lava into the sea. The various stages of the eruption and its features are pictured with considerable detail and illustrated by many fine half-tone plates and figures in the text. Professor Koto believes that the disturbance was a normal one for the volcano according to the periodic recurrence of activity in Japanese volcanoes of about 120-130 years ; following Jensen, he thinks individual volcanoes, like Asama, may have a 60-year period, but that the regional activity of deep origin revives after the double length of the 60-year cycle, and quotes cases to illustrate this. The bilateral eruptions he suggests may have been caused by horizontal ejections of considerable magnitude into the flanks of the volcano, and that relief from pressure in these satellitic injection chambers took place directly upward, giving rise to subordinate vents.

The petrography of the ejected material is fully given, with a number of chemical analyses.

The work is an important contribution to vulcanology, especially in respect to the manifestations of volcanic phenomena in the Japanese islands. L. V. P.

9. On Synantectic Minerals and Related Phenomena; by J. J. SEDERHOLM. Bull. de la Comm. Géol. de Finlande, No. Pp. 148, pls. viii, 1916.—This work deals with certain mineral structures found in igneous and other rocks, known as reaction rims, corona minerals, kelyphite, myrmekite, etc. It may be recalled that in 1897 in certain rocks in Finland the author proposed the name of myrmekite for certain micropegmatitic intergrowths, which, however, were not composed of orthoclase and quartz, but of plagioclase and quartz; this occurs as masses with convex outline projecting into potash feldspar. The study of this has led him to consider other cases, where it is characteristic of certain mineral groupings in igneous rocks, that they occur only where two definite minerals meet. The coronas around olivine in gabbros are an example. Minerals in such associations he designates as synantectic (from the Greek, meaning to meet). They are found in a great variety of rocks, and some petrologists have been inclined to consider them as a structure produced in the original consolidation of the magma, whereas others have

seen in them evidence of secondary, in some cases, metamorphic action. The author is inclined to think, after study of the literature on the subject and much material of his own, that these structures are too complicated in their relations to be explained by any one simple process. He rather believes that those occurring in granitic rocks are primary, forming in the last stages of consolidation when fluids and gases play a prominent rôle; whereas they are secondary, or metamorphic in the mafic rocks.

L. V. P. 10. Bibliography of Australian Mineralogy. Bull. 22, Mineral Resources, Dept. of Mines, N. S. W.; by C. ANDERSON. 1916.—This bulletin gives first an exhaustive list of papers in which Australian minerals have been described and secondly locality indices and mineral lists for the different States.

W. E. F.

11. *Rings*; by G. F. KUNZ. Pp. 381, 3 colored pls., more than 100 doubletone pls. Philadelphia, 1916 (Lippincott Co.).— Dr. Kunz is an authority on the subject of jewels and ornaments and anything from him on this subject is certain to be of great interest. This is the third book by him on this general subject, the two earlier ones being The Curious Lore of Precious Stones and The Magic of Jewels and Charms. The following brief outline of the chapter headings will give a good idea of the scope of the book : The Origin of the Ring, Forms and Materials of Rings, Signet Rings, Rings of Historic Interest, Betrothal and Wedding Rings, Religious Use of Rings, Magic Rings, Rings of Healing. The book is finely printed and bound and profusely illustrated. W. E. F.

12. Economic Geology; by HEINRICH RIES.—In the notice of this work on p. 252, by a typographical error, the space assigned to Ore Deposits in the book is stated to be 329 pages instead of 398 pages.

13. The Geological History of Australian Flowering Plants; by E. C. ANDREWS, pp. 171-232, September, 1916.—The author calls attention to the following erratum on page 173, line 27: for absence of read absence from. He also suggests the insertion of the names of the following genera on page 232, line 16:

"Leucopogon (140 sp.), Pimelea (76 sp.), Eremophila (90 sp.), Bæckea (70 sp.), Daviesia (65 sp.), Boronia (75 sp.), Prostanthera (50 sp.), Olearia (75 sp.)."

# III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The Indians of Cuzco and the Apurimac; by H. B. FER-RIS, M.D. Memoirs American Anthropological Association, vol. III, No. 2, 1916.—This work is a study of the Anthropometric data collected by Dr. Luther T. Nelson, surgeon of the Peruvian Expedition of 1912, under the auspices of Yale University and the National Geographic Society, the director of the Exhibition being Professor Bingham.

Of the 145 Quichua Indians measured, 124 were from 54 localities in the Department of Cuzco, and 21 were from 9 localities in the Department of Apurimac. The average from each locality was thus only a little over two. All but one were males. Eighteen measures were taken on the body and extremities, six on the head, and twelve on the face. In addition to these, observations were made on the eyes, teeth, skin and its modifications, deformations, and anomalies. Some of the measures employed are not on the list approved by International Agreement. Of the 145 cases measured, 124 were adjudged pure and 24 mixed. The criteria of racial purity were skin, color, and features. The author wisely admits the possibilities of error in the matter of purity. It is probable that his ratio of 124 Indians of pure blood to 24 of mixed is too high. The ages of the subjects measured ranged from 17 to 88. Measurements on youths of 17 to 20 are of little value and should have been omitted. Fortunately the series contains only 14 cases of this class.

To summarize, the stature is low, the forearm long, and thigh short relatively; the skin color varies from light to dark brown; the hair black, straight, and abundant; grayness and baldness are rare; very little hair on the face; lips medium to thick; head proportions average mesocephalic with frequent examples of hypsicephaly; corpulency rare; teeth remarkably well preserved except on sugar plantations.

The memoir is accompanied by instructive tables and a series of sixty plates; it was published at the expense of The National Geographic Society. There is apparently no connection between the numbers accompanying the illustrations and the subject numbers of the tables. It is also to be regretted that in taking the photographs there was no uniformity of orientation. Seldom is the subject correctly posed either for a front view or for a profile; and one is left to guess whether the profile is of the same subject as the accompanying front view. The Expedition is to be commended on having made a beginning in the field of Quichua anthropometry. G. G. MACCURDY.

2. Carnegie Institution of Washington; ROBERT S. WOOD-WARD, President. Year Book No. 15, 1916. Pp. 404, 1 pl. Washington, Feb. 15, 1917.-The completion of the fifteenth year of the Carnegie Institution has found it with an income of \$1,351,-200, largely derived from its endowment fund of \$22,000,000. Notwithstanding this very considerable amount received annually, the president states most distinctly that the income of the Institution not only falls far short of popular estimate, but is not even equal to the proper demands upon it for research. This is in part due to the fact that the purchasing power of all income has materially declined in recent years; but, aside from this, the legitimate demands upon the Institution increase still more rapidly. This limitation is particularly to be regretted, since the system of Research Associates, finally evolved after various preliminary stages, has proved to be so valuable that its extension is much to be desired. It is added, however, that the current activities of the Institution can continue without serious danger of lessening the efficiency, although expansion cannot be hoped for.

Of the total sum appropriated for 1916, somewhat more than one-half (\$654,700) was given to the special Departments recognized as constituting the chief work of the Institution. In addition, \$120,000 was allotted for the minor grants, and \$74,000 for publication, giving the remainder to administration, insurance, and the reserve fund (the latter receives \$250,000). During the year, thirty-five volumes have been issued, having an aggregate of about 9,500 octavo and 2,400 quarto pages. Since its beginning in 1902, the impressive total of three hundred and thirtyfour volumes, with 91,000 pages, have been issued.

The administrative reports which occupy the first fifty pages are followed by special reports—each in detail and full of interest—from the Directors of the special Departments, eleven in number, in their different lines of work; a summary of the contents of recent publications closes the volume. It is interesting to note the extension of the work in the Geophysical Laboratory, under Dr. A. L. Day; also of the Mt. Wilson Solar Observatory, under Dr. George E. Hale, where the 100-inch reflecting telescope has now reached essential completion. In the Department of Terrestrial Magnetism, Dr. L. A. Bauer tells how the non-magnetic ship "Carnegie" has recently completed an extended voyage in the sub-antarctic region with important results. The total length of the cruises of the "Carnegie" and its predecessor the "Galilee" now amounts to 224,000 nautical miles, as strikingly portrayed on a map of the world on the Mercator's projection.

Recent publications of the Institution are noted in the following list (continued from Dec. 1916, vol. xlii, pp. 508, 509):

No. 224. Contributions to Embryology. Volume IV, 4to. Nos. 10, 11, 12, 13. Pp. 106; 4 pls.

No. 228. Studies on the Variation, Distribution, and Evolution of the Genus Partula. The Species inhabiting Tahiti; by HENRY E. CRAMPTON. 4to. Pp. 313; 34 pls.

No. 234. Descriptive Catalogue of the Documents relating to the History of the United States in Papeles Procedentes de Cuba, deposited in the Archivo General de Indias at Seville; by ROSCOE R. HILL. Pp. xliii, 594.

No. 239. Guide to Materials for American History in Russian Archives; by FRANK A. GOLDER. Pp. viii, 177.

No. 244. Sissano: Movements of Migration within and through Melanesia; by WILLIAM CHURCHILL. Pp. 181; 17 charts.

No. 249. The Interferometry of Reversed and Non-Reversed Spectra; by CARL BARUS. Pp. 158; 99 figs.

List of Publications of the Carnegie Institution of Washington. Pp. 155. Issued December 1, 1916.

Also the following additions to the Series of Classics of International Law. Edited by JAMES BROWN SCOTT (see p. 509).

Synopsis Juris Gentium, by JOHANN WOLFGANG TEXTOR. Edited by LUDWIG VON BAR. Volume I. Pp. 28*a*, 168. A Reproduction of the First Edition with Introduction by Ludwig von Bar and Errata. Volume II, A Translation of the Text, by JOHN P. BATE, with index of authors cited. Pp. 26a, 348.

3. Observatory Publications.—The following publications from certain of the Observatories in the country call for mention:

U. S. NAVAL OBSERVATORY. Reprint, Second Series, volume IX, Appendix.—Determination of the Difference of Longitude between Washington and Paris 1913-1914; reduced under the direction of F. B. LITTELL and G. A. HILL. Pp. E 100; 5 pls. Washington, 1916. Annual Report for 1916. Pp. 21; 3 plates.

ALLEGHENY OBSERVATORY of the University of Pittsburgh. Vol. III, No. 22. The orbit and spectrum of  $\sigma$  Aquilæ; by FRANK C. JORDAN. Pp. 189–196. No. 23. On the orbit of T Vulpeculæ; by A. F. BEAL. Pp. 197–199.

CINCINNATI OBSERVATORY.—No. 18. Part II. Catalogue of Proper Motion Stars. Pp. 113; by JERMAIN G. PORTER, Director; EVERETT I. YOWELL and ELLIOTT SMITH, astronomers. Cincinnati, 1916.

PRINCETON UNIVERSITY OBSERVATORY.—No. 4. Photometric Researches. The eclipsing variables R V Ophiuchi, R Z Cassiopeiae; by RAYMOND S. DUGAN. Pp. 38; tables and illustrations.

DETROIT OBSERVATORY.—Publications of the Astronomical Observatory of the University of Michigan. Volume II. Pp. 186; 11 pls. Ann Arbor, 1916.

CAROTHERS OBSERVATORY (*Private Astronomical*), Houston, Texas, March, 1916.—Bulletins, No. 1. The Correlation of Solar and Weather Phenomena (Weather). Pp. 5, 1 chart. Also the same subject (Solar). Pp. 6, 8 maps.

4. Publications of the Museum of the Brooklyn Institute of Arts and Sciences.—Science Bulletin. Vol. 2, No. 6. A Contribution to the Ornithology of the Orinoco Region; by GEORGE K. CHERRIE. Pp. 133 a—374. Brooklyn, 1916.

5. Tables and Other Data for Engineers and Business Men; compiled by CHAS. E. FERRIS. Twentieth Edition. Pp. 220. Knoxville, Tenn. (Published by the University Press.)—This is a new edition of a useful little pocket-book which many have been glad to avail themselves of in the past. As stated in the preface, the tables and engineering data here given have been compiled with a view to securing a medium for bringing to the attention of prominent men in the South strong "arguments in favor of technical education as a means of developing undeveloped resources."

# OBITUARY.

PROFESSOR WILLIAM BEEBE, for forty-one years an important member of the mathematical Faculty of Yale College, died in New Haven on March 11 at the age of sixty-five years.

PROFESSOR THOMAS PURDIE, who held the chair of chemistry in St. Andrew's University, died in December at the age of seventy-three years.

DR. N. H. J. MILLER of Harpenden, England, who made important contributions to agricultural chemistry, died on January 12 in his thirty-seventh year.

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J-128. Live Pupae. Zoology: J-116. Material for Dissection. J-26. Compara-

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## THE

# AMERICAN JOURNAL OF SCIENCE

# [FOURTH SERIES.]

ART. XXXI.—The Geology of the Lau Islands; by Wilbur GARLAND FOYE.

## OUTLINE.

Introduction Geography Previous work General statement of results Classification of the islands Detailed geology 1—Vanua Mbalavu 2—Lakemba Application of the results of the expedition to coral reef theories.

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INTRODUCTION.

THE following paper presents in outline a few of the more important results obtained during a geological study of the Lau Islands, Fiji. The study was made while a Sheldon Traveling Fellow of Harvard University and occupied the months between August and November, 1915. A complete account of the expedition will be published later as a Shaler Memorial report.

## Geography.

The Lau group consists of fifty or more islands lying east of the two main islands of Fiji. They are scattered over 300 miles of the ocean floor from the 17th to the 21st parallels of south latitude and between the 178th and 179th meridians of west longitude. The average island is, perhaps, 4 or 5 miles in diameter and 300 or 400 feet in height. Vanua Mbalavu, lying at the west side of the lagoon inclosing the Exploring group, is one of the largest islands. It is 20 miles long and 1 or 2 miles wide.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 257.—MAY, 1917. 24 PREVIOUS WORK.

J. Stanley Gardiner\* of Cambridge University, England, E. C. Andrewst of Sydney, Australia, Alexander Agassiz, ‡ and W. M. Davis§ are the scientists who have contributed the most to the geological knowledge of the islands.

GENERAL STATEMENT OF THE RESULTS.

The Lau islands are believed to have been formed by volcanic activity about the middle of the Tertiary period. They were later maturely eroded, submerged, and overlain unconformably by 300 to 500 feet of coraliferous limestone. Still later they were elevated, eroded, and a second period of basaltic eruptivity spread its debris over the eroded complex. In Recent times certain of the islands in which limestones are alone exposed have been eroded to submerged platforms by atmospheric solution and, aided by a recent subsidence, atolls have developed in their place.

CLASSIFICATION OF THE ISLANDS.

In a later paper a genetic classification of the Lau islands will be given, but for the purposes of this paper it is sufficient to distinguish:

1—Islands composed of limestone and volcanic rocks;

2-Islands composed of limestone alone;

3—Islands composed of volcanic rocks alone.

The members of group 3 are in general younger than the other groups and only two islands, Munia and Kanathea, were visited. Among the more important members of group 1, the Exploring Group, Tuvuthà, Lakemba, Ono-i-Lau, and Kambara were studied. Fulanga, Ongea, Vatoa, Wangava, and Vekai of group 2 were also visited. Of the islands just mentioned, Vanua Mbalavu of the Exploring Group and Lakemba will alone be described. The geological facts characteristic of these islands may be considered as typical of the other islands as well.

DETAILED GEOLOGY.

1. Vanua Mbalavu (fig. 1).

Vanua Mbalavu is nearly twenty miles long from N. to S. and of variable width. It is shaped something like a question mark and has its greatest width (2 to 3 miles) near the center

\*J. Stanley Gardiner, "Coral Reefs of Funafuti, Rotuma, and Fiji," Proc. Camb. Phil. Soc., vol. ix, pt. 8, pp. 417-503, 1898. † E. C. Andrews, "Limestones of the Fiji Islands," Bull. Mus. Comp.

Zoöl., Harvard College, vol. xxxviii, 1900. ‡ Alexander Agassiz, "Coral Reefs of Fiji," Bull. Mus. Comp. Zoöl., Har-vard College, vol. xxxiii, 1899. § W. M. Davis, "A Shaler Memorial Study of Coral Reefs," this Journal,

vol. xl, pp. 223-271, 1915.

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FIG. 1. The Exploring group and adjacent Reefs and Islands. Black=elevated limestone.



FIG. 2. Island of Lakemba. Black=limestone. White=andesite. Lined=coastal flat.

of the upper curve. Here, near the center of the island, is situated its highest peak, Koro Mbasanga, which rises 930 feet. North of this peak the country slopes down in wide, spoonshaped valleys to a limestone platform, having a broken surface which forms the northern end of the island. The average elevation of the platform is 350 feet. It swings southward on the western side of Koro Mbasanga and terminates just west of the peak, wedging out along the shore.

Southward from this peak a broken ridge forms a serrate backbone to the island. The map shows hills 500 and 700 feet high along this ridge, but the usual altitude is but 300 or 400 feet. The hills are low and rounded.

At the southern end of the island the low ridge dips southward beneath a small area of limestone standing at an elevation of about 300 feet. The peak, Koro Mbasanga, has an amphitheater-like depression on its eastern side. The southern limb of the ridge inclosing the amphitheater was followed southward and it was found that lavas from this peak had overflowed an area of limestone and baked it red. The limestone was a foraminiferal variety containing little or no coral. Just north of Koro Mbasanga a similar limestone, but silver-grey in color, was found in patches overlying an eroded volcanic surface. Here it included bits of the underlying rock and formed an undoubted basal layer.

From the facts just recorded it was inferred that an eroded surface of volcanic rocks had been submerged and overlain unconformably by limestone. The evidence was inconclusive, however, as to whether the limestone had been elevated and eroded before the extrusion of the volcanic rocks of the second period. This question was answered by exposures in the small island of Andivathi, lying off the northwestern coast of Vanua Mbalavu within the upper curve of the question mark.

The larger part of Andivathi is composed of andesite agglomerate and ash dipping 30° E. The western beds, representing the lower members of the series, are of coarse agglomerate with vesicular blocks of lava a foot or more in diameter. The upper beds become increasingly finer and show many small fragments of pumice. The total thickness of these beds is about 200 feet. The eastern side of Andivathi is composed of elevated coraliferous limestone. Both ash and limestone are cut by a network of basic dikes, the largest observed being 20 feet in width. It is deeply lateritized and outcrops as a long, well-defined depression in the limestone into which it was intruded. The limestone stands up in nearly perpendicular walls on either side of the depression which was once filled with the dike, indicating that in this climate the igneous rock weathers more rapidly than the sedimentary. On the N.E. side of

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Andivathi ash beds rest on an irregular surface of limestone and dip S.E. toward the eroded and nearly vertical walls of limestone, forming the coast of Vanua Mbalavu less than a hundred yards away. The irregularity of the surface beneath the ash makes it apparent that the limestone was elevated and eroded before the volcanic rocks of the second period were extruded.

The central ridge south of Koro Mbasanga is more deeply lateritized than the rocks of the highest peak, and bits of silicified coral often occur in the laterite. The writer inferred that the corals were residuals of a limestone cover which once mantled the volcanic rocks. The andesites, lateritized to a depth of 20 feet or more, strengthen this inference since it is apparent that they are of a very different age than the rocks of Koro Mbasanga. A petrographic study shows that the latter rocks are olivine basalts whereas the former are andesites.

The limestone area at the northern end of the island covers 10 to 12 square miles. Its surface is very irregular and in places almost impassable because of the tangled mass of solution remnants. It is covered with a red residual soil, having an average thickness of one or two feet. Skeats found that 17 limestones from this district showed less than 1/10th of one per cent of insoluble matter. It follows that the limestone lost by solution must be reckoned in hundreds of feet.

The general elevation of the limestone plateau is 300 to 350 feet. Nearly perpendicular walls bound this area along the coast and in these walls may be traced a slight folding of very low curvature. There is no evidence here that the limestones have been deposited on the eroded stumps of Tertiary strata, as Agassiz's theory would postulate. Coral heads occur in place from top to bottom of these cliffs and are usually surrounded by a paste of shell and coral rubble similar to that filling in around the heads of a modern reef. Since these cliffs are higher than the vertical limit within which corals grow beneath the sea, and since, moreover, they must have retreated laterally, as well as vertically, by solution and wave-cutting, the writer sees no escape from the conclusion that they were formed by vertical subsidence.

Distinctive features of the limestone of the island are the narrow fingering bays, inclosed by nearly vertical walls of limestone, extending far inland. Many of the bay-heads rest against the volcanic rocks and the writer believes that underground solution cavities, formed along the contact between the limestone and volcanic rocks, have in most cases been the initial stage in the production of such bays. Most of the rainfall percolates easily into the porous limestone and flows away to the sea on the surface of the volcanic rocks. Large solution cavities are thus formed and the collapse of their roofs gradually develops the ramifying bays. The writer does not agree with Davis that these bays are necessarily evidence of subsidence in sub-recent times.

# 2. Lakemba (fig. 2).

The island of Lakemba was probably never completely covered with limestone. The volcanic surface, reaching a maximum elevation of nearly 800 feet, is composed of wellrounded, mature forms. The rocks are deeply lateritized and support a scant vegetation.

Along the boundary of the volcanic area are isolated remnants of elevated limestone which once encircled the island. These remnants unconformably overlie the volcanic rocks and rise to a maximum elevation of 320 feet. Near the northern side of the island spur-ridges 100 feet high and their intervening valleys are covered with a mantle of shell and coral rubble containing volcanic pebbles. Traced west and south, this basal deposit is transitional upward into coral-reef limestone.

The remnants of limestone decrease in altitude along the coast towards the eastern side of the island. They reach a maximum elevation, as noted above, of 320 feet at its northwestern side but do not occur on the side hills of the eastern half.

These facts show that the island, bearing an unknown number of andesitic cones, underwent nature erosion and subsided. The mature topography was not entirely submerged since 400 feet of the island still remained above sea-level. The sunken portion was overlain by 320 feet, or more, of coraliferous limestone and was later uplifted.

The disappearance of the limestone from the eastern side of the island may be explained in two ways. It may be due to more rapid solution on the rain side of the island, or it may be due to tilting during uplift. If erosion were the cause it would seem that the rainy side of the island should show a more mature topography than the dry side. It is significant that the topographic forms on the western side show greater erosion than on the east. This fact, with others, leads the writer to believe that the island has been tilted toward the east.

The reef on the western side of Lakemba is narrow and fringing but sweeps far out and includes a lagoon 8 or 10 miles wide on the northeastern side. The mouths of the rivers on the eastern side are deeply embayed. The width of the western reef would suggest that it has been established in subrecent times by uplift, whereas the eastern reef has either been long established or recently submerged. The recent uplift of the western coast would favor a tilting to the east.

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# W. G. Foys—Geology of the Lau Islands.

In this connection it is important to note that the Lakemba lagoon has a maximum depth of 14 fathoms, the Aiwa lagoon slightly to the southeast, 21 fathoms, and the lagoons of the Argo reefs, 15 miles to the east, have a depth on the western side of 20 fathoms, on the eastern side of 35 fathoms. These lagoon depths are much greater than the average for the Lau Islands and may possibly be attributed to the eastern tilting movement described above.

# Application of the Results of the Expedition to Coral Reef Theories.

From the facts just stated it is apparent that the elevated limestones of the Lau Islands were deposited on an eroded surface of volcanic rocks which subsided in accordance with the principles of Darwin's theory. It has been questioned whether this process explains the development of modern atolls. Alexander Agassiz inferred that coral banks similar to the Florida banks were the result. Likewise Daly considers atolls as special, post-Pleistocene, forms of coral reefs.

According to Daly, Kambara is an atoll which developed on a platform carved on Tertiary limestones, during the Pleistocene, and which has since been elevated. The coraliferous limestones of the island now stand at an elevation of 400 feet, or more, above the sea. Since the rise of the waters after the Glacial period, as stated by this writer, was between 250 and 300 feet, it would seem that there should be evidence of an unconformity between the Tertiary platform and the post-Pleistocene reef exposed in the sea-cliffs; no evidence of such an unconformity was seen either in Kambara or any similar island, although the cliffs have been cut back sufficiently to expose such unconformities if they were present.

That the uplift of the limestone islands is comparatively recent in date is apparent from the fact that the included corals are Pleistocene or Recent. Their age was kindly determined for the writer by Dr. T. W. Vaughan. Assuming that Fulanga owes its atoll form to post-Pleistocene growth on a Pleistocene, wave cut platform, this platform should now stand near the present sea-level, as the summit of the uplifted atoll-rim is 240 feet above that level. It is apparent, therefore, that the present level lagoon, which is from 10 to 12 fathoms in depth, cannot be ascribed to Pleistocene wave-cutting. Hence it is inferred that atolls developed as a result of the subsidence of the Tertiary volcanoes.

The limestone rim of Lakemba has the appearance of a barrier-reef formed during subsidence. The exact location of the reef-edge is not known, for it is almost impossible to recognize ancient reef-edges in masses of elevated limestone. If the observations of the writer are correct the growing reef is continually being destroyed and its débris cast into the lagoon; the reef grows on a mass of its own waste containing only a limited number of coral heads *in situ*. There is more chance of the rounded heads of the lagoon being preserved than the fungus-like growth of the reef-edge.

There is, therefore, positive evidence of subsidence in the Lau islands, and very good evidence that barrier reefs and atolls were developed during such subsidence. Thus far the Darwinian theory is supported, but the irregular uplifts and subsidences negative the idea of a general depression of the Pacific islands, a further conception of the theory. The earth movements are here irregular and seem to be confined to individual foci whose instability is the result of isostatic adjustment of large fault blocks, of secular cooling after volcanism, or of the transfer of large quantities of molten rock from the interior to the exterior of the earth's crust.

There is another method by which atolls develop. The limestone islands are rapidly eroded to sea-level by atmospheric solution. Evidence of this process may be seen in the diminishing limestone masses within the lagoons of many of the Lau islands. By tidal-scour and wave action, platforms are developed slightly below sea-level. Examples of such platforms may be seen about Fulanga and Ongea. It is significant, however, that most of these islands have lagoons 10 to 15 fathoms in depth. Such depths cannot be ascribed to erosion but must be the result of recent submergence. In time, the erosion of the elevated limestone of Fulanga will lead to the development of an atoll of the second generation replacing the older uplifted mass.

In conclusion, it should be stated that the evidence from the unstable islands of the Lau Group should not be given too wide application. The writer is convinced that the Glacialcontrol theory has a large body of facts in its favor but these facts are gathered from other, more stable, portions of the earth's surface.

Middlebury College, Middlebury, Vt.

Spencer—Origin and Age of the Ontario Shore-Line. 351

# ART. XXXII.—Origin and Age of the Ontario Shore-line, —Birth of the Modern Saint Lawrence River; by J. W. SPENCER, Ph.D., LL.D.

Introduction.—The modern beach of Lake Ontario is the last of the shore-lines about the lake basin to be studied with sufficient precision for writing its history, although seemingly obvious. Much attention had been given, during the last three decades, to the higher water-planes, especially to the Iroquois Beach (of Spencer\*), not only skirting the lake at a high level, but tilted by subsequent earth-movements, so that it now rises 540 feet between the head of the lake and the Galops Rapids of the St. Lawrence River (66 miles below the lake outlet), which form the first rocky barrier to the lake basin. In contrast with this deformation, I have recently determined the horizontality of the modern shore.<sup>‡</sup> In sinking from the higher beach, the waters fell to more than 200 feet below the present level (at Niagara River), before the warping of the earth's crust raised the barrier to the lake basin, so that the waters rose to a few feet above the present Ontario shoreline, from which they have since been lowered, owing to the scour of the St. Lawrence River, after the river sunk within its channel. Pursuing the investigation of these features, with the aid of the most comprehensive surveys, soundings and borings for the Toronto Water Supply, especially those of Messrs. Chipman and Power, I have been able to approximate the age of the present shore-line of Lake Ontario and that of the St. Lawrence River.

# Cessation of Earth-Movements.

# Birth of the Post-Glacial Saint Lawrence River.

Intermittent subsiding of the waters below the Iroquois Beach is seen in minor beaches and terraces, best developed in the valleys tributary to that of the lake. Terraces or terraceplains occur at 70–75, 40, 15, and 5 feet, near the head of the lake and along the lower Niagara River, but the question of their deformation and the amount of lowering of the lake level

<sup>\* &</sup>quot;Science," vol. ii, p. 49, 1888 (abstract); this Journal, vol. xl, pp. 445-451, 1890.

<sup>&</sup>lt;sup>†</sup>Deformation measured between head of lake and Watertown, N. Y., is 367 feet, and calculated to the Galops Rapids (where the country is low) 540 feet.

<sup>&</sup>lt;sup>‡</sup>Bull. Geol. Soc. Am., vol. xxvii, p. 79, 1916 (abstract).



FIG. 1. Map and chart in the vicinity of Toronto, showing soundings, etc. (After Chipman and Powers' maps.)

due to the scour of its outlet had not been investigated. Between 1911–1914, I found that the terraces at about 15 feet\* and 5 feet recur from one end of the lake to the other, thus showing that the deformation had ceased when the waters were at these levels. But, as stated before, the water level had been more than 200 feet lower than now before the deformation which barricaded the basin, thereby causing the lake to rise again.

The banks of the St. Lawrence River, except at some of the rapids, are composed of drift rising seldom higher than 20 feet, with broad plains beyond formerly covered by a pre-Ontario Where rocky isllake. ands, in the upper part of the river, rise higher, deep channels occur between them. These are pre-Glacial features, while the modern river was first established when it was confined by the terrace about 15 feet above the present sur face, such as may be seen Gananoque, carved at out of banks of drift. This terrace is especially well-defined at Mill Haven (12 miles west of Kingston), being there carved out of shaly rock; so that the term Mill Haven Terrace may approximately be given

\*Bull. Geol. Soc. Am., vol. xxvii, p. 79, 1916 (abstract).

to the lake stage, corresponding to the birth of the St. Lawrence River.

Upon the river being confined within its banks, as here defined, the currents removed the drift from the St. Lawrence channel, thus lowering the Ontario level by about 10 feet, thereby uncovering the underlying flat rock floor at and above the first rapids, which form the rim of the lake basin (to which point the river slopes only 2 feet). The rock spur at the rapids is less than a mile across and has been partly penetrated so as to lower the lake by nearly 5 feet more.

This rocky barrier has caused the present lake level to continue longer than that which obtained during the Mill Haven stage, when only drift was being removed by the river currents. The higher stage of the Ontario shore-line (3-5 feet) is well illustrated at the head of the Gulf of Quinté, at the eastern end of Burlington Beach, near Hamilton, at the mouth of Niagara River, and in lower reaches of tributary streams.

The Ontario Beach.—Passing to the present stage of the beach, its variability is striking. Encroachments of the lake upon the shore prevail in many places. East of Burlington village, the waves are cutting a terrace in shaly rock. The greatest encroachments are those upon the drift of Scarboro Bluffs (see fig. 1) east of Toronto, and farther east near Port Hope, where it was necessary to shift the original railway bed farther inland. Again, so weak is the wave action that the low plains slope almost imperceptibly to the water edge, leaving little or no beach form to mark the lowering level, as at Colborne or near the lake outlet.

In contrast are the great sand deposits and bars at the base of the peninsula of Prince Edward County formerly accumulated by the late Algonquin River and its successor the modern Trent River. Only a few tributary streams, as those at Port Darlington and Frenchman's Bay, are obstructed by barrier beaches across their mouths. However, there are two most conspicuous and abnormal features,—those of Burlington Beach and Toronto Island, which if studied alone would give an erroneous idea of the Ontario shore and its history.

Burlington Beach is a barrier of sand and gravel, 200-300 feet wide, 2-3 feet high and 5 miles long, crossing Lake Ontario 5 miles from its head. This beach is not a delta and contains no material brought down by the streams through Dundas Valley, at the head of the bay. Its sands and gravel (of Hudson River limestone) are immediately derived from the stony drift by the assorting action of the waves, and transported by the currents across the lake from its northwestern side. At both ends of the barrier, the beach material is thin, resting on clayey drift or on shales. Toronto Island.—The enormous mass of sand deposited here is of more than local interest, having given rise to fatal chronological speculations. Its origin is much more complex than that of wave-assorted beach materials transported by currents from the drift bluffs of Scarboro and deposited in front of Toronto Harbour. Its history could not be separated from that of the whole Ontario shore, nor understood without the study of the invaluable surveys made for the Toronto Water Supply.

The floor of Lake Ontario is generally a uniform plain, sloping outward from its northern shore, at about 50 feet per mile to a depth of more than 300 feet, in contrast with the steps, which occur beneath the southern side of the lake. In the vicinity of Toronto, the map of Chipman and Powers (fig. 1) shows the lake deepening gradually to 50 feet, from a mile to a mile and a half from the shore, beyond which the 75-foot contour is irregular, varying from 2 to  $3\frac{1}{2}$  miles. This encircles the great Humber Embayment, and the smaller indentations off the Woodbine and off Victoria Park. A steeper slope, beginning at 75-100 feet and reaching to a depth of 175 or even 250 feet, extends along the coast for 12 miles, thus producing a slight shelf-like form, which disappears at The shelf sends out a tongue either end of this section. between the embayments of Woodbine and Victoria Park, (where the wave action is of little consequence) to a distance These indentations, as well as of 3 miles from the low shore. the Humbar Embayment, are partly re-filled inter-Glacial or pre-Ontario land valleys.

One of the inter-Glacial valleys in the floor of Lake Ontario is brought to light by borings in front of Victoria Park (section B, fig. 2). An older inter-Glacial valley to the east in Scarboro Bluffs was discovered by Dr. G. J. Hinde, and redescribed by Prof. A. P. Coleman, but its natural extension to the lake is re-filled, concealing its corresponding embayment.

The line of borings outward from Victoria Park shows that the rocky basement beneath the lake is covered by only about 30 feet of inter-Glacial clays and sands. Another line of borings,  $4\frac{1}{2}$  miles to the east, in front of Scarboro Bluffs, also shows 30 feet of sand and clay covering the rocky basement of the lake (section C, fig. 2). The lake floor here slopes uniformly for 2 miles to a depth of 85 or 90 feet, and somewhat more rapidly beyond. On either side of this point, the border of the shelf varies from  $1\frac{1}{2}-2\frac{1}{2}$  miles from the shore. Thus a uniformity of the lake floor is shown in front of either the lower or the higher shore and where there is both little or rapid encroachment of the lake.

In contrast with these features are those of Toronto bay and



FIG. 2. A—section from shore at Toronto, across Island to the Filter basin; see map, fig. 1. (From Toronto Water Supply Report.) B—section outward from Victoria Park. (Chipman & Powers.) C—section outward from Scarboro Bluffs. (Chipman & Powers.)

Island, the outer margin of which is 10,800 feet from the shore (section A, fig. 2). At the shore, only a few feet of sand cover the basement shales, but at the outer edge of the island variable beds of sand with clay (180 feet) rest on transition and clay beds to a depth of 230 feet, overlying the basement shales. Their origin is complex. Only the upper 30 feet are composed of coarse sands and gravels, washed as are beach materials. These alone can be regarded as belonging to the Ontario beach, and their thickness corresponds to the maximum depth of the bay behind the island. Below are 10 feet of transition beds with some clay, which limit the waterbearing strata. Beneath, are 100 feet of variable beds of very fine sand and clayey sands, not well-washed. These rest upon very fine, closely packed sand without clay (40 feet), beneath which is a transition bed of clay nodules in sand (10 feet) overlying 40 feet of blue clay beds covering the basement shales,\* The fine clayey sands below the coarse beach sands are the covered post-Iroquois delta deposits of the Don River.

The Toronto beach, in front of Ashbridge Bay and Toronto Harbour, is a barrier nearly 6 miles long, leaving the main lake shore near the Woodbine (see map, fig. 1). By comparing the various maps of it, made since 1788, the beach is seen to have had a rapid westward growth--the waves building up a succession of spurs and hooks, with intervening ponds and marshes, until they coalesced (see fig. 3). Early in the Nineteenth Century the western end of the Harbour was open. Here a spur, 4,000 feet long, was developed between 1841 and 1882 (forming Hanlan's bay; see B, fig. 3). In 1854, the western end of the Harbour was being further silted up so as to occasion concern. In 1891, and again in 1912, piers were constructed for keeping open the deepened western channel, now otherwise closed. The materials for the westward growth of the barrier have been mostly obtained by robbing the southern shore of the beach.

About 1850, the waves forced a passage between the lake and the bay (B, fig. 3). This was further opened in 1852, '3 and '5, when a steamer passed through. The gap was closed in 1856 owing to low water, but it became permanent in 1857. By 1882 the beach had been washed away for a length of 1,800 feet and a depth of 5 feet, leaving the site of the tavern of 1841 some hundreds of feet outward in the lake, as also the triangulation station of 1818. Thus, Toronto Island became separated from the peninsula at dates mentioned. No considerable amount of drift from the east re-entered the gap. In 1883 the channel through it was deepened by a canal and the

\*This geological section was obtained from borings at the Filter basin, near the southwestern point of the barrier beach.



FIG. 3. Maps of Toronto Harbour, showing development of the Island, the barrier broken by the waves, and gap again closed artificially and by redeposits due to protective works (after Chipman). A, B, C.

remainder of the gap closed by crib-work and piling, and the deepened canal is now protected by transverse piers nearly half a mile long.

The sands and gravels were originally derived from the remains of the drifts of Scarboro Bluffs, which upon being undermined and wave-washed were current-borne westward. However, these features were insufficient to explain the origin of Toronto Island until soundings and borings had revealed the character of the underlying delta deposits hitherto unknown. The source of these is found in the excavation of the Don valley\* (behind the barrier to Toronto and Ashbridge bays (see map) which, below a height of 190 feet above the lake, has been excavated since the Iroquois epoch. The delta basement (with the closely packed very fine sand which may be inter-Glacial) is more than six times the thickness of the Ontario beach itself.

The now buried delta was accumulated while the lake surface was rising from its lowest level (some 200 feet) to that of Mill-Haven stage, which is now represented by the "bottom" of the present valley, before the waters fell again to the existing shore, when the beach materials from Scarboro Bluffs were brought by the waves to cover the delta mass.

While elsewhere the lake deepens gradually to 75–100 feet or more, the slope of its floor is only 17 feet in a distance of 1,600 feet at the southwestern angle of the Island, but immediately beyond it descends abruptly to 69 feet (in 1,400 feet) and to 150 feet just beyond (section A, fig. 2). Such is in strong contrast with the gentle gradient elsewhere. This changing slope also shows the approximate limit of wave action to 20 feet as appears farther east. No features below 20–30 feet can be correlated with the Ontario Beach.

The materials of both the older delta and the newer beach have been dumped into the eastern side of the Humber Embayment, producing the peculiar configuration of the southwestern extremity of the Island. But the Humber is unlike the Don Valley, the former being of inter-Glacial age, with a later mantle but without a post-Iroquois delta as has the Don.

# Age of Lake Ontario and of the Saint Lawrence River.

Investigations about Toronto Island alone furnish no clue of the age of the Ontario Beach; but from the encroachments of the lake upon Scarboro Bluffs, for over 9 miles between Victoria Park and Port Union, and from the topography of the

<sup>\*</sup>Such materials as were removed may be seen at the Don brick yard; till 3 feet; stratified sand with grit and layers of clay 20-25 feet; laminated drab clay (sandy) about 25 feet; clay with fine sandy laminations 35-40 feet; sand coarser 6 feet; fine sandy clay 40 feet covered with sand.

region the approximate age of the Ontario Beach is determinable. Between these two points, the encroachment of the lake has been measured along 18 lines coördinate to the lake shore. These points\* are indicated on the map (fig. 4). The recession of the two terminal points has been unimportant (respectively 8 and 3 feet in 50 years), but between them the mean lake encroachment has been 2 feet a year.

The total recession of Scarboro bluffs, since the establishment of the Ontario Beach, is determinable from the topography. While the bluffs reach to 350 feet above the lake, the Iroquois terrace skirts their face except for less than half a mile, where it has been undermined by the waves (see fig. 4). This shows that the post-Iroquois surface, removed by the lake, rose less than 200 feet above it, and its slope should correspond to that of the country between the Iroquois Beach and the low shore, just west of Victoria Park, a distance of 4,000-4,400 feet. Such would indicate the original extension of the Ontario shore in front of Scarboro Bluffs.

This location is confirmed by the restoration of the natural shore-line in front of the indentation in the bluffs (see figs. 1 and 4), where their truncation represents the recession of the original Ontario shore. Combining the mean rate of recession of 2 feet a year with the amount of encroachment determined, the age of the Ontario Beach is found to be approximately 2,000 years.

\* Mr. F.M. Passmore marked by 18 cornerstones the position of the bluffs in 1882–3. Messrs. Speight and Van Nostrand re-surveyed them in 1912 (for the Toronto Water Supply). By comparison of these surveys the mean recession has been found.



FIG. 4. Map showing Scarboro Bluffs, Iroquois Beach and later encroachments on the shore.

Am. Jour. Sci.—Fourth Series, Vol. XLIII, No. 257.—May, 1917. 25 But the age of the lake itself is somewhat older—its surface having been lowered a few feet, while the St. Lawrence was deepening its channel, but there is no direct measurement derivable from the St. Lawrence River itself.

Researches, relating to the great accession of water to the Niagara River, show that the terrestrial tilting about the northeastern angle of Lake Huron occurred as late as some 3,500 years ago. This earth movement extending to the St. Lawrence River was that which gave birth to the great modern river itself. No appreciable deformation has since occurred. Consequently, Lake Ontario is found to be some 3,500 years old. The difference between this figure and 2,000 years for the age of the Ontario Beach seems ample for the lowering of the lake level from the Mill Haven to the present shore-line.

New Results.—Lake Ontario and the St. Lawrence River date only from the time when the discharge was first confined to the river channel, since lowered some 15 feet by current scour. The former earth movements of some 3,500 years ago have disappeared in the higher and present Ontario shore-lines. The age of the Ontario Beach is satisfactorily determined at about 2,000 years, while the age of the lake itself, and that of the St. Lawrence River, is 3,500 years or perhaps slightly less, as based upon the data so far discovered, without any great probable variation indicated.

# Speculations relating to the Age of Lake Ontario and Post-Glacial Time.

To close this study and not analyze the speculations would leave the subject in confusion, as few have the available data or opportunities for investigation. Furthermore, a discussion introduces other important features. A notable attempt to find the time value for the Ontario Beach has been made by Prof. A. P. Coleman,\* who based his estimate on beach accumulations artificially obstructed by the canal piers crossing the beach at Toronto Island (see fig. 3); and according to his assumed rate of deposit and the gross quantity of sand under Toronto Island he concluded that the age of the Ontario shore is 8,000 years. Plausible as this method might seem, such assumptions are contrary to the observations and mechanics of wave action, as well as the mass of sand, being derived from one source.

In transportation, the wave-action varies as the sixth power of velocity. Reduce the velocity one-half and the transportation power is reduced to one sixty-fourth. Thus, a slight obstruction will cause a deposition of the wave-carried sand,

\*Estimate of Post-Glacial Time, by A. P. Coleman. Trans. International Geol. Congress, for 1913, pp. 455-472.
not merely that drifting along the shore, but also that washed by the waves from greater depths.

An illustration of new-formed land is seen at Atlantic City, where groins or piers were built outward to check the force of the waves encroaching upon the coast. But the groins led to the deposition of sand between them. By extending these and adding others a strip of new land was acquired in 40 years for a length of three-fourths of a mile, with breadth reaching to one-fourth of a mile, curiously leaving the lighthouse inland.

During high water of 1908, the lake waves washed away the shore road around Humber Bay. Here also protective groins were built (see map, fig. 1), and already the interspaces are being filled with beach material.

Without artificial impediments, a barrier beach 3 miles long was formed at Asseagua Light, on the coast of Maryland, in 40 years; and another spit or barrier, 4,000 feet long, was developed on the western side of Toronto Harbour, between 1841–1882 (see b, fig. 3) and now completely separates the bay from the lake, while the southern side of the beach is being washed away.

After the formation of the gap through the Toronto barrier, no considerable deposit of beach material from the east was carried through the opening into the quieter waters of Toronto Bay; and only when the gap was artificially closed in 1883 and further obstructed by the canal piers, did the sand and gravel accumulate here, although such were naturally closing the western end of the harbour. These were the deposits which Prof. Coleman unfortunately used as a basis for his speculations of geological time. The above examples illustrate the effects of artificial impediments upon wave action and natural changes of current, showing the worthlessness of any deductions as to time that can be derived from them. Furthermore they are contrary to the laws of mechanics. Prof. Coleman also failed to distinguish the underlying clayey sands of the Don delta from the overlying beach materials of the Ontario shore, thereby greatly lengthening his conjectures as to geological time.

We are indebted to Prof. Coleman for calling our attention to the not-well-known surveys of the recession of Scarboro bluffs, which had been made for the Toronto Water Supply. By his selection of the figures, rejecting measurements of the greater erosion, while retaining those of reduced amount (which were compensatory in the variable conditions), he assumes 1.62 feet as the mean rate of recession in place of 2 feet per annum, which latter is the mean of 16 measurements between the points of practically no encroachment.

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In the recession of Scarboro bluffs the author, just mentioned, seeks to confirm his estimate of the age of the Ontario Beach derived from Toronto Island. Such requires a knowledge of the amount of the wave encroachment since the birth of the Ontario Beach. From the gentle slope of the lake floor to a depth of 100 feet, at a point 13,000 feet outward, where it declines more rapidly, he concluded that the Ontario beach had an amplitude of 100 (in place of 20) feet and had risen this amount, but from the soundings he could with equal value have selected 8,000 or 18,000 feet. From his assumptions here he again gets 8,000 years as the age of the Ontario Beach. Using the other figures, just mentioned, a student could just as well obtain an age of 5,000 or 11,000 years. Any hypothesis based on such variables can not be accepted. But more, he includes in the Ontario Beach epoch the time of the water rising 100 feet to its present level, thus unconsciously embracing with the time of the Ontario Beach a long period before the beginning of that stage, which further throws confusion into his hypothesis.

To this disjointed speculation of the age of the Ontario Beach (8,000 years) the same author assigns, without offering any evidence, an equal time for the Iroquois Beach, and then adds another 8,000 years (which he himself recognizes as only a "guess") for the time intervening between the Ontario and Iroquois beaches-thus making 24,000 (or perhaps 27,000) years as the duration of post-Glacial time.\* But a further contradiction appears, for the professor has shown elsewhere that Lake Iroquois was a Glacial lake, consequently, his 8,000 years as the age of the Iroquois Beach must be taken away from his post-Glacial time, leaving 16,000 years. Such à priori philosophy leaves a suspicion that its author had some speculation to support, but the analyses of the data show that a confusion is thereby thrown into the problem of Geological time, when he had within his grasp the material for a lasting scientific contribution of great value; and if the confusion be not expunged such must lead to the retardation of scientific research.

Washington, D. C.

\* From resemblances between the Iroquois and Ontario beaches their relative duration might be inferred within an error of 100 per cent; but the time required for the work performed between these epochs is not comparable to either, for during this intervening period the lake level fell more than 500 feet, with pauses, and rose again 200 feet with the partial submergence of some of the terraces. During this intervening period great denudation was effected, as shown by the large valley excavated by the Don. The varied work performed at this time was vastly greater than that of building either the Iroquois or the Ontario Beach.

# ART. XXXIII.—Granite Bowlders in (?) the Pennsylvanian Strata of Kansas; by W. H. TWENHOFEL.

### Introduction.

FROM time to time granite has been reported from deep wells of different parts of east Kansas. On investigation many of the reported granites were found to be other kinds of rocks, or without basis in fact. In a few instances final judgment had to be reserved. The 1915 boom in oil development together with very conspicuous cases of granites reported from two wells near Zeandale, a small village about eight miles east of Manhattan, Kansas, brought so many inquiries to the Kansas University Geological Survey, and the possibility of encountering granites in drilling was having such a depreciative effect on further development, that Professor E. Haworth, the State Geologist, carefully investigated all of the reported cases of granite in order to definitely ascertain, if it were possible, whether such actually had been reached in any of the deep wells.\*

In each of the Zeandale wells granite was reported at a stratigraphic level in the upper part of the interval between the Oread and Iola limestones. In one it was struck at nine hundred and fifty-eight feet and drilling was continued to one thousand and ninety-three feet without penetrating the granite, although curiously, the log of the well showed that thirty-two feet from the top of the granite the drill had passed through a twelve-inch bed of shale. In the other well granite was struck at nine hundred and forty-five feet and continued drilling encountered no lithic change. A careful examination of the cuttings which are said to have come from the wells showed unquestionable fragments of unweathered granite. Haworth's conclusions were to the effect that the granitic rocks which were derived from these two wells, and which perhaps had also been found in others, are probably firmly cemented sediments which came from rocks of a granitic character and, by way of illustration, he called attention to a rock of Tertiary age which occurs in Phillips County, Kansas, and is composed of firmly cemented granitic gravels derived from the Rocky Mountains. This rock resembles granite so closely that it has been quarried and used as paving blocks under that name.

During the field season of 1916, while examining territory in Wilson and Woodson counties in the interest of the Fredonia Gas Company, the present writer found granite bowlders which it is fairly certain came from Pennsylvanian strata.

\* Haworth, Bull. 2, Kansas Univ. Geol. Sur., 1915.

The locality is in Eminence Township, Woodson County, about eight miles almost due south of Yates Center and one mile west and a half mile south of the Missouri Pacific Railway station, Rose, the locality being on the very headwaters of a small tributary of the Verdigris River, into which it empties about twelve miles to the southwest. The bowlders lie on the northern edge of a low hill which has been determined by a small anticlinal structure. A little valley extends almost entirely around the hill and beyond this valley other hills, immediately or ultimately, rise to higher elevations.

Since the occurrence is of interest not only because of the rocks themselves, their stratigraphic position and the geological history they reveal; but because their presence may help to explain the finding of granite in deep wells, a description of the lithology of the bowlders, of their manner of occurrence and of their relation to the strata with which they are associated is warranted. The facts will be given in considerable detail because of the uniqueness and importance of the subject.

The distribution, characteristics and lithology of the bowlders will first be given. This will be followed by an examination of every possible way by which the bowlders might have attained the positions where they are found. Then will be considered their stratigraphic position and a conclusion will be sought which satisfies the available data. Lastly, various deductions will be developed from the conclusions which have been reached.

For assistance in the field study of the bowlders, the writer is extremely grateful to one of his students, Mr. E. M. Stryker of Fredonia, Kansas, and also to Messrs. C. V. LaDow and Maurice Stryker of the same place, since it was largely through the aid of these three men that the territory within a radius of from ten to fifty miles of the place of occurrence of the bowlders was able to be examined.

## Areal Distribution and Size of the Bowlders.

The bowlders are distributed over an area of about one hundred and twenty acres which are so placed that eighty acres in a tract eighty rods wide lie on the west side of the north-south road and forty acres on the opposite side of the road in a tract of the same width. Most of them and also the largest occur on the southwest twenty acres (1 on the map), where the greatest number are found on four low mounds or elevations which rise from four to six feet above the general level of the surface. The most western mound is the largest and highest and has an area of about an acre, and it also has the bowlders in far greater abundance than elsewhere. They are



FIG. 1.—Outline map of eastern Kansas, showing the position of Rose and its relation to other parts of Kansas. The dashed line shows the approximate position of the southern limit of the Kansan ice sheet. The dot and dashed line shows the position of the southern limit of Kansan glacial bowlders. Glacial data are taken from Todd, Trans. Kan. Acad. Sci., vol. xxiv, 1910, pp. 211–218, and Science, vol. xxxix, Feb. 1914, pp. 263–274. so numerous on this mound that about one-fourth of the surface is covered and they have made impossible its cultivation, so that at present it is given over to the growth of bushes, and such appears to have always been the case. None of the other mounds contains a twentieth as many bowlders as does this. In addition to the larger mounds, there are about a half dozen others of much smaller height and area which have not been mowed or plowed because of projecting bowlders. These smaller elevations are situated between and for about a hundred feet on either side of the larger and they also extend much



FIG. 2. Outline map of the region of the bowlders. Each square represents forty acres. The section on the right of the north-south road is T. 26 S., R. XVI E., S. 18, Eminence township; while the area on the left is in T. 26 S., R. XV E., S. 13. The area within the dashed line carries bowlders which appear to be in approximately natural position. The large mounds extend from A to B, A being the position of the most western mound.

farther east, but there are none toward the west. The four largest mounds are aligned in a direction a little south of east and they extend through about a thousand feet. The alignment coincides with the outcrop of the shales with which the bowlders are associated.

The most western of the large mounds has a dozen or more bowlders with diameters of about four feet and there are probably between fifty and a hundred that are more than a foot and a half in diameter. The largest bowlder observed is on one of the smaller mounds and it has a diameter of nearly seven feet.

FIG. 2.

Every one of the mounds owes its origin to the resistance of the bowlders as compared with the resistance of the surrounding and underlying rock, the former having been eroded away, while the latter was protected. It should be noted, however, that one of the larger mounds has no bowlders on it, but there are no reasons for disbelieving that they were once there, and have either crumbled under the forces of weathering, or perhaps some of the people of the region hauled them away. On this mound, the shales are at the surface.

The twenty acres due north of the tract just considered (2 on the map) were lower down the slope and hence lower in stratigraphic position. Through a portion of the northern edge a small creek has cut through the shales associated with the bowlders and has reached the underlying Stanton limestone. Bowlders, some of which are more than a foot in diameter, are scattered over the slopes on which the shales outcrop and a few are present in the bed of the small creek, where it is clear they were thrown to dispose of them. On the road to the east, where the land is nearly as high as at the mounds, several have been plowed out in the grading. There are not nearly so many bowlders on this tract as on the twenty acres due south.

On the forty acres to the south of the twenty first considered (3 on the map) bowlders are very rare. There are probably not a dozen on the whole tract; every one is small, none weighs over a pound, and there is little doubt that man is responsible for their occurrence on this field. On the forty acres to the north (4 on the map) granite bowlders up to eighteen inches in diameter occur quite thickly scattered over parts of the higher land on the southern side and are most abundant on the southeast corner of the area. On this corner the soil is extremely thin in many places and in some places it is altogether wanting and the shales, thickly studded with small granite bowlders, are at the surface. The small creek, which has already been noted, flows through this tract and has the Stanton limestone exposed in its bed. A few granite bowlders are present in the creek bed, but it is quite evident that they were thrown there to get rid of them.

It is possible that there was at one time an extension of the bowlders to the west, since from the top of the largest mound there is a comparatively rapid descent—a grade of five to six per cent—to exposures of the Stanton limestone which outcrops about three hundred feet beyond the western edge of the mound. No bowlders, however, are present within about one hundred and fifty feet of the outcrop, so that it is quite probable that the bowlders in their distribution ended abruptly westward.

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On the forty acres east of the road (5 on the map) small granite bowlders are not uncommon and a few large chunks were seen in the hollows and hedges where it is clear they had been thrown. No one of these exceeded a weight estimated at twenty-five pounds. The forty acres to the north (6 on the map) has the Stanton limestone over most of its area as the surface rock and, save for the southwest corner, no bowlders are present, while the tract of forty acres to the south has a very few small ones and these were probably carried through human agencies to the places where they occur. On the forty acres to the east of 5 (8 on the map) a few small bowlders are



FIG. 3. View of one group of bowlders on the most western mound. Bowlders are quite thick in the bushes on the right background. The handle of the hammer is sixteen inches long.

present which have been brought there in cultivation, or they may be the last surviving fragments of large bowlders which may once have been over the field. It is deeply eroded so far as the shales are concerned and the surface is nearly on the Stanton limestone, which is also true of 7.

These are all the places where granite bowlders were observed. The surrounding country for from ten to fifty miles in every direction was quite thoroughly examined and at no place was a single granite bowlder found, and, so far as the writer is aware, none has ever been reported, and the nearest locality where such are known to occur is about seventy-five miles to the north in the drift of the Kansas ice sheet.

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#### Characteristics and Lithology of the Bowlders.

Many of the bowlders are almost completely decayed and are so soft that they can be dug through with a spade, Mr. E. M. Stryker having thus dug about fifteen inches into one which was buried in the ground. The most badly decayed ones are in the ground; but, as shown by fragments, there were others in the midst of the solid bowlders now on the surface which fell to pieces as fast as they became exposed. Some of those on the surface have the constituent minerals so poorly held together that they can be crumbled with the hands. Others which are still compact have deep corrosion pits which reach into the stone for six or more inches. It appears quite probable that the greater number of the smaller bowlders have been produced by the breaking up since deposition of the larger, for in many instances the former have the minerals poorly held together and are of angular and irregular outlines. They have the appearance of having been separated from larger pieces and where the bowlders are numerous there are not a great many small ones except in those places where a large one is crumbling to pieces. It is plainly evident that the granite bowlders are very old and have been where they now occur a very long time.

The minerals composing the rock of the Rose bowlders are glassy white and pale bluish-white quartz and gray orthoclase and oligoclase feldspar, considerable proportions of the latter being present as phenocrysts, of which some are fully threefourths of an inch across in their greatest dimension. Quartz is also present as phenocrysts of which the largest are about half an inch across. Compared to the quartz, the feldspars predominate in a proportion estimated at about two to one. Α few grains of magnetite are present together with a few grains of some ferro-magnesian mineral which has been chloritized so as to be unrecognizable. Originally it was probably either hornblende or biotite. Professor Joseph Barrell, to whom some of the specimens were submitted for examination, confirmed the identifications and stated that "the rock has been shattered, but the fragments are still largely in their original juxtaposition. In connection with this shattering there was a recementation with fine-grained quartz and feldspar showing a trace of poikilitic tendency."\* The shattering of the rock is not apparent on all of the granite bowlders although it is plain from every one that they are closely related and were evidently derived from the same mass of rock. The intimate dovetailing of the minerals absolutely puts out of consideration any possibility that the rock is an arkose or a breccia.

\* Personal communication, August 17, 1916.

There is much variation in texture, but every specimen is porphyritic. In some the texture is very coarse with the average grain approximating one fourth inch and in no bowlder was a microscopic texture observed. Bowlders of coarse and fine grain occur together and some are coarse-grained on one portion and fine on another with the dividing line between the two textures quite sharply defined. This juxtaposition of the two textures may have been produced by the recementation following the shattering, the fine-grained granite being the cement.

In addition to the granite porphyry bowlders, three or four of chert were seen and on the most western mound were found two of quartzite of which the larger is about two feet in diameter and is composed of glassy gray sands of fine grain. Most of this bowlder is still on the mound. The smaller of the two bowlders weighs about half a pound and, while the quartz is of the glassy type, it is of a greenish shade. This bowlder is in the writer's collection. The larger quartzite bowlder is so deeply corroded as to have a spongy appearance.

Every one of the porphyry bowlders is more or less obscurely subangular in shape; but, as previously stated, the surface of every one of them is much weathered and, hence, rough and pitted, so that little data relating to the character of the original surface could be obtained. In fact, the original shapes may have been anything, while the present shapes may be altogether due to weathering. The smaller quartite bowlder appears originally to have had one side flat.

## Possible Methods of Origin of the Bowlders.

Four hypotheses may be considered. They are as follows: (1) the bowlders are firmly cemented masses of coarser sediments in which large unworn crystals of feldspar were important as constituents; (2) they are bowlders of weathering derived from a sheet, dike, or flow of igneous rock which is there enclosed in the sediments; (3) they were carried to their present positions by streams; (4) ice was the transporting agent.

The disposition of three of these hypotheses is readily accomplished. The bowlders are certainly not firmly cemented coarse sediments, for such a possibility is precluded by the absence of rounded fragments, the presence of well-formed crystals of feldspar, the intimate dovetailing of the minerals and the total absence of any signs of deposition in the material composing the bowlders. Every one of the granitic bowlders is true granite and each was directly derived from a common parent igneous mass. It is absolutely impossible to hold to the first hypothesis.

The only thing supporting the hypothesis that the bowlders are the surface exposures of an intrusion or extrusion is the alignment of the large mounds, which is linear and, therefore, in harmony with the idea that the bowlders came from either a dike, sheet or flow. A sheet or flow is the more probable because of the correspondence between strike of strata and alignment of mounds. However, if an intrusion be responsible for the bowlders, it must have been large, if coarse-grained textures be criteria of size of intrusion, and this fact of coarse texture thoroughly disposes of any possibility that the large mounds are the outcroppings of a flow. If an intrusion be present, the shales ought to be modified to some extent, especially if the intrusion be large, as must have been the case. There is, however, absolutely no evidence of any alteration. Furthermore, the presence of the flint and quartzite bowlders offers difficulties to this hypothesis. Lastly, if either a dike, sheet, or flow exist here, somewhere the parent rock ought to have been seen in place; but so far as observed, every bowlder rests on shales. It appears quite positively certain, therefore, that this hypothesis can not be held.

The hypothesis that the bowlders are water-borne makes necessary an inquiry as to the sources from which they might have been so carried and the competency of present and past streams to have brought about the transportation. The present streams of Kansas are not of high gradient and throughout this region they do not appear to have been so since their The drainage is eastward and such has been its direcorigin. tion since early in the Tertiary. Prior to the Tertiary the drainage was westward. The nearest western points from which granite bowlders might have been carried by streams since the beginning of the Tertiary are in the Rocky Mountains, fully five hundred miles away, and for streams of such gradient as those of Kansas possess, or have possessed since the early Tertiary, the task would have been an absolutely impossible one. Moreover, not one of the present large streams of Kansas, which heads in regions of igneous rocks, flows within seventy-five miles of the locality of the bowlders which, as previously stated, lie on the extreme headwaters of a small tributary of the Verdigris. If a Tertiary or later stream deposited the bowlders where they now occur, very great changes of drainage must be assumed and this necessitates such great erosion that it is difficult to understand how the bowlders could have avoided destruction. The Rocky Mountains as a source for the bowlders, hence, can be eliminated, and all Kansas streams which head, or since early Tertiary times have headed in the Rocky Mountains, as transporting agents, must be eliminated from consideration.

A possible source for the bowlders is the drift of the Kansan ice sheet. The nearest locality of its occurrence is about seventy-five miles to the north, where bowlders are present in considerable numbers in the valley of Wakarusa Creek and a few occur on the hill slopes which limit the valley on the south. The map, fig. 1, shows the general facts of the distribution of the Kansan drift and the nearest southern limit of the ice. Between the Wakarusa Valley and Rose there are no bowlders, the bowlders at the former place are dominantly red quartzite and there is no drainage from the former to the latter and has been none since the Kansan glacial advance. This must also, therefore, be eliminated as a source.

Other sources from which the bowlders might have come are the Arbuckle and Wichita mountains of Oklahoma, and the old mountains of southeastern Missouri, the former being about two hundred and twenty-five miles away and the latter more than three hundred. There has been no drainage in the direction of Rose from these regions since the Cretaceous. The reverse was true during parts of the Mesozoic, but there is no evidence that any of these ancient streams were of high gradient in the region of Rose and hence it is quite improbable that the bowlders could have been carried by them, and, if so carried, unless they were covered by Mesozoic sediments, for which there is no evidence whatever, it is impossible to explain how they could have been preserved through the long interval of time which has elapsed since the drainage was reversed and through the erosion which the region has undergone. They might have been deposited by streams of Pennsylvanian age and subsequently covered by Pennsylvanian sediments. In this way they could have been preserved. The sediments, however, with which they appear to be associated were deposited in quiet waters—waters absolutely unable to transport bowlders of the sizes of those which are present. Streams, hence, must be discarded as possible agents of deposition.

It may be assumed that somewhere in this region in Pennsylvanian times there rose a granite mass from which bowlders rolled as talus to the places where they are now found. The strata of the region are almost horizontal and if a granite mass projecting above the present level of the bowlders were once present, it seems that somewhere in the region it should still project through the sediments which lie at the same level as the bowlders. There is absolutely no evidence that such is the case.

The last possibility is that ice was the agent of transportation. This alone appears to be competent to carry bowlders of the sizes which are present. Ice could have brought about the transportation either in the form of a glacier or as floating ice. If the bowlders are in the Pennsylvanian strata, then they must have been deposited by floating ice, for only in such a way could the very local distribution have been effected and the deposition have been made in the midst of muds laid down in quiet waters. If the bowlders are of comparatively recent time, that is Tertiary or early Pleistocene, they must have been laid down either by a glacier or ice floating in a stream flowing from its margin.

In seeking for the place of origin of the bowlders, comparison was made with specimens of Missouri and Lake Superior granites of which the University of Wisconsin has collections containing about all the varieties, while the literature was examined for data relating to the granites of the Wichita and Arbuckle mountains. This search has yielded negative or uncertain results. In addition, Professor E. Haworth very kindly loaned for comparison a specimen of the rock which was reported to have come from one of the Zeandale wells. The latter, mineralogically and texturally, is altogether unlike the Rose bowlders and the same is essentially the case with respect to the Missouri granites. So far as the literature is concerned, it appears quite unlikely that a granite of the characteristics of that composing the Rose bowlders is present in either the Arbuckle or Wichita mountains.

In respect to the granites of the Lake Superior region, the examination was limited to those of the Vermilion Range of northern Minnesota which Doctor C. K. Leith suggested most nearly resembled that of the Rose bowlders. The specimens which are most similar came from the recomposed granite of Lake Saganaga. According to Grant, the original Saganaga granite "is coarse-grained gray to reddish granite . . . of which the chief constituents are quartz, orthoclase, acid plagioclase and hornblende. A peculiar and characteristic feature of this granite is in its large grains of quartz, which are conspicuous on weathered surfaces. The quartzes are commonly a quarter of an inch in diameter and they frequently become larger." In the recomposed granites which developed from these "the hornblende of the true granite is wanting."\* This description approximates that of the Rose bowlders, but the similarity comes far from approaching identity, and the examination of specimens of the recomposed granite made this much clearer since the textures of the two rocks are quite different. In the Rose bowlders the phenocrysts of quartz are larger and this mineral has a different appearance, the proportion of quartz is less, the average grain is larger, while there are no large phenocrysts of feldspar in the recomposed Saganaga

\* Grant, Geol. and Nat. Hist. Surv. Minn., vol. iv, p. 322, 1897.

W. H. Twenhofel-Granite Bowlders in (?)

granites. Furthermore, the general appearance of the two rocks is quite different, and the recementation appears to have been accomplished by different methods.

The Rocky Mountain granites were not examined since it does not seem likely that any of the known conditions of present and past drainage would permit the bowlders to be derived therefrom.\*

### Stratigraphic Position of the Bowlders.

The local section of the region under consideration belongs to the Douglas and Pottawatomie formations of the Pennsylvanian system and consists at the base of the Stanton-Allen limestones with a thickness estimated at about fifty feet. The former limestone is above the latter and there is generally a separating shale. Overlying the limestones are the LeRoy shales and sandstones. The local thickness of this member slightly exceeds two hundred feet. These two divisions are the only ones exposed on the hills at Rose. Tothe east lower strata appear and to the west higher ones. The LeRov shales and sandstones consist of black shales throughout the basal eighty or ninety feet while the upper portion is composed of red and yellow sandstones and sandy shales. These sediments are probably of deltaic and fluvial origin in the region under consideration.

Succeeding the LeRoy shales are the Iatan (Kickapoo) limestone and the Lawrence shales and sandstones. Below the Allen limestone are the Lane shales and this is preceded by the Iola limestone.

At present the bowlders are on the surface of a hill at a level varying from eight or ten feet above the Stanton limestone to about fifteen feet above, the largest and best preserved being at the latter level and the large mounds previously described lie at this upper level. The associated strata belong to the black shale division of the LeRoy shales and sandstones and these shales underlie the entire hill top on which the bowlders were seen, the shales immediately underlying the bowlders being nearly the highest exposed on the hill. The nearer the surface is to the top of the Stanton limestone, the fewer, the smaller and the more poorly preserved are the granite bowlders, and where the shales are altogether removed

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<sup>\*</sup> It was also considered whether the bowlders might not have been brought to their present position by man. The hypothesis was rejected as altogether untenable.

<sup>(</sup>Since going to press, cuttings from three other recently drilled wells of central Kansas which have been reported to have reached granites have been sent to the writer for examination. There is no resemblance between the materials from these wells and the granite of the Rose bowlders.)

there are no granitic fragments excepting such as have clearly been carried down the slope and they, in general, are so rare as to be negligible. On the south, east and west sides of the anticlinal structure no bowlders were observed, although exposures are equally as good as on the north side, since erosion in numerous places has reached the Stanton limestone. Stating the matter differently, the large bowlders occur over a quite limited area and appear to coincide with a definite and limited horizon in the LeRoy shales. In every instance they rest on shales and shales arise around some of them, but in no instance were shales seen to overlie bowlders. A few quartz veins were observed in the shales just in front of the school house (see map, fig. 2), but these can have no significance in relation to the granite bowlders.

Two alternative views are therefore presented; namely, the bowlders are not in the Pennsylvanian strata and are of comparatively recent age, or the bowlders are in the Pennsylvanian strata and are contemporaneous in origin with the shales on which they rest and which in some instances rise above their bases. Each of these two views will be examined in detail.

The evidence for the first view is that the bowlders lie on the surface and that in no instance were shales seen to cover them. Not even a small bowlder was seen overlain by shales ; but, as already has been stated, it appears quite probable that no or few small bowlders were originally present. Opposing this view are the facts favoring the other, which will be considered in a subsequent paragraph, and the difficulty of explaining how the bowlders attained their present positions on the headwaters of a very small stream. As has already been shown, ice was in all probability the agent of transportation, but the bowlders are not of the same age as the Kansan glacial bowlders farther north. They are certainly older. The bowlders of the Kansan ice sheet are dominantly red quartzite, probably seventy-five per cent of them being composed of that rock, but not a single red quartzite bowlder occurs at Rose, while the two quartzite bowlders which were seen there resemble quartzites which outcrop near the village of Middletown, five or six miles to the southwest, and they may have come from there; but the resemblance is not sufficiently close to say positively that they do. Perhaps the Rose bowlders are the deposits of a glacial advance of pre-Kansan time, that is, very early Pleistocene-the sub-Aftonian,-or perhaps Tertiary. In that case, the ice advancing from the north crossed and filled the valleys of the Wakarusa, Osage and Neosho rivers, each of which is now trenched from one hundred to two hundred feet below the level of the uplands; or perhaps these valleys were not in existence at that time. On this

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view the bowlders may be considered either a remnant of a once extensive sheet of drift, or a local deposit of ice floating from the glacial margin with the main body of the drift lying a little farther to the north.

If the bowlders are a remnant of a once extensive sheet of drift, then the rest of it has been altogether removed from the surrounding country without leaving a single trace of its one time presence and all marks of glacial erosion have been completely effaced so that the valleys mentioned above show no evidence whatever of having been filled and crossed by glaciers. If the bowlders are the deposits of early Pleistocene or Tertiary floating ice, the problem is rendered no simpler, since the drift-covered and glacier-eroded area lav but a short distance to the north.

This view postulates great erosion, which took place in such a way so as not to destroy the Rose bowlders, but at the same time altogether swept away similar deposits from neighboring areas, some of which were higher and others apparently lower than the hill at Rose. Such preservation calls for extremely special conditions and there is nothing in the region that lends itself to the view that such were present. It would appear that the final stages of removal of the supposed drift sheet would be marked by gravels of small size remaining here and there over a great stretch of country instead of a well-preserved deposit in one place.

The impossible, however, in the past has not infrequently been proved the possible and it may be that the Rose bowlders are of early Pleistocene or Tertiary age. If such be the case, the only early Pleistocene glacial material with which it is possible to compare them is the sub-Aftonian drift of Beyer, \* in his description of the Oelwein section, charlowa. acterized the sub-Aftonian drift sheet as "a massive gray-blue till with a marked greenish tone when unoxidized. Theupper portion contains much humus and gives off a characteristic marsh-like odor when wet. The distinctive characters which serve to distinguish the bowlder clay from the preceding (Kansan) are its color, the predominance of greenstone, and vein quartz pebbles and a less tendency to joint on exposure. Granific pebbles and bowlders are almost if not entirely wanting." Savage who studied the same section, in his description says substantially the same things.+ The sub-Aftonian drift of the Grand River section was described by Bain as "Boulder clay . . . containing mainly small pebbles, predominantly of vein quartz, but with a fair proportion of granite"; while

\* Beyer, Proc. Iowa Acad. Sci., vol. iv. pp. 58-62, 1897.

† Savage, Ann. Rept. Iowa Geol. Surv., vol. xv, p. 522, 1904. † Bain, Proc. Iowa Acad. Sc., vol. v, p. 97, 1898; Am. Geol., vol. xxi, p. 255, 1898.

Chamberlin and Salisbury, in a general statement of the sub-Aftonian drift, describe it as "typical sheet of till notable for the relatively high percentage of its greenstone erratics."\*

It is significant that while greenstone and vein quartz pebbles and bowlders are very prominent among those of the sub-Aftonian drift, not a single greenstone or vein quartz pebble or bowlder occurs among the many observed in the locality under consideration, and if the material of the latter were related in time and origin to the bowlders of the sub-Aftonian drift there should be present some material of the character typical of that drift. The greenstones might have decayed, but the vein quartzes should certainly have outlasted the granites. Furthermore, so far as published descriptions observed by the writer are concerned, not a single one of the sub-Aftonian bowlders is anyways nearly so large as the large bowlders of the Rose region. There is no Tertiary material on the western plains with which the Rose bowlders can be compared, nor is there any evidence that such was ever present.

It is therefore considered that the hypothesis that the bowlders are of early Pleistocene or Tertiary age is not in harmony with the available facts, and while it still must be considered as a possibility, it does not appear that it can be strongly maintained.

The chief evidence for the second view is the close correspondence between the outcrop of the shales and the distribution of the large bowlders. As already noted, the large bowlders occur on the surface following the outcrop of a definite and relatively narrow horizon in the shales. Also along the north-south road decayed bowlders are present which lie almost surrounded by decayed shales. Residual soil is not meant when delayed shales are referred to, but shales in which the bedding has not been entirely obliterated. Furthermore, in every instance where a bowlder was observed in undisturbed position it rested on shales without an intervening soil. In no instance, however, were shales seen overlying bowlders. Could this observation have been made, it would, of course, have definitely decided the problem; but it was not observed and probably never will be since the bowlders are local and the cover, if once present, in the immediate vicinity has been totally removed. Higher shales are present on the hill, but they are a little farther south.

If the bowlders are in the shales, the explanation of how they reached their present positions is quite simple. The Le-Roy shales have been stated to be deltaic in origin, and in strata a little above the horizon of the bowlders there is decisive evidence of deposition in tumultuous non-marine waters. This

\*Chamberlin and Salisbury, Geology, vol. iii, p. 384, 1907.

evidence is both in the manner of deposition and the deposits themselves. Somewhere near the headwaters of the stream which brought in the sediments and which are believed to have been to the south or southeast, there were highlands on some of which snow and ice may have accumulated to form glaciers. Masses of ice breaking away from these floated down stream to become stranded or stopped in quiet waters where they melted and deposited the débris which they carried. Murray and Hjort have stated that bowlders dropped from floating ice take position in the muds into which they fall with the long axes in perpendicular position.\* It is not possible to apply this test to the Rose bowlders since erosion has warped all of those which were elongated out of what may have been their original positions so that they now lie with the greatest areas downward.

To the extent that the facts are available it appears that the more probable view of the position of the bowlders is that they are in the shales and contemporaneous therewith.

If the second view outlined above be correct, the sequence of events, so far as the Rose bowlders are concerned, must have been something as follows: (a) In Pennsylvanian times the region of Rose was on a broad delta or river flood plain on which masses of ice becoming detached from glaciers which lay on high lands assumed to have been situated to the south or east from time to time became lodged in local areas and melted there. (b) Long afterward, probably about the close of the Permian, the strata of the region of eastern Kansas were warped and numerous low anticlinal structures were developed, one of which involved the strata containing the Rose bowlders. (c) A long period of erosion followed. The anticlinal structure gave erosion favorable points of attack which led to the rapid removal of the less resistant strata so that the area of structural elevation became from time to time a topographic depression, these times coinciding with the appearance of weak strata at the surface. The LeRoy shales and sandstones constitute one of the weak members and they were removed to the bowlders whose comparative resistance retarded erosion. When the Stanton limestone was reached, the streams followed it down the structural slope and thus was developed the valley which practically surrounds the Rose hill.

The relation that the Rose bowlders bear to the occurrence of granitic material in the Zeandale wells is still problematical. It may be that the latter reached its position in the same manner as did the bowlders at Rose. Evidence, however, has lately come to the writer from many sources that granitic

\* Murray and Hjort, Depths of the Ocean, London, 1912, p. 207.

rocks in place locally underlie the Pennsylvanian strata of central Kansas and it is possible that the Zeandale granites hold a similar position. Furthermore, the evidence in the writer's possession, which has been derived from at least five independent sources, points to the conclusion that these granites are older than the overlying strata. If this view be correct, and the Rose bowlders be of the origin indicated by the available data, it follows that there is no connection between the two occurrences.

### Conclusions from the Known Data.

(1) The bowlders reached the positions where they are found through the agency of ice, either glacial or floating; but more probably the latter.

(2) The view is strongly favored that they are of the same age and hold the same stratigraphic position as the shales with which they are associated, that is, they are the deposits of Pennsylvanian floating ice.

(3) It is barely possible that they are a remnant of an early Pleistocene or Tertiary drift deposit which resulted from a great glacial advance in pre-Kansan times, or the bowlders may have been laid down by floating ice derived from the glacier's margin.

### Corollaries of the Conclusions.

(1) If the bowlders are not of Pennsylvanian age, they may belong to the sub-Aftonian drift, to the bowlders of which, however, they bear little resemblance. Should they belong therewith, it follows that the sub-Aftonian stage of glaciation in Kansas extended farther south than the glaciers of any other stage are known to have done. If not of sub-Aftonian age, then perhaps they should be correlated with the Tertiary glacial deposits of southwestern Colorado, recently described by Atwood;\* but, so far as known, there is no information whatever on which to base a synchrony.

If the bowlders are in the LeRoy shales and sandstones and are of Pennsylvanian age, as appears the more probable view, they add another link to the chain of evidence for cool climates in Pennsylvanian times. In the Old World and South America the evidence for such cool climates is fairly complete, but for North America it has been more or less scanty. The finding of bowlders, probably ice transported, in the base of the Caney shale of Oklahoma,<sup>+</sup> which Ulrich considers of Pottsvillian

\* Atwood, U. S. Geol., Prof. Paper 9 5-B, 1916.

<sup>†</sup>Taff, Science, vol. xxix, p. 637, April 1909, Bull. Geol. Soc. Am., vol. xx, p. 701, 1910. Woodworth, Bull. Geol. Soc. Am., vol. xxiii, p. 457, 1913.

age,\* extended the probability of cool climates for this continent to the early Pennsylvanian. It is not possible to correlate the Rose bowlders with those in the Canev shale, but it is possible that they may be correlated with the Squantum tillite near Boston.<sup>+</sup> This is a part of the Roxbury conglomerate and supposedly of Permian age, although the age determination is based merely on the resemblance that this conglomerate bears to Permo-Carboniferous conglomerates of the Narragansett and Norfolk basins, an extremely hazardous feature on which to base a correlation. If the correlation of the Rose bowlders with the Squantum tillite can be made, the position of the former, if they are situated where this article assumes, definitely fixes the age of both and also the time relations of the beginning of the Permo-Carboniferous cold climates so far as the North American continent is concerned. The LeRoy shales have been correlated in a general way by Schuchert<sup>‡</sup> with the Conemaugh of Pennsylvania. The cold conditions of the late Paleozoic have usually been assumed to have occurred during the Permian which for the Kansas section is generally not considered to have begun until the close of Wabaunsee deposition, which is separated from what is considered the probable stratigraphic position of the bowlders by between thirteen and fourteen feet of sediments.§ Some writers have begun the Permian at a slightly lower position, but no one has attempted to include the Douglas formation of which the LeRoy member is a part, since the faunas of that and the two overlying formations are typically upper Pennsylvanian. It follows, therefore, if the assumptions which have been made respecting the stratigraphic position of the bowlders be correct, that glaciers existed over the higher lands during parts of the later half of Pennsylvanian time.

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\* Ulrich, Bull. Geol. Soc. Am., vol. xxii, pl. 29.

† Sayles, Bull. Mus. Comp. Zool., vol. lvi, No. 2, Geol. Ser., vol. x, pp. 141-175, 1914.

‡ Schuchert, Bull. Geol. Soc. Am., vol. xx, p. 558, 1909.

§Haworth, Kan. Univ. Geol. Surv., vol. ix, pl. III, 1908.

# ART. XXXIV.—An Oligocene Camel, Poëbrotherium andersoni n. sp.; by Edward L. TROXELL.

#### CONTENTS.

Introduction; Summary and conclusions; Observations on the skull, teeth and atlas; Related forms; Similarities and distinctions; Measurements and Bibliography.

Introduction.—The osteology of the skull of *Poëbrotherium* has been given, especially by Scott, 1891, and Wortman, 1898; therefore only the features of interest which are seen in the new specimen and the differences between it and the known species will be discussed in the following pages.

The specimen, a nearly complete skull, jaws and atlas, found near Harrison, Nebraska, comes from the Oligocene, Oreodon Zone and was contemporaneous with, and about the size of *Mesohippus*, the early three-toed horse.

Summary and conclusions.—As a result of the study of the specimen, the following points present themselves:

The upper canine is very small, but the third incisor, greatly enlarged, performs the function of a canine. Especially long diastemas bound the first premolars, both in the upper and lower jaws, thus sharply distinguishing the species from *Poëbrotherium eximium*. A cingular ridge and an internal basal pillar on M<sup>3</sup>, as well as the cusps and grooves in the third premolars, above and below, are characters not usually found in *Poëbrotherium*.

The cement coating on the lower molars, and also their straight, perpendicular sides and long enamel covering—a first step toward hypsodonty—indicates an animal of considerable advancement. Posteriorly the orbit is not inclosed with a bony ring as in *Gomphotherium* and the later camels; this is a primitive character.

The present specimen shows so many features not found in the other related forms, that it is here made the type of a new species: *Poëbrotherium andersoni*.\*

Morphology.—The whole skull and jaws are long and slender, a form made possible, partly by the short crowned teeth and partly by the diastemata before and behind the first premolars.

A conspicuous feature in these early camels is the large otic bulla. In the genus generally it is large and round, but in the present specimen, which in this respect resembles the later camels, the form is roughly triangular and consists of two por-

\*Note: The species is named in honor of Mr. John Anderson of Harrison, Nebraska, who, because of his keen interest in natural science and his exceeding generosity, has been of such great assistance to western explorers.

### E. L. Troxell—An Oligocene Camel.

tions, marked off especially by a postero-exterior groove for the junction of the stylo-hyoid bone. This groove, instead of following along the bottom of the bulla as in *P. wilsoni*, leads from the original pit upward, leaving the outer portion a pendant lobe whose upper end envelops the external auditory



FIG. 1. Side view of skull and jaws of *Poëbrotherium andersoni* n. sp., one-half natural size.

FIG. 2.



FIG. 2. Skull, base view, and jaws, crown view. One-half natural size.

meatus. This opening is directed upward and backward as it leads from the bulla.

The inner parts of each of the bullæ, which measure from 6 to  $9^{mm}$  in thickness, extend parallel to each other and to the longer axis of the skull. They are quite flat except where the posterior border ends in the paraoccipital, which, thick at first,

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comes quickly to a thin edge and flares outward; the process itself, which is a sharp point about  $6^{mm}$  long, is directed slightly backward. A deep fossa separates this from the occipital condyle.

The glenoid cavity consists of two flat surfaces at right angles and completely united. Such an articulation with the small condyle of the ramus allows very free motion of the jaw and the spacing of the teeth requires a different position of the condyle for interlocking the front teeth and the molar-premolar series respectively.

In the occipital condyles there is no anterior basal facet as an accessory articulation with the inferior border of the atlas and consequently the lower border of the latter shows no rounded articular edge. The condyle is situated forward and is overhung slightly by the supraoccipital. For more than half its extent the crest is strong and single; then it bifurcates and leads to the supraorbital, bony shelf extending over the eye. Lateral ridges from the supraoccipital prominence extend to the external, auditory meatus and thence a sharp border follows the temporal groove and joins the superior border of the zygomatic arch.

The width across the supraorbitals is  $6 \cdot 3^{\text{mm}}$ . The rear border of the post-orbital process is at right angles to the long axis, causing an abrupt narrowing of the skull posteriorly and a widening of the forehead over the eyes. This is characteristic of camels and gives the head a triangular appearance. Anteriorly there is an insweep of the orbital margin, directing the eyes somewhat forward.

In place of the usual supraorbital notch of other specimens, in the present skull there is an inclosed foramen on one side; on the other, there is a very narrow slit in the outer margin of the bony shelf leading into the pseudo-foramen. Over the middle of  $P^4$  and the length of the tooth above it is the mental foramen: the postpalatine foramen lies between  $P^3$  and  $P^4$ .

In this specimen as in all the species of *Poëbrotherium*, the orbit is not inclosed behind; this is a primitive character and distinguishes the genus from *Gomphotherium*. The orbits are so close together that only a thin septum intervenes. The lower border of the jugal is a straight line, sloping downward and forward; its posterior notch, which receives the squamosal, is not deep. There is a parapet or flange along the lower rim of the orbit. In front the zygomatic arch ends definitely above a point between  $M^2$ ,  $M^3$  and there is a slight pit over  $M^2$ . The pit over  $P^2$ , near the top of the maxillary, measures over a centimeter in diameter; it constricts the nasal passage considerably and gives this region of the skull a narrow appearance. The suture scar on the upper inner edge

shows that the nasal extended anteriorly on the premaxillary to the point where the latter dips downward. The masseteric fossa occupies the middle of the ascending ramus and fades out below at the level of the molars.

The teeth.—Although the size of the upper canine teeth in these early camels may vary with sex, it is important to note that they are very small; the length in the new species is about  $5^{mm}$ . The anterior and posterior edges are only slightly compressed, so that the diameters are about equal; they are slightly recurved, situated  $3^{mm}$  from the incisors, 7 to  $9^{mm}$  from the first premolar, and the premaxillary suture leads directly to the anterior edge of the tooth.

 $C_i$ , the canine of the lower jaw, is considerably larger than that above; it is more flattened, being oval in section; the edges are thin and it is also recurved. The enamel covers only about two-thirds of the length of the crown. Through contact with the third upper incisor the anterior thin edge is much worn. Though set at an angle in the body of the ramus, the canine is not at all procumbent in the sense that the lower incisors are, for they extend forward almost parallel to each other and to the lower edge of the ramus at that point. The lower incisors are semi-spatulate with a diagonal cutting edge. Because the upper incisor are set at right angles to them, these precumbent, lower teeth are worn off squarely on the ends. The anterior incisor is smallest; the third is largest.

Only the second and third upper incisors are known, although the alveolus of I<sup>4</sup> is present and the premaxillary seems to be complete. I<sup>2</sup> is erect, standing almost at right angles to the line of the premolars, but does not touch I<sup>3</sup>. It is fairly long, curved backward, circular in cross section and is worn on the posterior edge from contact with incisors 2 and 3 below. The alveolus of I<sup>4</sup> indicates a smaller tooth of the form and posture of I<sup>2</sup>.

I<sup>s</sup> is of unusual interest because it is canine in form. It is regularly recurved; it interlocks with and passes in front of the lower canine. This third incisor is set solidly in the very heavy premaxillary and is a tooth of considerable strength. Although the point is worn it is still  $10^{\text{mm}}$  long; the enamel covers only about two-fifths of the length. The palatal portion of the maxillary extends forward to a point even with the posterior part of I<sup>s</sup>.

*Premolars.*—The first premolar is a thin, low, but long (antero-posteriorly) tooth; it is bounded by diastemas fore and aft which vary from 6 to  $9^{mm}$  on the right or left. The right P<sup>1</sup>, 7.5<sup>mm</sup> long, is located  $2^{mm}$  behind the one on the other side, which measures but  $6.5^{mm}$ ; both are simple, compressed, trenchant and elongated. It is difficult to see how this tooth,

which is so long antero-posteriorly, could be changed into the caniniform tooth found in the later genera, viz: *Procamelus*, etc. There is one prominent central and one anterior cusp and in general P<sup>1</sup> resembles somewhat the lower  $P_1$  which, however, is already more nearly caniniform.

This lower tooth, through the prominence of its anterior and middle cusps, has a chisel edge with the posterior corner beveled off at an angle. It stands higher than the first premolar of the upper jaw, but is not so long antero-posteriorly (height  $3 \cdot 3^{mm}$ , length ant-post.  $5^{mm}$ ). Its greatest thickness near the roots is nearly  $3^{mm}$  and apparently the tooth is set with a single heavy root. The diastema before is about  $3^{mm}$ , that behind,  $9^{mm}$ .

The second premolars in the maxillary are of the same long, trenchant form in general, though they emphasize the ridges and show distinct valleys externally (and internally, to a less extent) before and behind the central cone. The cutting edge, slightly worn, faces inward and backward.

Upper premolar three, through the elongation of its tetartocone, has a festoon inclosing a distinct lake in the posterior portion. Antero-interiorly there is a cusp, the deuterocone of Scott, corresponding in position to the protocone of the molars, which may in some cases, as for example on the right side, mark the outer boundary of a lake or backward trending groove between it and its own protocone. A heavy buttress leads from this cusp and appears to form a separate, third root. The outer wall of the tooth, which is marked by two valleys and three ridges, the anterior one of which is a rather prominent style, stands high as a cutting edge because the worn surface slopes inward at an oblique angle.

 $P^*$  seems extremely simple and, like that of most ruminants, consists of the ordinary two crescents inclosing a shallow lake. At the present stage of wear the junction of the protocone and deuterocone is not entirely complete. The outer surface of the tooth resembles  $P^3$  and  $P^2$  and all have rather prominent anterior styles.

 $P_2$  of the lower jaw is, like the ramus at this point, very thin transversely, but its antero-posterior diameter,  $7 \cdot 5^{min}$ , is long. It is separated by an extensive diastema from the tooth in front, but is in conjunction with the premolar behind.

The central cone of  $P_3$  is very prominent and from its narnow, acute point there extends backward two ridges, one the main, trenchant edge joining the single posterior cusp, the hypoconid; the other, the deuteroconid, incloses a very narrow lake or valley which opens on the inner side of the tooth. Its anterior cusp, the paraconid, is set off conspicuously by the short sharp groove behind it.

Thus the third premolars both above and below are of exceptional interest in the formation of cusps and grooves. It has been pointed out (Scott) that in many animals the premolars may be even more complicated than the molars.

 $\mathring{\mathrm{P}}_{_{4}}$  is in almost every detail like  $\mathrm{P}_{_{3}}$  except that it is broader, especially posteriorly where it meets the first true molar, and is



FIG. 3. Left, upper, third molar of Poëbrotherium andersoni n. sp., natural size. (Cusp nomenclature according to Osborn's Evolution of Mam-malian Molar Teeth, 1907.) *Pr*, protocone; *Hy*, hypocone or enlarged metaconule; *Met*, metacone: *Pa*, paracone; *Pas*, parastyle; *Ms*, mesostyle; *Mts*, metastyle; *Ibp*, internal, basal pillar: *Cing*, cingulum; *L*, lakes.

FIG. 4. Left, upper. third and fourth premolars, natural size. *Pr*, proto-cone; *Pa*, paracone; *Deut*, deuterocone; *Trit*, tritocone; *Tet*, tetartocone.



FIG. 5. Left, lower, third molar, natural size. *Pr*, protoconid; *Met*, metaconid; *Ent*, entoconid; *Hy*, hypoconid; *Tal*, talonid or hypoconulid. FIG. 6. Left, lower, third and fourth premolars, natural size. *Pr*, protoconid: *Pa*, paraconid; *Hy*, hypoconid (metaconid or tritoconid of Scott): *Tet*, entoconid (tetartoconid of Scott); *Deut*, metaconid (deuteroconid of Scott) Scott).

worn down to a greater extent. The lake in the hinder portion is almost obliterated, but still retains the internal outlet. The elements of the wide heel may be identified as the entoconid and the hypoconid of Osborn (tritoconid and tetartoconid of Scott).

Molars.-In each of the upper molars the anterior lobe is the broader, except in M' where they are about equal, and thus each tooth over-reaches in lateral extent the adjacent surface of the tooth before it.  $M^1$  is less in longitudinal diameter than M<sup>2</sup> and because of its greater time of wear has its lakes obliterated.

M<sup>3</sup> has fairly prominent ribs on each lobe and an anterior, a median and a posterior style; the mesostyle is especially sharp.  $M^2$  has a prominent median style and a moderate rib and style anteriorly.  $M^1$  shows scarcely more than the median style and the valley in front of it, to break the smooth outer surface. On the posterior, internal corner of  $M^3$  there is a cingular ridge or cusp which appears again between the internal lobes as a rudimentary, internal, basal pillar; this is entirely absent in *Poëbrotherium* generally (Wortman, '98, p. 106).

The lower molars, as earlier suggested by Scott, show a distinct trend toward hypsodonty; the enamel on M<sup>3</sup> especially is very deep, reaching to the alveolar border in places. An unusual feature is the presence of cement on the lower molars, indicating the extreme advancement of these early camels; this is further shown by the fact that the lower teeth are flattened considerably on the inner side as well as by their sub-hypsodonty.

M<sup>3</sup> has a large third lobe or fifth crescent which occupies one fourth of the length of the whole tooth and is over half the transverse width of the adjacent lobe. The outer surfaces of the lower molars are not rounded, but as shown by the enamel border, are angular.

Related forms.—The new specimen is distinguished from P. eximium (Hay) by the greater diastemas, especially before and after the first premolars, and also by the crowding of the lower incisors. The upper canine is relatively much smaller and the third upper incisor is very much larger and is caniniform. The upper incisors are erect and conical or cylindrical, while the lower incisors are procumbent, semi-spatulate and crowded together. In P. eximium the incisors, canines and first premolars are quite regularly spaced, except that  $P^1$  is set far back, are of uniform size and are somewhat compressed.

The supraoccipital crest in *P. labiatum* far overhangs the condyles, but the crest of the new specimen is only moderately extended. Other characters of *P. labiatum* are: <sup>1</sup> the otic bullae are rounded; <sup>2</sup> the lower border of the ramus is rather straight, like that of *P. wilsoni*; <sup>3</sup> the alveolar bone encroaches on the orbit; <sup>4</sup> the paraoccipitals seem to flare widely back-and outward; <sup>5</sup> M<sup>3</sup> is set far in front of the ascending portion of the ramus; <sup>6</sup> in the atlas there is a gap in the posterior border of the inferior arch; <sup>7</sup> the outer and inner sides of the laterial processes are rounded and converge gradually.

On the other hand in *Poëbrotherium andersoni* n. sp., 'the otic bullæ are sub-triangular; 'the lower border of the ramus has a double, reverse curve; 'but little of the maxillary bone projects into the region of the orbit; 'the posterior border of the paraoccipital stands vertical; 'M<sub>3</sub> is close to the anterior border of the ascending ramus; 'in the atlas there is no gap on the inner surface of the lower arch, posterior; 'the atlas is

generally more squarely cut, including the borders of the lateral, posterior processes. The dorsal arch, posteriorly, is set in and, anteriorly, it overhangs the canal.

As is general in the Camelidæ the vertebral artery traverses the transverse process and opens on the border of the axial articular surface. These surfaces, which are nearly in a single plane at right angles to the neural canal, are reflected upon the inner surface of the arch on the lower half only; the upper half of the cavity, therefore, is wider, differing in this respect also from *P. labiatum*. Rather deep notches are found on the outer border of the anterior cotyles.

Gomphotherium sternbergi Cope is distinguished from the present species by the following characters: the strongly pointed and recurved canine, the deeper skull, the anterior and posterior lobes of the molars which are more nearly equal (each tooth does not greatly over-reach the one in front of it), the similarity in size of the outer and inner parts of the otic bullæ and finally by the orbit which is entirely encircled by bone.

Measurements :---

				G.s	ternber	gi	N.sp.		P. eximium
					mm.	ratio %	mm.	ratio 9	% mm.
Lengt	h from	$P^2$ to	) M <sup>3</sup>	inclusive	60	99	59	82	65
	66	P, to	$M_{3}$	66	65	99	64	87	72.5
66	entire	infer	ior d	lentition	110	94	103	96	107.5

Measurements of the new specimen, Poëbrotherium andersoni :--

Diameter of	Ant-post.	Transverse
$\mathbf{P}^{_{1}}$	7.6	2.3
$\mathbf{P}^{2}$	8.8	3.5
$\mathbf{P}^{s}$	9.4	5.0
$\mathbf{P}^{4}$	8•4	7.4
$\mathbf{M}^{1}$	11.0	10.0
${ m M}^{2}$	12.0	11.2
${ m M}^{ m s}$	12.2	12.4
P,	5.0	2.8
P,	7.6	2.5
P,	9.5	3.0
$\mathbf{P}_{_{4}}^{^{s}}$	10.0	4.2
$\mathbf{M}_{1}$	10.3	7.0
M,	11.7	7.8
M	15.5	8.2

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## ART. XXXV.—Sand Fusions from Gun Cotton; by CHARLES E. MUNROE.

WHILE engaged in a series of tests on means of exploding gun cotton wherein the charges were fired imbedded in sand on an old sea beach, it was observed on excavating after one of the tests that the loose sand had in places been fused into forms analogous to those of the disks of gun cotton used.

In the experiments the charges were enclosed in cast iron shells of a size designed to closely confine the charge, the walls of the shells being  $1\frac{1}{3}$  inches in thickness, and the whole buried to a depth of three feet in the compacted sand of the beach, which was of a very uniform granulation. In the particular experiment in which the sand fusions were formed the shell contained one disk of dry gun cotton and three of gun cotton wet with 20 per cent of water, and the charge was primed with 4 ounces of gunpowder. On firing the sand was slightly disturbed, the base plug of the shell thrown out to a small distance and the shell broken into large fragments which remained imbedded, but no "crater" was formed as was the case in all other of the experiments. There were three of these fusions found on excavation some five minutes after the

## 390 C. E. Munroe-Sand Fusions from Gun Cotton.

charge was fired and each then contained burning gun cotton. It is believed that each fusion figure was formed about a wet disk of the gun cotton and is a cast of the partly burned disk. They are shown in the photograph where No. 1 is a disk of such gun cotton as was used originally. It measured 3.5 inches in diameter by 2 inches in height. The sand fusions are numbered 2, 3 and 4 in the photograph. They were coated on the



interior with a greyish glaze not over a millimeter in thickness to the exterior of which grains of sand was adherent. They at once on appearance suggested fulgurites, but as a fulgurite has been defined as "a vertical tube with fused walls formed in sand, rarely in compact rock, by the passage of lightning," these may simply be styled sand fusions produced by the burning of wet compressed pulped military gun cotton in sand impregnated with sea salts.

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## ART. XXXVI.—Electrolytic Analysis with Small Platinum Electrodes; by F. A. GOOCH and MATSUSUKE KOBAYASHI.

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

IN a former article from this laboratory<sup>\*</sup> it was shown that certain processes of electrolytic analysis may be carried out successfully with the aid of small platinum electrodes of light weight and a weighable cell, any difficulty due to the detach-

ment of particles of material deposited at high current density upon the small electrode surfaces being overcome by drawing off the residual liquid through a small filtering tube which was finally weighed with the electrodes and the electrolytic cell. The feasibility of the process was demon-strated in determinations of copper and nickel, taken in the form of sulphates, from solutions of small volume. The results of the determinations were good, but the criticism has been made<sup>+</sup> that the use of solutions of the small volume (about 15 cm<sup>3</sup>) appropriate to the cell which was employed is impracticable. Although the former experimental results show that such a conclusion is unwarranted, we have thought it desirable to test the small electrodes in an apparatus modified to permit the use of volumes of solution which are comparable with those ordinarily employed in electrolytic analysis.

In the experiments to be described, the rotating electrode (fig. 1) was made of a small piece of platinum gauze (1.2<sup>cm</sup> square) into the central meshes of which the tapered end of a lead glass rod was fused. The electrical connection between the gauze and the metal shaft of the motor, which formed a part of the electrical circuit, was made by means of a doubled and twisted platinum wire, 0.03<sup>cm</sup> in diameter, wound about the glass rod and held to the shaft by means of a twist of copper wire (see fig. 3). The stationary electrode was a strip of thin platinum foil  $(5^{\text{cm}} \times 0.5^{\text{cm}})$  welded to the connecting wire by means of which it was hung to the side of a thin glass beaker of about 120 cm<sup>3</sup> capacity.

The small filtering tube (fig. 2) was made by fusing the flared end of a lead glass tube to a little disc of platinum gauze, and coating the disc with a filtering mat by dipping it in an emulsion

> \* Gooch and Burdick, this Journal, xxxiv, 109, 1912. + Fresenius, Zeitschr. anal. Chem., lii, 209, 1913.

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- - FIG. 2.

of asbestos and applying suction. The filtering tube thus made may be dried, or even ignited, without difficulty.

In using this apparatus, the beaker, both electrodes, and the filtering tube were first dried and weighed together, the total weight amounting to about 20 grm. The material for analysis was electrolyzed in the apparatus, assembled as shown in fig. 3, the beaker being covered with a split watch-glass. At the end



of the electrolysis the liquid remaining was drawn off by suction through the filtering tube, and the washed beaker, electrodes, and filtering tube were dried and again weighed together.

With this apparatus, determinations, the details of which are given below, were made of copper and nickel deposited upon the rotating cathode from sulphate solutions, and of lead dioxide, deposited upon the rotating electrode used as the anode, from a solution of lead nitrate.

### The Determination of Copper.

In the determinations of copper the material used was recrystallized copper sulphate,  $CuSO_4.5H_2O$ , and a separately weighed portion (0.5 grm., as nearly as might be) was taken for each analysis. In each case the electrolysis was continued

some minutes after the solution had been completely decolorized and thereafter was brought to an end only when the ferrocyanide test failed to give any indication of copper in a portion of the solution removed for testing.

In the first three experiments the deposit of copper was washed, as is usual, with a water-jet and the results indicate that there must have been included in the somewhat porous copper deposited at a high current density  $(N\dot{D}_{100} = 30$  to 45 amp.) traces of sulphuric acid which the superficial washing failed to remove. In the remaining experiments, therefore, the cathode deposit was several times dipped and allowed to stand for a few minutes in distilled water to permit the escape of included acid by the process of diffusion.

#### TABLE I.

Electrolysis of Copper Sulphate. (Cathode revolutions, 600 per minute.)

Copper taken as sulphate grm.	Copper found grm.	Error grm. Superficial x	Initial amp. vashing	Current volt only.	$Vol-ume cm^3$	H₂SO₄ added drops	Time min.
0.1273	0.1279	+0.0006	0.6	7.8	30	5	40
0.1273	0.1282	+0.0009	0.4	8	50	5	40
0.1273	0.1293	+0.0020	0.6	7.8	100	10	50
Super	rficial was	hing supplem	ented b	y diffusio	on in v	vater.	
0.1273	0.1271	-0.0005	0.2*	4	100	30	55
0.1273	0.1274	+0.0001	0.2*	4	100	30	60
0.1273	0.1271	-0.0005	0.2*	3.8	100	30	60
0.1273	0.1275	+0.0005	0.2*	3.8	100	30	60
0.1275	0.1276	+0.0001	0.2*	3.9	100	39	60
		$*ND_{100} = 15 s$	amp. (ap	prox)			

The results of the latter group of experiments show that with the use of the small electrodes the copper in half a gram of crystallized copper sulphate may be completely precipitated within an hour from 100 cm<sup>3</sup> solution acidulated with sulphuric acid, and determined with a high degree of accuracy, by means of a current of about 0.2 amp. In the experiments described the adjustment of conditions was such that this current was delivered under a potential of about 4 volts between the elec-Experience shows that the amperage rises as the trodes. action proceeds, presumably in consequence of the heating of the liquid.

#### The Determination of Nickel.

The material used in the determinations of nickel was nickel sulphate, NiSO<sub>4</sub>.6H<sub>2</sub>O, taken in a solution containing approximately 0.1 grm. of nickel in every portion of 50 cm<sup>3</sup>. The

solution was standardized by the electrolysis of such portions with a platinum crucible used as the rotating cathode.<sup>\*</sup> In every case correction was made for change of volume due to the difference between the temperature at the time of the experiment and that at the time of standardization, upon the assumption that the coefficient of change was that of pure water.

In the procedure adopted after the preliminary experimentation, portions of the solution were drawn from a burette and concentrated by evaporation. Ammonia and ammonium sulphate were added, the volume was adjusted to 100 cm<sup>3</sup>, and the electrolysis was continued for some minutes after the solution became colorless and always until dimethyl-glyoxime gave no indication for nickel in a small portion removed for testing. The washing of the cathode deposit was completed by soaking in water, as in the approved procedure described above for the determination of copper.

#### Electrolysis of Nickel Sulphate.

(Volume, 100 cm<sup>3</sup>; cathode revolutions, 600 per minute; washing completed by soaking of cathode in water.)

Nickel taken as sulphate grm.	Nickel found grm.	Error grm.	Initial amp.	Cur- rent volt.	$(\mathrm{NH}_4)_2$ SO <sub>4</sub> added grm.	${ m NH_4OH}\ { m added}\ { m cm^3}$	Time min.
		Preliminary	Experin	nents.			
0.0989	0.0985	-0.0004	0.2	9.8	2	50	90
0.0989	0.0972	-0.0017+	0.5	7.2	3	50	105
0.0989	0.0990	+0.0001	0.6	9.3	4	100	135

Adopted Procedure :  $ND_{100} = 60$  to 75 amp. (approx.)

0.0989	0.0994	+0.0002	0.8	9•4	4	55	90
0.0989	0.0989	0.0000	0.8	9.4	4	55	100
0.0989	9.0990	+0.0001	0.8	9.9	4	55	100
0.0989	0.0991	+0.0005	1.0	12.2	4	55	90
0.0989	0 <b>·</b> 098 <b>6</b>	-0.0003	1.0	11.7	4	55	90
0.0989	0.0992	+0.0003	1.0	11.1	4	55	100

These results show that with the use of the small electrodes approximately 0.1 grm. of nickel may be deposited completely in an hour and a half from 100 cm<sup>3</sup> of solution charged with ammonia and ammonium sulphate by means of a current of 0.8 to 1 amp. The voltage required under the conditions of the experiments described was approximately 10 or 12 volts.

> \* Gooch and Medway, this Journal, xv, 320, 1903. † Deposition incomplete:

#### The Determination of Lead.

Lead nitrate, recrystallized and dried at  $200^{\circ}$  was used as the source of lead to be deposited electrolytically from solution as dioxide upon the anode of small dimensions. The volume of the solution was fixed at 100 cm<sup>3</sup> and, in order that metallic lead might not be deposited on the cathode,\* this was generally made up to contain 30 cm<sup>3</sup> of strong nitric acid.

Preliminary experimentation developed the fact that a too rapid rotation of the anode results in the detachment of large amounts of the anode deposit in the early stage of action during the first half-hour—and that the detached dioxide may be entirely dissolved in the electrolyte, from which it is again deposited on the anode as the electrolysis pro-

gresses. The later deposit from the more dilute solution adheres firmly to the anode. It was found, further, that dissolved lead may be found in the electrolyte so long as any appreciable amount of the dioxide remains in suspension.

Acting upon the hypothesis that nitrous acid gradually and continually formed in the course of action is the active agent in bringing about the resolution of suspended dioxide, the attempt was made to hasten the process of solution by adding potassium nitrite, but this reagent and the nitrous acid formed from it are so rapidly decomposed that no appreciable advantage seems to be gained by its use. When the suspended dioxide nearly or entirely disappears and the anode deposit has become fixed, the addition of a little urea serves to destroy the nitrous acid in solution and prevent solvent action of the electrolyte upon the deposit after the stopping of the current.

Instead of waiting until the detached residue has been dissolved again, it is possible to separate the clear liquid from the suspended material by drawing it off through the filtering tube and again submitting it to electrolysis. For this separation,

a simple apparatus (fig. 4) made by attaching the filtering tube to a separating funnel into which the clear liquid may be drawn by suction and from which it may be returned to the electrolysis cell, after disconnecting the tube, is convenient.

The details of experiments upon the lines indicated are given in the table. In every case, at the end of the electrolysis, the liquid was drawn off from the beaker through the filtering tube. The entire apparatus—beaker, electrodes, and filtering tube—and the deposit were dried at 200° and weighed.

\*Gooch and Beyer, this Journal, xxvii, 59, 1909.

FIG. 4.

#### Electrolysis of Lead Nitrate.

(Volume of	solution,	$100 \text{ cm}^3$ : vol	ume of r	nitric a	acid prese	ent, $30 \text{ cm}^3$ .)
Lead					R	ovolutions
taken as	$\operatorname{Lead}$			Cur-	(	of anode
nitrate	$\mathbf{found}$	Error	Initial	$\mathbf{rent}$	$\operatorname{Time}$	per
grm.	grm.	grm.	amp.	$\operatorname{volt}$	min.	minute
Amoun	t of suspe	nded lead dio	cide larg	ge at ei	nd of elec	trolysis.
*0.1002	0.0929	-0.0023	2.9	$6 \cdot$	120	150
0.1015	0.0994	-0.0051	3.	5.8	110	100 approx.
0.1014	0.0991	-0.0053	3.5	6.7	120	100

Amount of suspended lead dioxide small at end of electrolysis : Urea added 20 minutes before end.

0.1001	0.0991	0.0010	<b>4</b> ·	6.5	90	150
0.1007	0.0996	-0.0011	$4 \cdot$	6.3	90	150
†0·1001	0.0988	-0.0013	4·	6.	90	150
10.1009	0.1000	-0.0009	4·	5.8	90	150

Amount of suspended lead dioxide inappreciable at end of electrolysis : Urea added 20 minutes before end.

0.1002	0.1008	+0.0006	3.	5.8	90	150
0.1009	0.1013	+0.0004	3.2	$7 \cdot$	90	150
0.1002	0.1003	-0.0005	4.	6•	90	150
0.1002	0.0998	$-0\ 0004$	3.5	6.2	90	150
0.0999	0.0992	-0.0004	3.5	5.8	100	150
0.1003	0.0998	-0.0002	3.7	6•	90	150
0.0995	0.0991	-0.0004	3.7	6.2	90	150
0.1010	0.1914	+0.0004	3.8	6.4	90	150

Suspended lead dioxide removed by filtration and the filtrate again electrolysed after addition of urea.

0.1012 0.1008 -0.0004 3.8 6.3 90 150

From these results it is apparent that lead may be determined accurately by the aid of platinum electrodes of small dimensions, the filtering tube, and the weighed cell. The process is successful when the electrolysis is prolonged until the lead dioxide which becomes detached from the anode in the early stages of the operation has been dissolved and again deposited on the anode, or when the electrolyte is filtered from any suspended lead dioxide and again submitted to electrolysis.

It is plain, therefore, that the use of the small electrodes, filtering tube, and weighed cell, modified in the manner described, may be extended to solutions of considerable volume  $(100 \text{ cm}^3)$ . The time required, however, to complete the deposition of a given amount of material naturally increases with the volume of the solution.

\* No urea added.

† Potassium nitrite added, and subsequently urea, before end of electrolysis.
#### ART. XXXVII.—Crystal Drawing and Modeling; by John M. Blake. (Article 5.)

It now remains to describe two other methods which become practicable when we use the plotting sphere.

#### Drawing.

In a former article a practical method of obtaining the gnomonic projection was given which was based upon the plotting of the crystal planes on the sphere. This gnomonic projection can be utilized as an aid in making crystal drawings. The general principle on which this adaptation is based is that the direction of a crystal-edge formed by the intersection of two planes will be at right angles to a line connecting the normal points of the planes on the gnomonic projection. By taking advantage of this fact, we can greatly simplify the making of drawings.

This principle was used by others in a limited way as far back as the fifties for making plan drawings, but it was done under exceptional conditions. We would here draw attention to the more general adaptability of this present method for use in both plan and perspective drawing. Either kind of drawing can be made at will, provided that in each instance we start from a tangent plane projection made from the proper view-point. The method in which a templet is depended upon to mark out the direction and length of the axes can be entirely dispensed with, since the new way is so entirely different. Furthermore, it may be said, there will now exist no valid reason for being restricted to certain fixed positions and axial lengths, such as would be the case when using the templet.

It may be stated that as a general principle the planes which are more nearly flat on when seen from the selected viewpoint, will be most clearly presented and brought out by their intersections; while those planes which are viewed nearly edgewise, and are marginal, are most likely to be confused in their intersections on the drawing. It is well, therefore, to make a point of avoiding this nearly edgewise position for any of the planes.

When we have the position of the planes plotted on the sphere, it is easy to test for the above conditions by moving the sphere in the equatorial ring until a position is found where a projection made from this view-point will not give a tangent length in the projection exceeding, at the utmost, that of seventy-five or eighty degrees. In case of a plan drawing, we would select the view-point that would give the most compact grouping of the planes in a tangent plane projection; and, in case of a perspective drawing, we would make our view-point as near this first point as the case will allow. A second next best position should be found at or nearly at right angles to this first best position that would be suitable for making a correlated drawing to supplement the first.

When the view-point in any case tends, as sometimes happens, to give too long a tangent line on the projection, we must change our view-point to avoid this difficulty and allow the troublesome plane to come exactly edge on; or else make it overstep a sufficient distance into the other hemisphere.



This just mentioned trouble exists whatever the mode of drawing we employ, but we have, by the use of the sphere, a means provided to trace out the cause of the difficulty.

We begin our drawing by attaching the paper to the projection sheet. If we choose, we can carry on one, or even two, auxiliary or correlated drawings in connection with the main drawing, and by the methods of descriptive geometry, one drawing will supply dimensions which may be lacking in the In a case where we would need to utilize two or three other. corresponding projections at one time for this purpose, it would be desirable, in order to secure compactness, either to use a reduced scale of tangents, or to reduce the projections by Such reductions have been made in which an a pantograph. inked type was used. This type had a central dot inside a ring, the central dot making it easier to bring into alignment the two normal points that are used in obtaining the direction of a crystal edge.

One or both drawings can be in plan, or both be made in perspective. It is often well to make one in perspective and its correlated drawing in plan, and, if thought best, dispense with the latter after it has served its purpose. A T-square should be used in order to obtain sufficient span. We bring the two selected normal points in line under the square when this is placed in a vertical position. We next apply the square against the side of the board, and the edge of the square will then give the direction of the crystal edge. The usual procedure can, in general, be adopted in regard to other details.

Two drawings are shown, one in plan and one in perspective. They both relate to Gay-Lussite and were found together with a number of drawings pertaining to that species that were made by the writer in 1866. They will serve to illustrate the adaptability of this method of drawing to all positions. Plan drawings are as a rule more satisfactory for use during the correct proportioning and shaping of a crystal model from a descriptive drawing. The fact that plan drawings are better for shaping models also implies that when we have two correlated plan drawings from well selected view-points, we are provided with the means of gaining a clear conception of the crystal form. Perspective drawings have the advantage when we wish to show the back planes of a crystal.

The making of both kinds of drawings will be greatly facilitated by the use of the gnomonic projection method based on the plotting of the plane positions on the sphere.

#### Modeling.

During the progress of a crystal investigation it will be found a great help to be able to model any of the forms. The writer contrived a machine for this express purpose, which was successfully constructed shortly after the plotting sphere was made, the idea of such a machine naturally following the successful use of the sphere. A description of this machine will be given farther along.

Such models can be made so that the planes have the correct proportions of the natural crystal, or instead, we can make all the planes tangent to a sphere. This latter plan is frequently followed, and has the advantage of giving each plane an equal chance to appear.

The modeling of several varieties of the same mineral species with the true proportioning of the planes, when carried out on an isomorphous group of minerals, sometimes results in a very interesting series of models, as for instance in the chrysolite group, which includes the natural crystals, together with certain furnace products in which iron predominates. This series of models shows very wide variations in the development and appearance of the members, and yet the angles in the whole series are practically the same.

#### 400 J. M. Blake—Crystal Drawing and Modeling.

The machine contrived to cut these models is simple in principle. The plane positions are taken off the sphere in the same manner as when making the gnomonic projection, and the machine is set for each plane position before the cut is made.

To cut a model, a block of plaster is cemented on a stem which screws into a horizontal shaft. The other end of this shaft carries a graduated disk and the shaft can be rotated as required. This graduated disk corresponds to the equatorial ring of the sphere.

There is an iron table with a notch at one side into which



FIG. 3.

FIG. 3. J. M. Blake's Crystal Modeling Machine.

the block of plaster enters. This table can be rocked in a direction at right angles to the shaft, and has a graduated disk which reads from zero at each of the two vertical positions of the table to 90° at the horizontal position, so that one complete rotation of the shaft combined with the motion of the table through 180° covers the position of all possible planes on the model.

During the cutting, the saw and file are kept at the proper height above the table by attached supports on which they glide, and the depth of each cut is determined by adjusting the height of the table. The table slides up and down, and has a millimeter scale by which the radial distance from the center can be measured.

The radii required for proportioning a crystal model can be

obtained by measuring the perpendicular distance from each face to its opposite. The measuring apparatus can be made to enlarge this radial distance in any desired proportion, and with this help, a model can be made to any desired scale. If the same radius is kept throughout, the planes will necessarily be all tangent to a sphere of that radius.

A slice of material is cut off with the saw and the file follows at the proper depth. The file is rubbed across a stiff brush after each stroke to clear the teeth of plaster.

Plaster has certain qualities which render it ideal for cutting models. It has no grain, and has a certain toughness that prevents crumbling when cutting an acute edge. A medium degree of hardness is best for the reason that it is more easily cut. When there is to be considerable handling, a harder variety of plaster can be used. If desired, models can be mounted on a stem with a base to secure them from injury.

The components of a compound crystal can be modeled on the twin plane and the parts assembled. The model can be cut for this purpose with the twin plane square to the supporting stem. This can be done by making a projection from the twin plane view-point by which to set the machine.

These models admit of having the indices written on the planes, and two sets of indices in different colors are sometimes helpful in comparing two separate descriptions of the same mineral species. Salts that are not permanent may in this way be preserved in model. When tested by the hand goniometer these models show a very good approximation to the correct angles.

It may be of interest, as bearing on future applications, to mention that for the purpose of testing and identifying some minute artificial Gay-Lussite crystals a crystal was mounted on a pointed lead wire and brought under a one-fifth objective. The selected faces were leveled and compared directly with a plaster model. Calculation of the angles bordering the plane faces was in this instance rendered unnecessary by the possession of the model.

There are some further suggestions that have not as yet been presented relating to the possibility of more exact determination of certain crystal constants.

New Haven, Conn., Feb., 1917.

#### ART. XXXVIII.—Normal Anomalies of the Mean Annual Temperature Variation; by HENRYK ARCTOWSKI.

THE curves representing annual variations of atmospheric temperature are generally derived from monthly means. For many stations, belonging to different climates, these curves convey the impression of representing a cyclic variation, reflecting, with different amplitudes and more or less retardation, the seasonal changes of solar declination.

If, in the case of long series of observations, instead of monthly means, the averages for each day of the year are taken into consideration, the diagrams thus obtained display most remarkable anomalies. As typical examples I would refer to the curves of Koenigsberg, Munich, Catania and Valentia, published by Van Rijckevorsel\* and to the curve derived from observations made in Melbourne, published by R. J. A. Barnard.<sup>+</sup> Because of its simplicity, the Melbourne curve may be taken as a demonstrative example of the problem in view.

From the highest mean temperature, observed in January, the means decrease more or less regularly till the middle of March; then, suddenly, temperature increases about 2° F. Another characteristic break occurs between June 15th and 20th. After the minimum of July the increase of temperature is again interrupted in September and also at the end of November.

The annual variation for Melbourne may therefore be represented by the following diagram (fig. 1).



This diagram expresses graphically the opinion that the seasonal change of temperature in Melbourne is not what it should be: that at given dates of the year (x, y, y', x') the natural course of temperature, due to local conditions, is interrupted,

> \* Phil. Mag. (5), xlv, 459, 1898. † Phil. Mag. (5), 1, 408, 1900.

just as if the station had been shifted into another climate, similar, but colder than it ought to be during the summer, and warmer than it ought to be during the winter.

The annual variation proceeds by steps. The steps of ascent, occurring while the temperature is decreasing, correspond to similar steps of descent observed during the other half of the year.

Each successive stage marks the passage from one phase to another.

In the preceding example the annual variation is composed of three phases.

This opinion seems never to have been advanced and it is astonishing to notice that even the fact of the existence of steps during the autumn, corresponding to the steps of the spring, has, so far as I know, practically attracted no attention; though the frequently recurring temperature anomalies for given dates, in May and June, have been very extensively studied.

Researches of particular interest concerning these anomalies are those of G. Hellmann,\* W. v. Bezold,† Ch. Dufour,‡ W. Marten,§ R. Gautier and K. Almstedt.¶

The principal results gained by these authors may be summarized as follows:

(1). The temperature depressions are not strictly bound to given dates. Their occurrence varies slightly from year to year, but on the average, in Central Europe, the 11th-15th of May and the 4th-8th of June show a well pronounced deficiency of temperature.

(2). In all cases, of given years, the comparison of the records has shown a progressive displacement of the wave of cold.

(3). A characteristic distribution of atmospheric pressure over Europe is noticeable. On the ocean a high pressure area, extending an anticyclonic tongue eastward, moves slowly from the center of action of the Azores northward.

(4). The resultants of the observed wind directions change radically.

(5). Considering a long series of observations, groups of years may be distinguished for which the temperature depressions of May and June are well pronounced, while in other groups they occur only occasionally.

\* Ann. Phys. Chem., clix, 36, 1876. † Abh. math.-phys., Kl. K. Bay. Akad. Wiss., xiv, II, 69, 1883. ‡ Bull. Soc. Vaud. Sc. (3), xxix, 316, 1893. § Abh. K. Preuss. Met. Inst., ii, No. 3, 1902. [] Arch. Sc. Phys. et Nat. (4), xxxi, 497, 1911. T Meteor Zeit. xxxi, p. 426, 1914

¶ Meteor. Zeit., xxxi, p. 426, 1914.

This fact (5) applies at least to the Paris\* and Geneva+ observations.

The marked departures of temperature conditions of given dates, from the steady seasonal advance, may receive three different interpretations which are illustrated by the following diagram (fig. 2):



Curve "A" expresses the hypothesis that temperature is below the normal for given dates "k" and that "a'" is the continuation of curve "a". This represents the very generally admitted hypothesis.

Curve "B" represents the anomaly "p" as being due to such more or less sudden change in the distribution of the isotherms that "b" belongs to a curve identical to "a" but shifted downwards.

Curve "C" presupposes a radical modification of the annual variation. At "q" the curve "b" is supposed to have a greater amplitude than "a"; at "r" curve "c" is supposed to have a smaller amplitude than "b".

A careful examination of the available temperature curves shows that curve "A" may be discarded. On the contrary curves "B" and "C" must both be taken into consideration.

As a typical example I will cite the temperature curve for Warsaw.

The utilized daily means are those of the years 1826–1880.<sup>‡</sup> The following diagram (fig. 3) gives an interpretation of the detailed curve.

The variation is composed of phases 1, 2, 3 and 4 belonging to four concordant curves. The steps occur approximately at the following dates: Jan. 25, March 9, April 22, Oct. 2, Nov. 29, and Dec. 16.

Then during the summer, on the contrary, from June 9th till July 28th, we have practically a straight line of mean tem-

\* E. Renou, Annales Bur. Centr. Met. France, 1887, i, p. B. 195.
† R. Gautier et H. Duaime, Arch. Sc. Phys. (4), xv, 545, 1903.
‡ Jan Kowalczyk, Pam. Fizjogr., Warsaw, 1881.

peratures increasing from  $17.6^{\circ}$  to  $19.3^{\circ}$  C. This line 6 is evidently discordant: it cuts all the others. The summer maximum is 3° below the maximum which would be observed if curve 4 were fully developed. The summer temperature may, therefore, be considered abnormally low. Now, between 6 and 4 we observe the fragments of a curve 5 extending from May 22d to June 8th and July 29th to Aug. 26th. This curve intersects all the others: its amplitude is evidently much smaller than the amplitude of curves 1–4.

Although the temperature curve for Warsaw may be considered a most typical example of the normal anomalies of the annual temperature variation, the breaks being too well accentuated to be ascribed to chance circumstances, it is useful



to cite a few other examples in order to show how, gradually, we pass from one type of variation to another.

Hellmann has published\* a detailed curve of the daily means derived from the observations made in Berlin during the years 1848–1907. Referring to the diagram for Warsaw (fig. 3), the Berlin curve displays the fragments 1 to 4, 5 is missing and 6 is a well-developed curve extending from June 13th to Sept. 21st, with a maximum on July 22d.

From March 13th to April 7th the increase in temperature is abnormally rapid so that 3 is discordant with 2 and 4. The drop of temperature between 4 and 6 (June 6–11) is  $1.5^{\circ}$  C. This is perhaps the most characteristic feature of the curve. Besides, 4 and 6 are discordant. Phase 6 has a smaller amplitude than 4.

Evidently if many curves were available it would be interesting to follow the progressive change from station to station. That these anomalies do not occur simultaneously at different

\* Preuss. Met. Inst., Abh., v. 3, No. 6, Berlin, 1910.

stations but gradually propagate from place to place is a well established fact, at least for some of the temperature depressions of the spring. The curves for Arcachon, Greenwich, Berlin, Lemberg, Penza and Wologda, published by Almstedt,\* may serve as examples.

Without adopting in their integrity the ideas expressed long ago by Dove,<sup>†</sup> let me suppose now that the temperature curve for Melbourne, or the curve for Warsaw, or the curves for other places, exhibiting similar anomalies, express the result of an antagonism between maritime and continental climates, respectively characterized by a very small and a very large annual amplitude.

On the ocean, west of the coasts of France, the difference between the mean temperatures of the warmest and the coldest day of the year is certainly less than  $10^{\circ}$  C. In Paris it is  $18.7^{\circ}$ , in Warsaw  $24.7^{\circ}$ , in Barnaoul it is  $41.8^{\circ}$  and the observations of Nertchinsk give  $49.9^{\circ}$  C. I have traced the curves for Barnaoul (means of the observations made from 1838 to 1882) and Nertchinsk (1839–1881)‡ and have found, to my great astonishment, that from March 15th to November 1st these two curves are practically identical, whereas during the winter months they differ very greatly one from the other. The winter in Nertchinsk is very much colder than in Barnaoul. The temperatures are:

	Barnaoul	Nertchinsk
October 31	— 3·6°	$- 7.2^{\circ}$
January 2	$-18.3^{\circ}$	$-30.7^{\circ}$
March 15	$-10.8^{\circ}$	$-13.1^{\circ}$

The maxima of the summer are:

Barnaoul	$20.2^{\circ}$	on	July	the	$4  \mathrm{th}$
Nertchinsk	$19.2^{\circ}$	"	"	66	12th.

The temperature curve of Barnaoul belongs therefore to two climates. During the months of April to October it belongs to the excessive continental climate of Nertchinsk, while in the winter it belongs to a less continental climate.

The following diagram (fig. 4) gives the daily means of temperature in Nertchinsk for the months of May and June.

The diagram shows that the increase of temperature proceeds by steps. Going up, the curve slides down here and there and goes up again. The total depression of the yearly amplitude, due to these steps, may be estimated at 17°. Admit-

\* Loc. cit.

‡ Repert. f. Meteor., Suppl. 3, St. Petersbourg, 1886.

<sup>†</sup> Abh. K. Akad. Wiss. Berlin, 1856, p. 121.

ting this estimate and supposing that a curve of  $67^{\circ}$  (=50+17) amplitude would represent the variation corresponding to the coefficient of perfect atmospheric transparency\* at the latitude of Nertchinsk, the lowest temperature of January must be considered  $6.5^{\circ}$  too high and the highest July temperature  $11.5^{\circ}$  too low, since the extreme daily mean temperatures should be  $-37^{\circ}$  and  $+30^{\circ}$ .



Thus it may be that, in this case, the decrease in amplitude is in close connection with the annual variation of atmospheric moisture. During the summer months, the greater amount of aqueous vapor diminishes the coefficient of atmospheric (thermal) transparency very much more than during the winter months, and so it is evident that the summer temperatures differ more, from what they should be than the temperatures observed during the winter.

This leads to the question whether the steps of the Nertchinsk temperature curve, and perhaps also the steps of the curves of several other stations, are not partially due to a rhythmical transport of atmospheric moisture.

\* A. Angot, Ann. Bur. Centr. Met. France, 1883, i, p. B. 121.

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Fig. 4.

In the ascending part of the curve of Barnaoul the depressions following the crests generally precede by two to four days the corresponding details of the curve of Nertchinsk. The inflexions of the isotherms, characteristic for these changes, progress therefore across Siberia from the W. towards the E.

But, as a result of the international balloon ascents of May 13th, 1897, Hergesell has shown that the typical decrease of temperature observed then in Central Europe was very much more accentuated at high altitudes than it was near the ground.<sup>\*</sup> Similar observations have been made since. In consequence, the inflexion of the isotherms must be more pronounced at an altitude of 10,000 m. than it is at the surface of the earth's crust. After each step of the ascending temperature curve, the entire air mass above the station where the step has been observed is changed. The work of the progressive heating of the ground by solar radiation and the heating of the air mass above, by convection currents, must, to a certain extent, be begun anew, and probably under different conditions.

Evidently, to reach a definite conclusion it would be necessary to study the records of individual years and the weather maps as well. But the real difficulty, and at the same time the great interest of the study of these normal anomalies of the mean annual temperature variation, resides in the fact that we have to deal with a phenomenon showing intimate relationship between very far distant stations.

On the opposite side of the world, in Baltimore,<sup>+</sup> the temperature crests of February 22d, March 10th, April 14th and May 10th, there observed, belong also to the curves of Barnaoul and Nertchinsk. In Barnaoul they occur: February 18, March 9, April 21 and May 10. In Nertchinsk: February 22, March 12, April 20 (and May 12).

Already Dove<sup>‡</sup> noticed the fact that the anomaly occurring during the month of May is noticeable in the records collected in Arctic America and Greenland. On the other hand, according to R. C. Mossman,§ the cold period of May is well pronounced in Argentina and Chile, north of 40° S. lat., and it was also observed at the winter quarters of the "Discovery" in 1902 and 1903, at Cape Adare in 1899, at the South Orkneys during all the years of observation from 1903 to 1908, with the exception of 1906.

Mossman remarks that thus the temperature anomaly of May is a bipolar phenomenon and he adds that the curve of

\* Meteor. Zeit., xvii, 1, 1900.

†O. L. Fassig: The climate and weather of Baltimore, pl. 3, Baltimore, 1907.

‡ Loc. cit., p. 162.

§ Symon's Met. Mag., xliv, 1, 1909.

mean atmospheric pressure at the South Orkneys, for each day of the year, bears a close resemblance to that of Edinburgh.

Forcibly, therefore, we reach the conclusion that in a comparative study of the anomalies of the annual temperature variation, Teisserenc de Bort's conception of the great centers of action of atmospheric circulation will find an extensive application; because, although at present it would be premature to try to explain why it is that some changes of phase may occur simultaneously in Arctic and Antarctic regions, or in North America and Siberia, it seems impossible to conceive such correlations without supposing some relationship with the exchange of pressure between the seasonal and permanent centers of action.

New York City, November 2, 1916.

#### SCIENTIFIC INTELLIGENCE.

#### I. CHEMISTRY AND PHYSICS.

1. Attempt to Separate the Isotopic Forms of Lead by Fractional Recrystallization.—Although the complete inseparability of isotopes by chemical means has been frequently asserted, THEODORE W. RICHARDS and NORRIS F. HALL have deemed it desirable to test the possibility of such a separation still further and they have made a very elaborate attempt to do this with the radioactive lead from Australian carnotite. The low atomic weight of this sample of lead, previously determined by Richards and Wadsworth, indicated that it contained three or four parts of the isotope (usually assumed to be radium G) to one of lead, and its  $\beta$ -ray activity showed that it contained sufficient radium D to serve as a basis for testing the possible separation of this isotope from the inactive varieties. About 1 kilogram of this radioactive lead was converted into the nitrate, and this salt was subjected to systematic fractional crystallization by cooling the boiling, nearly saturated aqueous solutions, and carrying the crystals and mother liquors in opposite directions in the series. About 1000 separate crystallizations were thus made, where the end-products were combined when they became too small for convenient work, and a series of 18 members was finally obtained. Four of these members at the "more soluble" end and six at the "less soluble" end were united in each case, and these products were carefully purified, converted into chloride, and subjected to atomic weight

determination by finding the relation of the lead chloride to the silver required to combine with the chlorine, according to the highly refined methods in use in Professor Richards' laboratory. Two analyses of the chloride of ordinary lead had given 207.187 and 207.186 for the atomic weight.

The results with the end fractions of the isotopic lead were as follows:

	" More soluble "	" Less soluble "
	206.426	206.406
	206.409	206.422
	206.431	206.399
٩v.	206.422	206.409

These atomic weights agree so closely that it is obvious that no separation, or at most not more than an exceedingly small separation, of the isotopes was effected by the elaborate fractional crystallization. The end-products of the fractional crystallization, after purification, were tested as to their radioactivity in order to find if there had been any separation of "radium D" which is supposed to have an atomic weight of 210, and is supposed to be present in this lead in the proportion of about one part in ten million. The results agreed within the experimental error of 1 per cent, so that no evidence of any concentration was found.— Jour. Amer. Chem. Soc., xxxix, 531. H. L. W.

2. Manganese in Soils.-MAXWELL O. JOHNSON of the Hawaii Agricultural Experiment Station has devised a remedy for a serious local difficulty in the culture of pineapples. The chief pineapple district of the Islands lies on the island of Oahu in a region where the water supply is insufficient for the growth of sugar cane. In this district, in distinction from the usual red soils, there occur various areas of dark or black manganiferous soils where, as has been known for 10 or 12 years, pineapples make a very poor growth. The leaves of the plants gradually become yellow, and the plants often die or finally produce very small fruit of inferior quality. As these dark soils, where the yellowing of pineapples occurs, aggregate from 6,000 to 10,000 acres of the lowest lying, most accessible and most easily cultivated land of the region, the matter is of considerable economic importance. Several years ago this trouble was attributed by Kelly, of the same experiment station, to the presence of an abnormal amount of manganese in the black soils. He found that one of the black soils contained about 6 per cent of manganese oxide, while a red one contained only about 0.3 per cent of it. He analyzed also the ashes of a number of plants grown on the black soil, some of which were affected by the presence of manganese while others were not affected by it. From a study of the ash analyses Johnson came to the conclusion that the. affected plants were abnormally low in iron, and that the presence of manganese causes a suppression of the assimilation of iron

by the plants. Acting upon this suggestion, a practical method of controlling the trouble was found. Fields of yellow, unhealthy plants when sprayed with solutions of iron salts became green in a very short time. The effect on the fruit was most remarkable. The small, red, stunted pineapples, when sprayed, showed decided improvement within a week, becoming normally dark green, and commencing a vigorous growth within two or three weeks. When iron was applied to one side only of the unripe fruit, that side became green first and made such growth as to distort the shape of the fruit, but later the iron appeared to be distributed and the fruit became fairly symmetrical when ripe. Practically all the pineapple plantations have now applied spraying with ferrous sulphate solution on the manganiferous soils with apparently perfect success in profitable cultivation.—Jour. Indust. and Eng. Chem., ix, 47. H. L. W.

3. Preparation of Sulphurous Acid.—It is stated by EDWARD HART that the cheapest and most convenient method for preparing small amounts of sulphur dioxide in the laboratory consists in warming fuming sulphuric acid containing 30 per cent of SO<sub>3</sub> with sulphur in the form of lumps. The sulphur dissolves forming a blue solution from which, on warming, SO<sub>2</sub> is given off mixed with some SO<sub>3</sub>. If sulphuric acid is objectionable the resulting solution may be warmed and the gas again absorbed. The evolution of SO<sub>2</sub> ceases when the SO<sub>3</sub> has been acted upon and the sulphur melts. The sulphuric acid remaining contains only a small amount of dissolved sulphur and is fit for most uses.—Jour. Amer. Chem. Soc., xxxix, 376. H. L. W.

4. Gas Chemists' Handbook, Compiled by Technical Committee, Sub-Committee on Chemical Tests, THE AMERICAN GAS IN-STITUTE. 8vo, pp. 354. New York, 1916 (The American Gas Institute, New York City).—This compilation has been made by a committee of eleven prominent gas works chemists, of whom C. C. Tutwiler is chairman, under the editorship of A. F. Kunberger. It is a very useful book, not only for chemists connected with the gas industry for whose use it is particularly intended, but also for other analysts who may desire information in regard to the special methods used by these chemists. The book has a wider scope than would perhaps be expected, as it deals not only with the examination of the raw materials and the products of gas manufacture, but also with the tests of many miscellaneous materials, such as boiler-waters, paints, fire-clays, lubricating oils, solders, and other alloys, lime, cement, and both ordinary and special steels. The very important subject of sampling is well presented in connection with the various materials to be examined, and the book as a whole may be regarded as an excellent treatise, giving very full and clear directions of well-selected methods of examination and analysis. H. L. W.

5. Union of Glass in Optical Contact by Heat Treatment. – In many optical and spectroscopic investigations much annoyance and incomplete success arise from the fact that it seems to be impossible to obtain a suitable cement for fastening together the transparent parts of the various types of cells required. Cements cause trouble in, at least, three different ways. (a) They deform or strain glass which has been figured plane or spherical to the highest degree of accuracy. (b) No one cement is immune to chemical action when all kinds of liquids at various temperatures come in contact with it. (c) It is very difficult, if not practically impossible, to cement optically plane plates to a separating piece so as to obtain perfect parallelism between the surfaces. Certain experiments recently performed, in the research laboratories of Adam Hilger, by R. G. PARKER and A. J. DALLADAY give excellent promise of overcoming all of the disadvantages pertaining to the use of cements. The basic idea consists in heating the pieces of glass—while under pressure and in optical contact—until they unite and form one single object.

The necessary conditions of perfect figuring and absolute cleanliness present no insurmountable difficulties. The problem therefore resolves itself into a careful study of the proper thermal treatment. The temperature for complete union must not only be below the melting point of the particular kind of glass under investigation, but it must also be inferior to the annealing temperature, for, even at the lower temperature slight non-uniform stress will give rise to permanent deformation of the optically perfect surfaces. By keeping two pieces of the same kind of glass in optical contact, for about one hour, (under suitably applied pressure) at a temperature 60° C. or 70° C. below the annealing temperature, it was found that complete union, without deformation or appreciable strain, resulted.

This significant result was deduced from the empirical formula

established by the investigators. They found that  $S_T = S_{T_1} A^{\frac{T-T_1}{N}}$ , where  $S_T$  and  $S_{T_1}$  are the "mobilities" at the temperatures T and  $T_1$ , respectively,—measured by the rate of deformation of glass under constant stress,—and A and N are constants for the special sort of glass concerned. The authors say: "The quantity N is comparatively small, so that for quite small values of  $T - T_1$ , the index  $\frac{T - T_1}{N}$  would become equal to 1, 2, 3, ... If, for example, we take N = 8, A = 2, and compare the values of the mobility of the particular glass at temperatures of  $T = 560^{\circ}$  C. and  $T_1 = 552^{\circ}$  C., 544°, 536° successively, we find the respective values of the mobility to be

$$\frac{S_{T}}{S_{T_{1}}} = 2^{1} \text{ when } T_{1} = 552^{\circ} \text{ C.}$$
  
= 2<sup>2</sup> = 4 when  $T_{1} = 544^{\circ} \text{ C.}$   
= 2<sup>3</sup> = 8 when  $T_{1} = 536^{\circ} \text{ C.}$ 

That is, the glass becomes twice as "soft" for every rise of temperature of  $8^{\circ}$  C. Therefore, at  $60^{\circ}$  or  $70^{\circ}$  C. below the

annealing temperature a glass has become sufficiently hard to withstand very great local pressure for short periods without sensible deformation."

By taking suitable precautions in regulating the temperature of an electric furnace the experimenters have succeeded in making perfect cells of the type involved in the Rayleigh interferencerefractometer. The inner opposing walls were as plane and parallel as the outer surfaces of the cell windows. The parts of a polarimeter tube of soda-lime glass with end windows of plate glass were readily united at a temperature near  $470^{\circ}$  C. For obvious reasons, success was not attained in attempting to unify an object-glass the component parts of which were made of ordinary crown and flint glass. Although the problem of constructing ultra-violet absorption cells of fused silica has not been completely solved, the results thus far obtained give promise of ultimate success.—*Phil. Mag.*, xxxiii, p. 276, March, 1917.

6. The Flame Spectrum of Iron.—A promising method for differentiating and classifying the lines of complicated spectra has been recently developed, and applied to the case of iron, by G. A. HEMSALECH. The special features of the apparatus employed consist in the "electric sprayer" and the gas burners.

The most essential parts of the sprayer may be described as follows: An inverted bell-jar (height 10.5 in., diameter 5 in.) is closed at the lower, narrow end by a rubber stopper and at the upper, wide end by a flanged wooden disk. A stout wire, which passes up through the axis of the stopper, is rigidly attached to an iron electrode. The vertical portion of an L-shaped glass tube also passes through the stopper. The outer end of the glass tube is connected to an adjustable glass reservoir by a rubber tube. By means of a pinch-cock the liquid (perchloride of iron) is allowed to flow from the reservoir into the bell-jar until its free surface is just above the top of the lower electrode mentioned above. The upper electrode, likewise of iron, passes down axially through the wooden cover, its lower end being about 0.25 in. above the liquid. The iron wire is insulated by a glass tube throughout all of its length within the bell-jar except the lowest inch which is, of course, left bare. The inlet tube for various gases (air, oxygen, etc.) extends down through the wooden lid to within a short distance above the free-surface of the liquid in the jar. The outlet tube is flared conically at the end which projects only a short distance below the under surface of the wooden When a condensed spark (20,000-30,000 volts) passes cover. between the electrodes the material under investigation is broken up into particles of ultra-microscopic dimensions which are carried to the burner by the current of gas. Details of the refining collectors for keeping back the coarser particles, and of the method of mixing the spray-carrying gas with illuminating gas or hydrogen will be omitted.

Hemsalech states that the burners form the most important item in the instrumental equipment. Their tops were prepared

H. S. U.

by drilling holes in plates of brass 3<sup>mm</sup> thick. Burner No. 1 had 160 holes of 1<sup>mm</sup> diameter, the centers being 1.5<sup>mm</sup> apart. They were arranged in 8 rows of 20 holes each, consecutive rows being displaced in such a way that the gap between two flames of one row was opposite the flame of the next row. By this scheme an even distribution of light was obtained in a horizontal direction at right angles to the rows of holes. "When a low-pressure gas mixture is employed the cones obtained with this burner form an almost flat and continuous surface with only slight elevations over each hole. Seen end on, the cone region presents the appear-ance of a bright thin line. This burner is therefore particularly suited to studying the spectrum of the explosion region." Burner No. 2 had 12 holes of 2<sup>mm</sup> diameter, arranged in two rows of 6 each, the distances between the axes of the holes being 3<sup>mm</sup>. The direction of observation was such as to have five flames behind the first one. The gases in the air-coal gas mixture were so proportioned as to produce blue-colored cones the heights of which varied from 3 to 8<sup>mm</sup> according to the velocity of the gas. The burners for oxy-coal gas, oxy-hydrogen, and oxy-acetylene flames do not merit attention in this place.

The prism spectrograph was placed in a vertical position in order to have the slit horizontal. By using a good Zeiss objective (25<sup>cm</sup> focal length) with the non-astigmatic spectrograph the spectral details of the explosion region of burner No. 1 or of the alternating cones and flame of burner No. 2 were clearly differentiated on the spectrograms.

The following provisional classification of the iron lines has been adopted by Hemsalech as a consequence of his investigations. " Class I. Lines which are emitted by the mantle of the air-coal gas flame, and gain in intensity on passing to the hightemperature flames. They are specially sensitive to thermal actions, and may be regarded as true temperature lines. Class II. Lines which are particularly sensitive to the special chemical actions of which the explosion region of the air-coal gas flame is They are also, though feebly, emitted by the outer the seat. mantle. In the flames of higher temperatures their intensities increase, showing that they likewise respond to thermal changes, but to a lesser degree than Class I. lines. Class III. This class contains the bulk of the cone lines which form what M. de Watteville and myself had called the > supplementary spectrum." For details concerning the structure of the iron spectrum reference must be made to the original article.—Phil. Mag., xxxiii, p. 1, January, 1917. H. S. U.

7. The Nature of Matter and Electricity; by DANIEL F. COMSTOCK and LEONARD T. TROLAND. Pp. xxii, 203, with 11 plates. New York, 1917 (D. Van Nostrand Co.).—"This book attempts to give in broad, schematic form the conception of the structure of the material universe which has developed in the minds of modern students of physical science." The text is divided into two parts, the first of which is based on a series of articles contributed in 1911 by Comstock to "Science Conspectus." The material of Part I, which is presented in an extremely elementary manner, has been amplified and brought up to date by the original author Part II, from the pen of Troland, is virtually an appendix and it consists of fifty-six sections relating to specific problems and details appropriately omitted in the rapid survey of the entire field made in Part I. This field covers the following subjects: the properties and behavior of atoms and molecules; the nature of heat, Brownian movement, absolute zero, etc.; the electron and its behavior; electrons, chemical action, and light; electrons and magnetism; radio-activity; the structure of the atom; atomic numbers, the quantum hypothesis, radiation, and X-rays; atoms and life.

The material of Part I is presented in such a pleasing style that the writer of this notice was constrained to read every sentence in it. Frequent reference to Part II showed that it has also been written with care and that it constitutes an almost indispensable supplement to the earlier pages, in the sense that it contains just the right things to help satisfy the desire for more information so skilfully excited in Part I. The full-page plates are unusually good and no pains seem to have been spared by both authors and publishers to make the volume as attractive as possible. H. S. U.

8. Electric and Magnetic Measurements; by CHARLES MAR-QUIS SMITH. Pp. xii, 373, with 171 figures. New York, 1917 (The Macmillan Co.).-The degree of advancement of this text may be inferred from the facts that the equivalent of one year of general physics and some knowledge of the calculus are presupposed. Although the ground covered by the fifty-six laboratory exercises does not seem to afford anything especially novel, nevertheless the book possesses several valuable features. For illustration, much space is devoted to the general theory upon which the experiments are based, special attention being paid to definitions and to the precision of measurements. In other words, the text has been evolved from a course of lectures as well as from laboratory notes. Another salient feature is that most of the experiments are described in such a way as not to require particular types of apparatus. The exceptional cases involve apparatus which is well known and generally available. A few theoretical problems, for solution by the student, are given at the ends of the earlier chapters. The index is preceded by an appendix which contains an outline of the absolute measurement of current and of resistance, a table of constants, and a list of standard reference books. Because of the clearness and generality of the explanations the volume merits the serious attention of all who are engaged in conducting laboratory courses in pure as well as in applied physics. H. S. U.

9. Recreations in Mathematics; by H. E. LICKS. Pp. v, 155. New York, 1917 (D. Van Nostrand Co.).—" The object of this book is to afford recreation for an idle hour and to excite the interest of young students in further mathematical inquiries." The material selected is of such a heterogeneous character as to be susceptible only of the following very broad classification: arithmetic, algebra, geometry, trigonometry, analytic geometry, calculus, astronomy and the calendar, mechanics, and physics. The number of "recreations" is 180. These include puzzles, paradoxes, fallacies, historical memoranda, and serious remarks introductory to the study of the more advanced subjects.

Taken as a whole the book should be found both interesting and instructive by those to whom it is addressed. In two articles, however, the author makes statements which are either open to very serious objection or are altogether incorrect. In section 137 he concludes that mechanics ought to be omitted from courses in physics because the teacher of pure science makes use of dynes and poundals and since "... no apparatus for measuring forces in such units has ever been made or used." Article 138 contains several statements which are unqualifiedly wrong. For example, the unit of acceleration is given as "one unit of length per second." With regard to the dimensional equation  $[F] = [M L^{-1}]^{-2}$ he writes : "The student tries hard to comprehend this, but finds it impossible, for he knows that force is not  $M.L./T^2$  and he knows that there is no way to measure a force except by the number of units of force which it contains. The truth of the matter is that the equation F = m f is not true." H. S. U.

#### II. GEOLOGY AND MINERALOGY.

1. The Andes of Southern Peru; by ISAIAH BOWMAN, Director of the American Geographical Society. Pp. xi, 336, with 204 figures and 7 topographic sheets. New York, 1916 (Henry Holt and Company).-The attractively printed and beautifully illustrated "Andes of Southern Peru" is essentially the record of a reconnaissance along the seventy-third meridian, between parallels of latitude 12° and 16° 37' south. The book consists of two parts. In Part I, Dr. Bowman gives a well-composed picture of the life of the people, in which the factor of environment is emphasized. After reading the chapters on The Canyons of the Urubamba, The Rubber Forests, The Forest Indians, The Country of the Shepherds, and The Border Valleys of the Eastern Andes, one feels that he knows both the Indians and the Spanish planters. Two chapters on climate record and discuss the significance of observations made by the Yale Peruvian Expeditions, the Harvard Observatory, the Peruvian Government, and the Geographical Society of Lima.

The Physiography of the Peruvian Andes is treated under the headings: The Peruvian Landscape, The Western Andes, The Eastern Andes, The Coastal Terraces, Physiographic and Geologic Development, and Glacial Features. The most significant

topographic elements of southern Peru are: 1. A system of high level slopes of gentle gradient and great areal extent developed on rocks of various types and attitudes, deeply covered by soil and standing at an elevation 4,000 to 5,000 feet above the level at which they were formed; 2. deep, steep-walled, narrow-floored canyons sunk below the plateau surface; 3. lofty, residual, highly sculptured mountains; 4. volcanic cones and lava plateaus of the western Cordilleras; 5. glacial features at valley heads; 6. deep alluvial fill in valley bottoms, now in process of dissection. The system of high level slopes is substantially the surface of denudation elsewhere called the Inca peneplain (Gregory, H. E., A geologic reconnaissance of the Cuzco Valley, Peru: this Journal, vol. xli, pp. 1 to 100). Dr. Bowman finds that along the seventythird meridian a stage of maturity or post-maturity, but not peneplanation, has been reached and considers the well-marked peneplaned areas in the Cuzco region and in Bolivia as remnants of an older land surface. It appears that the extent of the Inca peneplain and its relation to other features must await further The canyons sunk below the level of the Peruvian field work. plateau are represented by the Urubamba (pp. 8 to 21) and the mountains rising above that surface by the Cordillera Vilcapampa (pp. 202 to 224). A separate chapter is devoted to glacial features.

The strictly geologic results of this geographic reconnaissance are appropriately meager. Geologic maps and measured sections are lacking, and conclusions drawn regarding geologic history necessarily rest on scant field evidence and are subject to radical The oldest sediments recognized along the seventyrevision. third meridian are unfossiliferous slates and shales, provisionally assigned to the Silurian, and underlain by early Paleozoic (?) schists. The Upper Pennsylvanian is widely represented and fossils were obtained at Huascatay, Pampaconas and Pongo de Mainique. Fossils from 2,000 feet of limestone at Cotahuasi were determined by Professor Schuchert as Lower Cretaceous. The physical history of the Tertiary of the Coastal region is presented in a new form. The lacustrine deposits of the Cuzco and other intermontane basins, also considered Tertiary, are probably late Pliocene or Pleistocene (Eaton, G. F., Vertebrate fossils from Ayusbamba, Peru: this Journal, vol. xxxvii, 1914, pp. 141 to 154, and papers by the present writer: this Journal, vol. xxxvii, 1914, pp. 125 to 140, and vol. xli, 1916, pp. 78 to 85).

When one realizes the advancement of geographic knowledge of the Andes represented by this book and notes that it has upwards of 40 smaller companions resulting from the devotion of Professor Hiram Bingham to pioneer scientific work, he can but regret that the work of the Yale Peruvian Expeditions has been suspended. The topographic maps of Kai Hendriksen and A. H. Bumstead alone justify the expenditure of time and money.

H. E. G.

2. Mount Rainier, A Record of Exploration; edited by Edmond S. MEANY. Pp. xi, 325, 17 pls. New York, 1916 (The

Macmillan Company).-Professor Meany's book on Mount Rainier bears the evidence of accuracy of statement and judicious selection of material. The discovery of the mountain by Captain Vancouver in 1792, its first approach by Doctor Tolmie in 1833, the first recorded trip through Naches Pass by Lieutenant Johnson in 1841, the attempted ascent of the mountain by Lieutenant Kautz in 1857, the successful ascent by General Stevens and by S. F. Emmons in 1870 are recorded in the explorers' own words. Professor Russell's account of explorations of the glaciers of Mount Rainier in 1896 is reproduced from the Annual Report of the United States Geological Survey. Chapters on Glaciers of Mount Rainier, by F. E. Matthes; on The Rocks of Mount Rainier, by George Otis Smith ; and on The Flora of Mount Rainier, by Professor Piper, are authoritative scientific descriptions. Accounts of Indian legends and an annoted list of place names are interesting and useful features. H. E. G.

3. Publications of the United States Geological Survey, GEORGE OTIS SMITH, Director.—Publications of the U.S. Geological Survey recently received are given in the following list (continued from vol. xlii, pp. 440, 441):

TOPOGRAPHIC ATLAS.—Seventy-two sheets.

FOLIOS.—NO. 200. Galena-Elizabeth Folio, Illinois-Iowa; by E. W. SHAW and A. C. TROWBRIDGE. Surveyed in coöperation with the Geological Survey of Illinois. Pp. 13; with 2 pls. topography, 2 colored pls. areal geology, 1 pl. of 13 half-tone illustrations.

No. 203. Colorado Springs Folio, Colorado; by GEORGE I. FINLAY. Pp. 15; 3 pp. sections, 2 pls. topography, 2 pls. areal geology, 2 pls. half-tone illustrations.

PROFESSIONAL PAPERS.—Shorter Contributions to General Geology. Chapter L, The Pliocene Citronelle Formation of the Gulf Coastal Plain and its Flora. Papers by GEORGE C. MATSON and EDWARD W. BERRY. Pp. iv, 167–204; pls. XXXII–XLVII, 3 figs. O. Relations of the Embar and Chugwater Formations in Central Wyoming; by D. DALE CONDIT. Pp. ii, 263–270; 3 pls., 2 figs. P. 1. Stratigraphy of a part of the Chaco River Valley, New Mexico; by CLYDE M. BAUER. Pp. ii, 271–278; pls. LXIV–LXXI, 1 fig.

BULLETINS.--No. 631. The Yukon-Koyukuk Region, Alaska; by HENRY M. EAKIN. Pp. 88; 10 pls, 2 figs.

No. 640, 641. Contributions to Economic Geology, 1919. 640, Part I. F-I. 641, Part II, G, H.

No. 642. Mineral Resources of Alaska—Report on progress of investigations in 1915; by ALFRED H. BROOKS and others. Pp. 279, x; 11 pls., 14 figs.

No. 648 Notes on some Mining Districts in Eastern Nevada; by JAMES M. HILL. Pp. 213; 6 pls., 18 figs.

Nos. 637, 639, 643, 646. Spirit Leveling, R. B. MARSHALL, Chief Geographer. No. 637. Texas, 1896-1915. Pp. 254; 1 pl. No. 639. Mississippi, 1901–1915. Pp. 80; 1 pl. No. 643. South Dakota, 1896–1915. Pp. 100; 1 pl. No. 646. North Carolina, 1896–1914. Pp. 71; 1 pl.

WATER SUPPLY PAPERS.—Surface Water Supply of the United States, 1914. N. C. GROVER, Chief Hydraulic Engineer. No. 381. Part I. North Atlantic Slope Drainage Basin. Pp. 195; xxxvii; 2 pls. No. 382. Part II. South Atlantic and Eastern Gulf of Mexico Basins. Pp. 66, xxx; 2 pls. No. 393. Part XII. North Pacific Drainage Basins, B. Snake River Basin. Pp. 248; 2 pls.

No. 400. Contributions to the Hydrology of the United States, 1916. Chapters B, C, D.

The Thirty-seventh Annual Report of the Director for the Year ending June 30, 1916, is announced as having been published under date of January 1, 1917; it has not as yet been received at this office.

4. West Virginia Geological Survey, I. C. WHITE, State Geologist. Jefferson, Berkeley, and Morgan Counties; by G. P. GRIMSLEY, Assistant Geologist. Pp. xxvi, 644; 3 maps in Atlas (under separate cover), 37 pls., 20 figs.—The area, covered by this detailed report, is especially noteworthy because it contains vast deposits of the purest limestones in the country; also immense deposits of pure dolomites and vast quantities of glasssands; also many other valuable and interesting mineral deposits, including clays, road materials, iron ores, etc. The price of the volume, including case of maps (delivery charges paid), is \$2.50; extra copies of geologic map, \$1.00 each, and of the topographic map, 50 cents each.

5. The Inorganic Constituents of Marine Invertebrates; by FRANK W. CLARKE and WALTER C. WHEELER. Prof. Paper 102, U. S. Geol. Survey, 1917, 56 pp.—This memoir, interesting alike to zoologists, paleontologists, and geologists, presents and discusses 250 new analyses, along with many old ones, of calcarcous algae and all of the chief shell-bearing marine invertebrates. It is shown that the foraminifers, alcyonarians, echinoderms, bryozoans, and crustaceans use in their skeletal structures from 5 to 25 per cent of magnesium carbonate, and that the quantity varies with the temperature of the water. The greatest amount is found in the warm waters and in association with calcite, whereas the aragonitic structures are essentially non-magnesian. c. s.

6. A Synopsis of American Early Tertiary Cheilostome Bryozoa; by FERDINAND CANU and RAY S. BASSLER. Bull. 96, U. S. National Museum, 1917, 87 pp., 6 pls.—In this very important synopsis relating to the classification of American Cenozoic Cheilostomata are also described 50 new genera and 42 new species. For four years the authors have been developing these bryozoans, which now number nearly 500 species from the Eocene and Oligocene. Eventually all will be described in an extensive monograph now in preparation. O. S. 7. Note on Goyazite; by OLIVER C. FARRINGTON (communicated).—The writer desires to express his thanks to Dr. W. T. Schaller for his kindness in pointing out an error in the writer's quotation of the percentage of  $P_2O_5$  in hamlinite.\* It is worth noting, however, that the corrected figure makes the difference in the percentage of  $P_2O_5$  in goyazite and hamlinite much greater than the value which the writer used. Corrected, the relation between goyazite and hamlinite is :

	Goyazite	Hamlinite .
Percent P <sub>a</sub> O <sub>5</sub>	14.87	28.92

This discrepancy seems too great to allow the two to be considered the same mineral, especially as no inaccuracy in Damour's determination has been proved. Moreover the statement of Damour in regard to goyazite that "it fuses with difficulty on the edges of the smallest fragments" does not describe a fusibility of 4. Again, Hussak† does not assert from his examination of Damour's goyazite that there was no calcium present, but simply that it possessed a "very strong" strontium content in comparison to that of calcium, ("einen im Vergleich zum Kalkgehalt sehr starken Strontiumgehalt besitzt"). The entire absence of calcium is especially noted by Penfield‡ as a feature of hamlinite, and Bowman found no calcium in the hamlinite which he analyzed.§ In view of these differences the identity of goyazite and hamlinite cannot be said to be yet proved.

8. Elements of Mineralogy, Crystallography and Blowpipe Analysis; by A. J. Moses and C. L. PARSONS. 5th edition. Pp. 631, 575 figs. New York, 1916 (Van Nostrand Co.) .- This is a new edition of a well known text-book. The changes in this edition, which have involved the addition of almost two hundred pages, have been chiefly as follows: The description of new species and economic groups, a more detailed discussion of the occurrence and genesis of minerals, an enlarged chapter on the optical properties of minerals and new determinative tables. An interesting addition to the latter is the inclusion of optical tests on fragments of the crushed mineral. These are given in addition to the ordinary chemical and physical tests. The book covers a very wide field and its method of treatment is necessarily very concise. At times one is inclined to wonder if this condensation, admirably as it is done, does not make some portions of the subject too difficult for the ordinary student. The book is excellently printed and illustrated. W. E. F.

9. The Optical Character of Sulphatic Cancrinite; a Correction; by E. S. LARSEN (communicated).—In the table in the middle of page 333 of volume xlii of this Journal (October, 1916), the optical characters of sulphatic cancrinite, cancrinite, and natrodavyne were inadvertently stated incorrectly but are stated correctly in the text. Sulphatic cancrinite and cancrinite are optically negative while natrodavyne is optically positive.

\* This Journal (4) xliii, p. 163, 1916. ‡ This Journal (4) iv, p. 314, 1897. † Tsch. Mitth., xxv, p. 340, 1906. § Min. Mag., xiv, p. 392, 1907.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

Morphology of Invertebrate Types; by ALEXANDER JNKEVITCH. Pp. xiii, 263, with 50 figures. New York, 1. PETRUNKEVITCH. 1916 (The Macmillan Company).-This book is essentially a laboratory guide to the dissection of the principal types of invertebrate animals. It differs in important respects from the other books in this field, particularly in insisting upon a more thorough and detailed study of invertebrate anatomy than has hitherto been possible for any except the most advanced students. To this end the book gives explicit directions for the complete dissection and study of all the organ systems of the animals included instead of a few superficial structures. Each chapter contains a brief summary of the anatomical features of the species to be This descriptive part explains the technical terms studied. employed and is accompanied by a general diagram of the animal's anatomy. It is to be read by the student before he begins the laboratory exercise. There are also brief directions for obtaining the materials required and for preparing them for study. W. R. C.

Microbiology: A. Text-book of Microorganisms General 2. and Applied; edited by CHARLES E. MARSHALL. Second edition, revised and enlarged. Pp. xxiv, 900, with 186 figures. Phila-delphia, 1917 (P. Blakiston's Son & Co.).-As in the first edition of this widely adopted text-book, the subject matter is arranged in three distinct parts: I, Morphology and Culture of Microorganisms, includes a general and systematic summary of the structure and classification of molds, yeasts, bacteria and protozoa, with a brief account of the invisible microorganisms. Part II, Physiology of Microorganisms, contains chapters on nutrition, products of metabolism, mechanism of metabolism, and the influence of moisture, temperature, light, electricity and other physical and chemical conditions on the life of the organisms. Part III, Applied Microbiology, is subdivided into chapters on the economic importance of the microorganisms of soil, water, sewage, milk and milk products, and special industries, together with the microbial diseases of plants, insects, domestic animals and man, and the methods of control of infectious diseases.

The work is in reality more than a text-book; it is a reliable and authoritative summary of the entire knowledge of the microorganisms of economic importance. It is the combined effort of many specialists, for in addition to the able work of the editor, the different features of the subject have been contributed by twenty-five of our foremost microbiologists. W. R. C.

3. Growth in Length: Embryological Essays; by RICHARD ASSHETON. Pp. xi, 104, with 42 figures. Cambridge, 1916 (University Press).—The first part of this little book contains three lectures on the formation of the embryo in the different groups of vertebrates, supporting the theory that the chordates have originated directly from a coelenterate ancestor rather than from the annelids, arthropods, or other highly specialized invertebrates. The second part consists of a reprint entitled "The Geometrical Relation of the Nuclei in an Invaginating Gastrula (e. g. Amphioxus) considered in connection with Cell Rhythm and Driesch's Conception of Entelechy." The early developmental stages may be explained by assuming the presence of a vital attractive force acting between the adjacent cells of the embryo. The book was prepared for the press by the author's widow.

W. R. C.

4. The Respiratory Exchange of Animals and Man; by AUGUST KROGH. Pp. viii, 173. London, 1916 (Longmans, Green & Co.).-This is a satisfactory attempt to "trace out a course through the ocean of literature" that has accumulated since Lavoisier's classic researches that first indicated more than a century ago something of the true nature of the respiratory exchange. The reputation of the author, reader in zoophysiology at the University of Copenhagen, as an expert in this field of science gives adequate assurance of intelligent treatment. The topics reviewed are grouped under the following headings: the physiological significance of the exchange of oxygen and carbon dioxide; methods for measuring the respiratory exchange; the exchange of nitrogen, hydrogen, methane, ammonia, and other gases of minor importance; the standard metabolism of the organism; definition and determination; the influence of internal factors upon the standard metabolism; the influence of chemical factors upon the respiratory exchange; the influence of physical factors upon the respiratory exchange; the variations in standard metabolism during the life cycle of the individual; the respiratory exchange in different animals. The volume is a fitting companion to the others in this series of monographs on biochemistry. L. B. M.

5. Memoirs of the Queensland Museum, Vol. V.; edited by the Director, R. HAMLYN-HARRIS. Pp. 234; 25 pls., 21 figs. Issued July 10, 1916. Brisbane (Anthony J. Cumming, Government Printer).—This new volume from the Queensland Museum is chiefly devoted, as were the earlier issues, to articles on natural history, especially zoology. Some fifteen of these appear, well illustrated by twenty-five plates. The opening paper by the Director, associated with Mr. Frank Smith, discusses fish poisoning and poisons employed by the aborigines of Queensland, where the practice of stupefying and killing fish by this means has been long in vogue. Queensland fishes are discussed at length by J. Douglas Ogilby and A. R. McCulloch; the two gentlemen together give an extended review of Australian therapons, while Mr. Ogilby continues his studies of the edible fish of the colony. (Parts iv-ix). Papers on Australian fish scales and on Queensland bees are contributed by Professor T. D. A. Cockerell of the University of Colorado.

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#### FOURTH SERIES

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WITH PLATE II.

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## **AMERICAN JOURNAL OF SCIENCE**

#### [FOURTH SERIES.]

ART. XXXIX.—The Geology of Pigeon Point, Minnesota; REGINALD A. DALY, Harvard University.

CONTENTS.

Introduction. Revised map. Main intrusive a sill. Tilting after injection of the sill. Stratiform structure of the sill. Segregation of red rock through gas tension. Ribbon injections. Time relations of the magmatic phases. Differentiation necessarily postulated. Nature of the magma differentiated. Evidences of assimilation. Red-rock shells surrounding xenoliths. Magmatic stoping. Capacity of the original magma for assimilation and contact fusion. Assimilation in the sill conduit. Summary on the origin of the red rock.

Introduction.—During the summer of 1916 the writer, in company with Professor Charles Palache of Harvard University, spent six days in a field examination of the intrusive body which has become celebrated through the able memoir by Bayley, entitled "The Eruptive and Sedimentary Rocks of Pigeon Point, Minnesota, and Their Contact Phenomena."\* With the kind assistance and personal guidance of Professor F. F. Grout of the University of Minnesota, the point was found to be easily accessible. Leaving the regular steamer from Duluth to Port Arthur at Grand Portage, six miles west of the point, the party there boarded the motor-boat of Mr. P. Gagnon and were soon comfortably camped in Little Portage Bay, an excellent center for the study of the whole eruptive area, especially

\* W. S. Bayley, Bulletin 109, United States Geological Survey, 1893.

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because transportation by the motor-boats of resident fishermen could be secured.

The objects of the visit were to secure personal acquaintance with the rocks so admirably described by Bayley, and to collect structural and petrographical material bearing on the origin of the local "red rock," which represents one of the main problems of Minnesota geology and, yet more significantly, falls under the general question regarding the origin of the world's granites.

The red rock has been called "quartz keratophyre" and also "soda granite." It is a highly micropegmatitic or granophyric rock, chemically very similar to many common granites, but locally it has a chemical composition much like a quartz syenite. The red rock passes gradually into "intermediate rock," that varies, chemically, from a monzonito-like type to a dioritelike type. The intermediate rock, always in small volume, in turn grades into gabbro. The latter is much the largest component of the main Pigeon Point intrusive. It has olivine-rich and olivine-free phases. Though possessing a somewhat low content of alkalies, the gabbro has nearly normal characters. For the full petrography of the eruptive and sedimentary rocks of the point, the reader is referred to Bayley's memoir.

Short as the field study was, it permitted a revision of the geological map and structure sections published in Plate XVI of Bayley's paper. A map showing necessary changes in the lines of contact is given in the accompanying fig. 1. So far as the outcrops allow a decision, the main intrusive appears to be a sill cutting the local Animikie sedimentaries, rather than a dike, as stated by Bayley. The red rock is concluded to be a gravitative differentiate from the magma which filled the sill chamber. As Bayley and others proved long ago, the origin of that magma is a question involving the possibility of the fusion of the Animikie quartzites and metargillites by primary gabbroid magma. While Bayley showed the probable reality of this melting-up, its absolute proof, here as so commonly at eruptive contacts, is obscured by the processes of differentiation.

A special novelty discovered is the existence of minute igneous bodies which are hereafter described under the name "linear or ribbon injections."

Professors Palache and Grout have greatly aided in the collection of facts and in clarifying the discussion, but neither should be held responsible for the theoretical views hereafter expressed.

*Revised Map.*—Pigeon Point is a peninsula stretching eastward from the main shore of Lake Superior, 150 statute miles (240 kilometers) northeast of Duluth. The peninsula is six

miles (10 kilometers) long; its maximum width is a little more than one mile. Its area is small; yet, on account of a dense growth of moss and trees over much of the interior, a correct delineation of all significant contacts of the rocks must take much time. The scant six days spent on the point did not suffice for a complete field review of the geology, but it was possible, with the liberal and highly expert help of Professor Palache, to trace most of the contacts in the eastern third of the peninsula, an area of about 2 square kilometers; and to run

FIG. 1.



FIG. 1. The eastern part of Pigeon Point. Animikie sediments, left blank; I, gabbro; 2, intermediate rock; 3, red rock. Diabase and gabbro dikes in solid black. Sediments and sill (1-3) dip about  $15^{\circ}$  in a direction somewhat east of south.

a few cross-sections in the broader part of the peninsula, to the westward.

In general, the maps of the western two-thirds of the peninsula, shown in Bayley's Plates XIV and XV, were found not to need any essential change. The eastern third is likewise accurately mapped by Bayley so far as the shore zones are concerned. Close study of the less well-exposed interior showed, however, the necessity of significant changes in the mapping of contacts, though no vital improvement can be offered on his remarkably thorough diagnosis of the kind of rocks occurring in the area.

The most important alterations of the geological map are noted in the isthmus at Little Portage Bay ("E" in fig. 1) and

to the eastward thereof. The red rock of the isthmus has throughout a general east-west contact with the mass of the intermediate rock and gabbro, and not a north-south contact, as indicated on Bayley's map. The patch of red rock and intermediate rock mapped by him, in a narrow band stretching south toward "D" from the little bay at "B," fig. 1, does not exist. Finally, the southern edge of the gabbro locally extends farther south, both to east and west of Little Portage Bay, than as drawn on Bayley's map. Special care was taken to be sure of these necessary changes and, in general, fig. 1 is believed to be essentially correct, in spite of the fact that the upper part of the gabbro carries some interstitial micropegmatite and is thus not always to be distinguished with ease from the intermediate rock.

It is seen that the map is distinctly simplified by these changes. The main gabbro is continuous and not cut across by any large body of red rock. The red rock is nearly continuous, lying between the main gabbro on the north and the quartzite-metargillite series of the south. The intermediate rock is nearly as continuous; it lies between the gabbro and the red rock, again with persistent trend of outcrop directed nearly east and west.

Main Intrusive a Sill.—R. D. Irving and Bayley considered the main intrusive to be a dike. In a letter N. H. Winchell has stated his belief that it is a sill.\* The decision between the two views is not obvious, on account of the few exposures of the Animikie sediments along the northern side of the eruptive mass. So far as the evidence goes, however, the sill hypothesis should be preferred. The matter is so important that some of the detailed field observations are worth stating.

Narrow dikes of red rock respectively cut the sediments, the main gabbro, the intermediate rock, and even rock phases which themselves closely approximate red rock in composition; nevertheless, every one must agree with Bayley and Winchell that the main gabbro, the intermediate rock, and the main body of red rock are transitional into one another, forming a single geological unit. The case is strikingly parallel to the associations of silicic, mediosilicic, and subsilicic rocks in the intrusive sheet at Sudbury, Ontario, in the (Moyie) sills of the Purcell mountains of British Columbia, and in several sills and laccoliths of South Africa. Since the red rock and the gabbro belong to one rock body, the contact of each with the Animikie sediments should be questioned concerning the structural relation of the intrusive.

The actual contact of the gabbro with the sediments is exposed at very few places. One of these is described by

\* See this Journal, vol. xx, page 200, 1905.

Bayley in the following words (page 23 of his paper): "On the north side of the point, at the mouth of Pigeon river, are slates and quartzites, capped by an overflow of a fine-grained variety of gabbro." Professor Palache and the writer visited that locality and found a dip-section as illustrated in fig. 2. It happens to be situated where two or more dikes of relatively fine-grained gabbro merge upward into the main gabbro mass, which itself, at least locally, has a concordant, sill contact with the quartzite-metargillite series. In the face of a steep cliff, 300 meters east of the fig. 2 locality and in the line



FIG. 2. Section of floor contact of sill, near mouth of Pigeon river. Gabbro dikes (dotted) pass upward into the sill gabbro (dotted). Q, Animikie sediments. Observed contacts shown by continuous lines; inferred contacts, by broken lines.

of Bayley's north-south section "a-b," the exact contact was again found, about 20 meters above lake-level. It could be traced for about 25 meters along the strike. Throughout this stretch the contact surface dips gently southward, rigorously parallel to bedding in the sediments except for strictly localized and quite minute transgressions, such as are common at most sill contacts.

At the only other area of sediments exposed in the peninsula, north of the main gabbro ("A" in fig. 1), the surface of contact cannot be located within a stratigraphically vertical interval of about 3 meters. On the small headland the quartzites have their regional, southward dip of 10° to 15°. They are cut by several trap dikes, one of which is composite.\* A few meters

\* The well-exposed composite dike runs north and south. The older component is a fresh diabase porphyrite, free from both olivine and quartz. Its width measures about 2 meters over all, that is, including the enclosed south of the most southerly outcrop of quartzite, the main gabbro appears in a low cliff. Here the gabbro bears feldspar phenocrysts ranging from 2 to 5 centimeters in length. These are commonly parallel, as if arranged by flow in the magma, and lie parallel to the bedding planes of the adjacent strata. The same parallelism of orientated feldspars to the regional dip-plane of the Animikie sediments was observed in the gabbro at several other localities. Such repetition in the arrangement of the gabbro phenocrysts, where that rock is distinctly porphyritic, is inexplicable on the dike hypothesis. As Bayley hints (page 23), the phenomenon rather suggests that the gabbro was injected after the manner of a typical sill.

#### FIG. 3.



FIG. 3. Section of roof contact of sill, made east of "C," fig. 1, and similar to other roof sections to the west. Q, contact-metamorphosed Animikie quartzite with metargillitic interbeds; 2, intermediate rock; 3, red rock. Blocky character of upper contact illustrated diagrammatically.

Again, the gabbro, especially near its northern contact, has a principal system of joints or rift, dipping 5° to 20° southward, the other joint systems being roughly perpendicular to that rift. These structural details are also consonant with the sill hypothesis.

The contact of the red rock with the sedimentary rocks is much better exposed. With a few short interruptions, quartzites and interbedded metargillites extend all along the southern

The geological relation of this good example of composite dikes to the sill, only a few meters distant, could not be determined.

younger component. After the consolidation of the porphyrite, this older dike was split, on a nearly-central plane, and a red granite dike was injected along that plane. The granite dike is a little over one meter in width; so that the whole composite, as far as visible, is composed of porphyrite and granite in nearly equal proportions. The porphyrite shows chilled edges. The granite does not, but is coarse-grained throughout and locally even pegmatitic. The granite, almost wholly made up of quartz and alkaline feldspar, has been much kaolinized and otherwise altered, as if hydrothermally. Its original structure was the hypidiomorphic-granular; no granophyric intergrowth is found in the thin section.
shore of the peninsula. At many places their contact with the red rock, for distances of from one to ten or more meters, measured down the dip, is seen to be clearly accordant (fig. 3). In general, the surface of contact dips southward, under the quartzites, at angles of from  $5^{\circ}$  to  $20^{\circ}$ , averaging about  $15^{\circ}$ . Parallel to that general direction is an unusually well developed system of rift joints in the red rock (see fig. 8 in Bayley's memoir). These are also parallel to a distinct, though less conspicuous, rift system in the adjacent intermediate rock; and roughly parallel to the main rift system in the gabbro, as already implied. Assuming that these rifts are parallel to the



FIG. 4. Dip-section of the Pigeon Point sill through "A," fig. 1, where the sill is relatively thin. Q, Animikie quartzite with metargillitic interbeds; D, diabase and gabbro dikes; 1, gabbro; 2, intermediate rock; 3, red rock.

original cooling surface of the complex intrusive—a probable interpretation—the conclusion that the intrusive is a sill is again indicated.\*

Nevertheless, the upper contact of the intrusive is by no means always concordant with the bedding of the roof quartzites. In the low cliffs of the south shore the red rock may be seen at some points to cross-cut the sedimentaries at high angles. There the red rock fills blocky re-entrants in the roof. The maximum observed degree of cross-cutting is a couple of meters, measured at right angles to the bedding of the sediments, but it may be locally several times that amount. Thus, in spite of the fact that bedding of the roof rock and the contact surface are on the whole roughly parallel, the roof exhibits re-entrants which seem to be small-scale analogues of those depicted in Barrell's study of the intrusive stock at Marysville, Montana.<sup>+</sup> As at Marysville such sharp-angled embayments

\*The wonderfully perfect rift in the red rock is clearly a primary structure and in no way related to relief of load by erosion or to the present topography. This Pigeon Point case strongly suggests that the rift in batholithic granite is similarly related, in a genetic way, to the forms of the corresponding batholithic roofs. For these larger granitic bodies also the explanation of the nearly flat rifting through cooling contraction still seems to be the best.

<sup>†</sup>J. Barrell, Professional Paper 57, U. S. Geol. Survey, 1907, page 72 and plate II.

in the country rock are best explained as due to its dislocation along fractures, accompanied by downstoping of the blocks immersed in the magma. At other points along the contact, much more intense shattering of the sedimentary rocks is in evidence, and swarms of quartzitic xenoliths show that magmatic stoping has, once again, been "caught in the act."

In summary, the field facts seem to show that the Pigeon Point body is a sill (fig. 4), modified, as to the detailed form of its roof, by heat shattering and moderate overhead stoping. So far as could be observed, the lower contact is more perfectly concordant with the Animikie beds, the cross-cutting there proved being restricted to rare local offsets of a few centimeters.\*

Tilting after Injection of the Sill.—Almost all of the many diabase and gabbro dikes cutting the sediments follow master joints, developed at right angles to bedding. The east-west dikes therefore now dip about 75° northward (see fig. 4), since the quartzites dip about 15° in a southerly direction. It is simplest to assume that the joints were formed when the strata lay flat; and that the dikes, some of which merge into the gabbro at its lower contact and thus seem to represent feeders for the sill, were injected before the Animikie beds were tilted. If so, the great sill was injected before being turned up into its present position. Yet absolute proof of this hypothesis has not been found. (See page 446.)

During or after the tilting the sill and sedimentaries have been affected by a few dip-faults of small displacement. One fault has offset a trap dike cutting the main gabbro at the extreme end of the point. Some of the irregularities in the ground-plan of the complex eruptive may, perhaps, be explained by similar faults.

Stratiform Structure of the Sill.—Bayley's view that the principal intrusive of Pigeon Point is a practically vertical dike, does not agree well with his explanation of the red rock as the product of the contact fusion of the sediments by the primary gabbro. Except for a few dikelets, the red rock is restricted to the southern side of the main gabbro. If the gabbro were injected as a dike, there is no apparent reason why the sediments along the northern contact should not be fused in the same way.

\* The time spent in the field did not permit of full study of the relations between the small patches of gabbro mapped by Bayley on Plate XV, to the southward of the red rock. The patch on Fisherman's Point is clearly a thick dike with normal chilled contacts. The other three patches may represent one or more other dikes older than the sill, or they may be residual chill phases of the sill magma, analogous to those observed locally at the roof of the Duluth laccolith. A dip fault may explain the offset of the red-rock band in the area mapped on Plate XIV of Bayley's memoir. These uncertainties do not seriously affect the conclusion that the main eruptive is a sill. On the other hand, the asymmetry of the complex presents no mystery if the whole igneous mass is, in essence, a sill dipping gently southward. (See figs. 1 and 4.) Many direct field observations, as well as numerous homologies among the sills of British Columbia, Ontario, South Africa, etc., indicate that the gabbro of the Pigeon Point body forms a thick layer at the sill floor; and that this is, in succession, overlain by much thinner layers of intermediate rock and red rock. The principle of gravitative differentiation is obviously suggested.

Segregation of Red Rock through Gas Tension.— Gravity has not been the sole control in the separation of the red rock magma. Narrow, short dikes of red rock cut the intermediate rock, the gabbro, and the quartzites underlying the sill gabbro. The dikes seen in those quartzites appeared in all cases to peter out within a distance of about 10 meters below the lower contact of the sill, and to be, in a sense, apophyses from the sill. The existence and location of these dikes imply that the red rock differentiate was fluid longer than the gabbroid differentiate; and that the red rock magma was injected into the sill floor, into the roof, or into the already solidified gabbroid phase, by virtue of strong gaseous tension in the red-rock magma.

That this magma was charged with gas in large amount is shown by the great development of miaroles or drusy cavities in the red rock of sill and dike. Similar miaroles were observed in the intermediate rock, but never in the gabbro. The unusual driving force which must have been resident in the red-rock magma is suggested also by the lengths of numerous, exceedingly thin veins of red rock in the sediments of the roof.

"Ribbon Injections."—A very striking proof of enormous tension in the red-rock magma was found in other minute, though locally numerous bodies, which may be called "linear injections" or, perhaps better, "ribbon injections." On the south shore, immediately west of the little bay marked "C" in fig. 1, the roof of the sill consists of micaceous and feldspathic quartzites enclosing thin, originally argillaceous beds. Into two different layers of the argillite, separated by about 12 decimeters of quartzite, the red rock has been injected in the form of nearly straight, flattened needles, or thin, narrow ribbons of relatively great lengths. The exposures in three dimensions here happen to be almost perfect, so that one can make out the form and relations characterizing this novel kind of intrusive body.

The smaller ribbons are one millimeter or less in thickness, 5 to 10 millimeters in width, and of various exposed lengths of 10 centimeters to one meter. The largest ribbon seen is one to two centimeters in thickness, 4 to 8 centimeters wide, and 2.5 meters in ascertained, minimum length. These lathlike bodies all lie in the bedding planes of the argillite. The low side walls of each ribbon are usually sharp and are perpendicular to the bedding. None of the smaller ribbons appears to have uparched the overlying sedimentary rock, or to



FIG. 5. Cross-sections (a, b, c) and partial ground-plan (d, e) of ribbon injections of red rock (dotted), cutting thin metargillitic layers (2), between beds of micaceous quartzite (1). Figs. d and e represent the two extremities of an observed ribbon seen in plan. With other ribbons the kind of termination shown in d is the more common. All drawings are to natural scale. Diagram c refers to the largest observed ribbon.

have caused the slightest depression in the rock underlying the ribbon. The cross-section is here conspicuously rectangular (fig. 5, a and b). On the other hand the largest ribbon has decidedly arched its roof (fig. 5, c). At their extremities the ribbons either thin out to sharp points (fig. 5, d) or end abruptly

at master joints in the country rock, with a square termination, like that of a commercial lath (fig. 5, e).

The injection mechanism of the largest ribbon is, in appearance, much like that of a laccolith with a lateral conduit. The thinner ribbons are not so obviously explained. They seem to follow joints in the argillite, and to have made room for themselves by crowding aside and compacting the argillaceous material on each side. No other feasible interpretation of the rectangular cross-section has yet been imagined. Where erosion has exposed the top of a ribbon as well as the argillaceous layer on each side, the ribbon looks like the filling of a sun-crack in the sediment. However, the cross-section of the same ribbon always shows normally bedded sediment immediately below the red rock; so that any genetic connection with sun-cracks is improbable. The explanation by lateral crowding presents patent difficulty. Each shale lamina concerned may have been prepared for the required sudden condensation through preliminary contact metamorphism; the main contact of the great sill is not more than about 10 meters below these gently dipping metargillites. Perhaps the heating of water, specially abundant in the shale, prepared the material for sudden condensation under great stress.

Some of the probable feeders of the ribbon injections are visible in low cliffs along the shore. The feeders are true dikes or veins, always very thin (one millimeter or less to three millimeters in maximum thickness) and often of capillary dimensions. They are interrupted and some seem to peter out, both above and below, in the cliff sections. None of these dikelets could be traced with certainty into a ribbon. The ribbons regularly cross the planes of the dikelets at high angles. In none of the observed ribbons is the immediate roof or floor diked by red rock. Hence the ribbons cannot be parts of coterminous dikelets abruptly widened at shaly horizons. Each ribbon chamber appears to have been forced open by magma which entered from one end. The forcing of a nail into wood by very strong, steady pressure is an analogy, though the injected red rock was, of course, not rigid. The viscosity of the ribbon magma must rather have been of an extremely low order.

Time Relations of the Magmatic Phases.—Because the Pigeon Point gabbro is cut by dikes of the red rock, a few observers have argued that all of the red rock here belongs to a magma distinctly younger than the gabbro magma. Accordingly, the intermediate rock has been explained as the product of the fusion of the older gabbro and its peripheral intermingling with the red-rock magma. This view has little to commend it. The irregular main layer of red rock averages

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probably less than 30 meters in thickness; it is hard to believe that its original content of heat could have sufficed to melt and impregnate the gabbro to the extent demanded by the hypoth-The contact of the two chief phases has not the charesis. acter of that between two members of the normal composite sill in other parts of the world. This hypothesis also fails to account for the practical restriction of the red rock, except for the small dikes above noted, to the upper contact of the gabbro. It fails to explain the micropegmatitic (red-rock) material often seen, under the microscope, to fill the interstices of the feldspar-pyroxene fabric in the gabbro, scores of meters stratigraphically below any level which could have been seriously affected by the hypothetical red-rock injection. Finally, this hypothesis fails to account for the local development of the intermediate rock between the main gabbro and the roof quartzites, with no red rock present in the cross-section at all; the intermediate rock, here as usual, passing gradually into the gabbro.

These objections have great cumulative weight. One is compelled to assume that at one stage much of the gabbro and much or all of the red rock were simultaneously molten; that the gabbro froze first and the red rock froze last, so as to be capable of diking both gabbro and intermediate rock.

In summary, the writer considers the main body of eruptive rock in the peninsula to be a unit, a sill which has been differentiated under gravity. The intermediate rock represents a shallow layer marking incomplete differentiation between the gabbro below and the red rock above. Because of special concentration of gas in the red rock, its temperature of consolidation was relatively low, and small tongues of its magma were driven down, into the gabbro, as well as upwards, into the sedimentary roof, because of the abnormally high gastension.

Differentiation necessarily Postulated.—At the close of his paper (p. 118), Bayley stated that the red rock "is only the final stage in the alteration of the slates and quartzites by the gabbro." In other words, he regards the red rock as the crystallized product of a secondary magma. Apparently he nowhere mentions the principle of differentiation in connection with the problem, but considers the red rock as sedimentaryrock material which has been fused *in situ*. Yet his average analyses of red rock and sedimentaries are systematically contrasted, as shown in the accompanying Table I, taken from p. 113 of his paper. The red rock is poorer in iron and magnesia, and, as distinctly, richer in soda and potash.

TABLE I.								
	1	2	3	4	5			
SiO,	74.00	72.42	70.31	73.64 - 74.22	59.71			
TiO	•34	•40	tr.		tr.			
Al <sub>2</sub> O <sub>3</sub>	12.04	13.04	12.81	10.61 - 11.25	18.32			
Fe <sub>2</sub> O <sub>3</sub>	•78	•68	7.26	6.24 - 7.45	8.11			
FeO	2.61	2.49	•88	•77- 1.04	·85			
MnO	.02	•09			none			
MgO	$\cdot 42$	•58	2.03	1.48 - 1.57	3.54			
CaO	•85	•66	•60	·36- ·56	1.02			
BaO	•12	•15						
SrO	tr.	tr.						
Na <sub>2</sub> O	3.47	3.44	2.19	1.67 - 3.04	1.93			
K <sub>2</sub> Õ	4.33	4.97	1.90	1.08 - 1.62	3.43			
Li <sub>2</sub> O	$\mathrm{tr.}?$	tr.						
H <sub>2</sub> O	•86	1.21	2.22		3.24			
$P_{2}O_{5}$	•06	•20						
CÍ	tr.	tr.						
	99.93	100.33	100.20		100.18			

1.—Analysis of the powder of three specimens of porphyritic red rock.

2.—Analysis of the powder of seven specimens of granular red rock. 3.—Mean of the analyses of three unaltered quartzites and one, slightly altered, metargillite.

4.—Range of oxides in three quartzites free from contact metamorphism. 5.—Analysis of one specimen of unaltered metargillite.

The present writer's field and microscopic study has led to the belief that the systematic differences are typical of red rock and sedimentary rock throughout practically the whole outcrop of the sill roof. Hence the mere fusion of the sediments by the heat of the gabbro magma probably cannot explain the red rock as now constituted. If part of the quartzite-metargillite roof has been simply fused in situ, without being dissolved in the gabbro, the red-rock magma could have originated from the fused product only if the latter had undergone some differentiation. Still more clearly, the red rock cannot be assumed to have originated from a solution of sediments in the gabbroid magma, unless the resulting hybrid magma has been differentiated. Competing with both of these hypotheses is a third : that the red rock and gabbro are the two poles of differentiation in a primary magma, which has never been affected by assimilation. In any case differentiation has to be reckoned with and it is this feature that, more than anything else, makes the genetic problem difficult.

As a preparation for further discussion it is well to note the approximate relative amounts of red rock and gabbro in the sill. Taking 15° as the average dip, the thickness of the exposed part of the sill varies from 125 meters to 200 meters or perhaps a little more, with an average of about 160 meters. Of the exposed mass, nearly one-eighth by weight is red rock; the remainder is gabbro, associated with an almost negligible proportion of intermediate rock.

Nature of the Magma Differentiated.—If the red-rock material were a differentiate of a purely primary magma, and if the actual weight ratio of red rock to gabbro is given by the surface exposure, the composition of the assumed parent solution (neglecting volatile substances which have escaped from the sill chamber) may be roughly calculated. The result is shown in Column 3 of Table II. Columns 4, 5, and 6 give respectively the average composition of diabase, gabbro, and basalt as world types.

TABLE II.

	1	2	3	4	5	6
SiO,	49.88	72.42	52.70	50.12	<b>48.24</b>	48.78
Al <sub>2</sub> Ô <sub>3</sub>	18.55	13.04	17.86	15.68	17.88	15.85
Fe <sub>2</sub> O <sub>3</sub>	2.06	•68	1.89	4.55	3.16	5.37
FeO	8.37	2.49	7.64	6.73	5.95	6.34
MgO	5.77	•58	5.12	5.85	7.51	6.03
CaO	9.72	•66	8.59	8.80	10.99	8.91
Na <sub>2</sub> O	2.59	3.44	2.70	2.95	2.55	3.18
K <sub>2</sub> Ò	•68	4.97	1.22	1.38	.89	1.63

1.-Analysis of mixed powders of five fresh specimens of Pigeon Point gabbro.

2.—Analysis of mixed powders of seven specimens of granular red rock.

3.-Calculated composition of the mean rock of the sill, giving "1" the weight of seven and "2" the weight of unity. 4.—Mean of analyses of 20 typical diabases. 5.—Mean of analyses of 41 typical gabbros.

6.—Mean of analyses of 161 typical basalts.

The calculated mean composition of the sill is seen to be not far from that of the average diabase, gabbro, or basalt of the world. The result would be little affected by considering also the volatile matter that has escaped from the chamber. Hence one must seriously entertain the hypothesis that the red rock has been differentiated from a gabbroid or diabasic magma essentially like that represented in the narrow, and therefore quickly chilled, dikes of Keweenawan age in Minnesota.

However, there are two chief objections to that view. Though red rock is similarly associated with gabbro or diabase in the Logan sills farther north, and in the gigantic Duluth laccolith to the west, many of the thick Keweenawan injections are constituted wholly of gabbro or diabase without any redrock phase. In other regions, many comparatively thick sills and dikes, of dates varying from the pre-Cambrian to the Tertiary, contain no acid differentiate which is comparable in purity and relative volume to the red rock at Pigeon Point. One or more special conditions must, therefore, be assumed in order to explain these remarkable Minnesota bodies, if due to pure differentiation. No such condition has yet been deduced from the field facts; until some are found, the pure-differentiation idea must remain in the realm of speculation.

On the other hand, specially rapid and thorough differentiation of an originally basic magma might be thought to have been induced by its absorption of much water from the walls of its conduit. The Pigeon Point magma rose through a great thickness of Animikie strata before reaching the level of the sill chamber. The sediments were then hydrous, probably more so than now. If the original gabbroid magma absorbed some water from them, the temperature of consolidation was lowered and the magmatic life thereby lengthened. Any tendency to spontaneous differentiation would become more effective merely because of the longer time available, and the resurgent water itself might be an independent cause of magmatic differentiation.

If this were true for the sill, similar differentiation might be regularly expected in the thick Keweenawan dikes cutting the upper Animikie sediments; since dikes, crossing the bedding, are favorably situated for the absorption of connate water. As far as known, the thicker Minnesota dikes show no special tendency to extreme differentiation.\*

Evidences of Assimilation.—The second objection to the pure-differentiation hypothesis is more telling. There is an unmistakable consanguinity between the red rock and the Animikie siliceous sediments, just as there is between the micropegmatitic phases of the Moyie sills of British Columbia and the quartzites invaded by them. The consanguinity is both mineralogical and chemical. In neither respect are sediment and red rock identical; yet qualitatively the two formations are closely parallel, and one cannot rest in the belief that their similarity is accidental. On the contrary, their qualitative likeness suggests that the red rock is the result of syntexis *plus* differentiation.

For a distance of from 5 to 20 meters, measured at right angles to the roof contact of the sill, the quartzites and metargillites have been strongly metamorphosed by the magma. Their maximum alteration is like that in the many xenoliths close to the shattered roof. Nearly always the contact between red rock and sedimentary rock is sharp and the bedding planes

<sup>\*</sup> Other things being equal, the volume of water absorbed by an ordinary dike would be less than that entering the magma of a conduit to a great sill, so that the postulated differentiating influence of water might be more conspicuous in the sill than in the dike; yet some effect should, by the hypothesis, be illustrated in visible thick dikes.

of the latter are usually evident. The originally gray or greenish quartzites become of a deeper and deeper red tint, according to the degree of their metamorphism. When most changed the quartzites have a color nearly identical with that of the red rock.

More locally, drusy cavities, lined with well-terminated quartz and feldspar crystals, are developed in the roof quartzites. These are of habit similar to that of the yet more abundant druses in the red rock.

Both the reddening and the formation of drusy cavities in the roof rocks might be regarded as effects of water-gas and other emanations from the red rock, in which the same features were developed because of its own content of these gases. By this hypothesis the color change is attributed to the chemical influence of the gas; the existence of the cavities, to its high tension. Thus, the two characteristics mentioned would be considered to have no significance in the problem of the red rock.

Yet some mode of origin for the emanating gas itself is demanded. A critic of the foregoing hypothesis may reply that it puts the cart before the horse, holding that the magmatic gas involved was largely water-gas derived from the sediments, as really implied in Bayley's theory of the red rock.

The consanguinity of red rock and sedimentary rock is more clearly suggested from the fact that each bears indigenous micrographic intergrowths, composed of quartz and feldspar. Some of this material has doubtless been introduced into the roof sediments, through impregnation, from the red-rock magma, but careful microscopic study shows this explanation to be unacceptable for much of the micropegmatite developed in the sediments.

The original quartzites and metargillites contain quartz, feldspar, sericite (also paragonite?), chlorite, biotite, and iron oxides. In an early stage of the contact metamorphism the quartz grains are seen to have been embayed by minute tongues of their alkaline and aluminous cement. These minute, but relatively long and narrow, tongues can only be due to mutual solution of quartz and feldspar, or quartz and general cement, aided by connate fluids. Where the mutual solution has not gone beyond the incipient stage, the product is generally obscure. In a slightly more advanced stage, most or all of the tongues in an attacked quartz grain are filled with alkaline feldspar, mixed with accessory material. The feldspathic parts of the tongues commonly extinguish simultaneously under the microscope. With further metamorphism this new feldspar is found to be intergrown micrographically with quartz, indicating a quite local, but complete, mutual solution. The micropegmatite so formed is indistinguishable from that in typical red rock, of which micropegmatite forms an essential part. The thin sections in which this series of changes can be traced show no sign of fracturing and no indication of any channel through which magmatic material has been introduced. In other words, the micropegmatite has apparently been formed of material original in the sediment, without importation.

Professor Grout, in a personal letter, has raised the question whether the intergrowths in the metamorphosed sediment have been produced through the agency of juvenile water-gas emanating from the magma. Of this there is no evidence in the thin section. On the other hand, chemical analysis of the sediments collected where they have not undergone any contact metamorphism proves that they now bear a relatively high percentage of connate water. In Keweenawan times these beds were less affected by regional (static) metamorphism and were, as above noted, probably even more hydrous. That the connate water must have acted as a solvent in the highly heated sediments is an obvious fact; to attribute the visible solution to the influence of juvenile gas is a speculative assumption, unsupported by facts won from a study of the thin sections. The matter is admittedly delicate, but the present writer prefers to dwell on the simpler inference from observed facts.

The indigenous character of the micropegmatite observed in the contact aureole is further suggested by its occurrence in the floor quartzites, next the gabbro, in which the granophyric material is almost or quite absent, and where, to judge from the actual mineralogy of the rocks, magmatic gases were never greatly concentrated.

The problem is identical with that studied in connection with the micropegmatite of the Moyie sills of British Columbia. There the roof aureoles are sometimes richly charged with typical micropegmatite, distributed through the bedded quartzites. Chemical analysis shows that little or none of this quartz-feldspar intergrowth is to be explained by emanation of feldspathic material from the magma.\* According to Professor Grout the same chemical relations hold at Pigeon Point.

While, then, feldspathization in many other contact aureoles is not to be doubted, that principle seems not to account for much of the micropegmatite in the country rocks of the Pigeon Point sill.

Nor is it likely that the close field association of micropegmatite in the red rock with micropegmatite in the metamorphosed sediments is a pure accident. The material is of a nature too specialized for that. The preferable explanation is probably to be found in the principle of "ultra-metamorphism,"

\* Cf. Memoir 38, Geological Survey of Canada, 1912, page 243.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, No. 258.—JUNE, 1917. 30 the red-rock material having been chiefly derived from dissolved quartzite aud metargillite.

Red-rock Shells Surrounding Xenoliths .- One set of field observations made by Bayley and repeated by the present writer at first sight appear to corroborate that theory most emphatically. In gabbro, in intermediate rock, and in red rock alike, are xenoliths of quartzite which are completely enclosed in shells of typical red rock. These small masses of red rock thus, in the field, look like direct contact fusions of the sediment. The shells vary from one centimeter to 50 centimeters or more in thickness. In general their contacts with the enclosed quartite and with the enclosing igneous rock are fairly sharp. The quartzite of the xenolith often shows clear bedding and always a texture different from that of the surrounding red rock, so that there is seldom much doubt as to the limiting surface of the non-magmatic material. Just east of the little bay marked "C" in fig. 1, a large group of these shelled xenoliths is exposed along the shore. In the group a series of xenoliths can be found, wherein the relative thickness (and volume) of the red-rock shell increases, the volume of the respective xenoliths decreasing, until thick shells of red rock are seen to enclose mere shreds of quartzite. Finally, at the end of the series, no quartzite is seen, the whole, roughly globular mass being composed of red rock. All of these bodies lie in a general matrix of intermediate rock. The masses of pure red rock, one or two decimeters in diameter, have the appearance of being "ghosts" of completely fused xenoliths. That explanation would seem the more probable since xenoliths of feldspathic gabbro (torn from a dike older than the sill) have no such envelopes of red rock; thus a genetic connection between sedimentary rock and red rock is the more readily credited.

Lawson found quartzite xenoliths in the diabase of the Logan sills, north of Pigeon Point, and noted the reddening of the diabase in their vicinity.\*

The importance of the red-rock shells first came to the writer's attention in the course of a personal discussion with Professor Grout. He seems to have been the first to see clearly that mere fusion of the xenoliths *in situ* is not the whole explanation of the red-rock shells. He has made a special study of the large rimmed xenolith in the intermediate rock at the locality mentioned on page 110 of Bayley's memoir. After a detailed microscopic and chemical investigation of this xenolith and its red-rock shell, Professor Grout has concluded that the shell is much richer in alkalies, especially potash, than

\* A. C. Lawson, Bulletin 8, Geological and Natural History Survey of Minnesota, 1893, page 30. the quartzite of the xenolith. The writer has confirmed his view by microscopic study of the same and of other rimmed inclusions in the intermediate rock. As shown by the thin sections, each shell contrasts with its xenolith in carrying at least twice as much potash and also more soda. Moreover, the shells examined are nearly uniform in composition and therein are equivalent to the main mass of typical red rock of the sill; while the xenoliths vary considerably in their original content of alkalies. As Professor Grout has pointed out, the differences of alkaline content between the shells and xenoliths are of the same order as those between the alkali content in the average analysis of the main red rock and the alkali content of the average Animikie sediment of the region. (See Table I.)

(1) Assuming the red-rock shell to have resulted from the fusion of the xenolith, without addition of material from the general magma, a large amount of silica, iron, and water must have been expelled from the secondary melt. It is conceivable that one or more compounds of iron and silica, aided by the water, might rapidly diffuse into the general magma, leaving behind the less volatile feldspar and some free silica. By such differential diffusion feldspar would be more concentrated in the shell than in the original quartzite. As yet no compelling evidence either for or against this hypothesis has been found ; however, one may well doubt the quantitative value of the imagined process.

(2) Is the red-rock shell rich in alkalies because these have been, as it were, sweated-out from the hot interior of the xenolith? The connate water of the inclusion must have attained high gas-tension, which might be conceived to have led to the expulsion of a water-feldspar-quartz solution, analogous to an ordinary, low-temperature pegmatitic magma. This second guess as to the cause of the concentration of feldspar in the shell at once meets the difficulty that certain shells have volumes greater than their respective enclosures.

(3) On the whole, it seems more probable that, while some fusion of each xenolith has taken place, some of the soda and potash, and perhaps alumina, concentrated in the red-rock shells have been derived from the general magma. How this was accomplished is a residual question, as yet without adequate answer. At least half of the soda and potash in the feldspar of the average shell must, apparently, have been imported, the remainder being the alkalies of the xenolith fused *in situ*. If the oxides of sodium, potassium, and aluminum, in the presence of water, were highly diffusible in the roof phase of the general magma, those oxides might conceivably have been fixed, both in chemical combination and in position, by the free silica of the partly melted xenolith. The mystery as to the phases actually present in a natural magma and as to their capacity for diffusion is so profound that this third speculation cannot be profitably discussed.

Difficulty of explanation cannot alter the fact that the redrock shells appear to be due in part to separation of material from the general magma. These envelopes are, therefore, not direct proofs of an origin of the main red-rock mass in mere contact fusion of the Animikie sediments. Nevertheless, the discovery of indigenous micropegmatite in the contactmetamorphosed sediments shows that *some* red-rock material has been generated by contact fusion.

Magmatic Stoping.-As Bayley noted, the roof rock of the sill is locally much shattered. Besides the isolated xenoliths, evidence of the disruptive action is given in comparatively thick breccias of roof quartzite, now cemented by subordinate amounts of red rock. Xenolith and breccia block still remain near or at the roof, evidently because the magma was nearly frozen when the enclosure of roof fragments took place. During the long preceding magmatic period, other shattering must have occurred, and, because of the smaller magmatic viscosity then ruling, the roof blocks sank into the heart of the sill.\* As in the case of the normal batholith, the efficiency of fusion and syntexis can here be estimated only after the fate of the sunken blocks is considered. In all batholiths the deeper levels are never exposed, so that the subsequent history of downstoped blocks can only be inferred. The outcrops of the Pigeon Point intrusive are sufficiently continuous to warrant the statement that xenoliths are very rare at depths greater than 20 meters below the roof. If the initial, hot magina did actually shatter and stope more effectively than the nearly frozen magma, one is compelled to believe the older xenoliths to have been melted and more or less completely dissolved in the primary gabbro magma. If this "abyssal" assimilation strongly supplemented any assimilation at the roof, some differentiation must be postulated, for the gabbro has been cleansed from nearly all the material which is not present in normal gabbro. The actual stratiform structure of the sill implies, as already noted, gravitative control in the separation, which would presumably progress simultaneously with the stoping and internal solution of blocks.

\*The lighter shales would float in the initial gabbro. Practically all xenoliths would sink in the acidified magma. Blocks of the dominant quartiztes would probably not sink all the way to the sill floor, but would come to rest at intermediate levels. There high temperature was long maintained, with the result that the blocks would tend to be completely dissolved or fused.

 $\dagger$  On the shore, east of the bay marked at "C" in fig. 1, the red rock cuts an older, nearly vertical dike of coarse anorthositic gabbro. For a distance of about 30 centimeters from their contact, the red rock is charged with The probable importance of stoping is indicated by the pronounced irregularity of the sill roof. The reader will recall that, at many places, the red rock sharply cross-cuts the roof strata for several meters, the eruptive occupying blocky reentrants in the roof. One result is the development of local, dike-like contacts, some of which were emphasized by Bayley.\* (See fig. 3.) On the other hand, the floor contact, where seen, is that characteristic of a typical sill, with observed cross-cutting to the extent of only, at most, a few centimeters, measured at right angles to bedding. Correspondingly, the eruptive at the floor, nearly the normal gabbro in composition, has a continuous chilled contact and shows little or no evidence of having there shattered or assimilated the sedimentary rock. Since roof and floor originally matched, the roof must have been roughened by some kind of magmatic activity; that roughening is most readily ascribable to stoping.

The reason for the practical restriction of stoping to the upper contact is discussed in a following paragraph.

Capacity of the Original Magma for Assimilation and Contact Fusion.—The syntectic theory is very commonly dismissed from sympathetic consideration by those who emphasize the "enormous" amount of latent and other heat required to fuse or dissolve rock. For the present case, as for many other debated cases, the heat demanded may be regarded as "enormous" in absolute measure but as small when compared with the initial heat supply.

In the Pigeon Point area, trap dikes and sills only a few centimeters thick were observed. Such thinness, combined with great length, demonstrates some superheat in their diabasic or gabbroid magma. The main sill itself, less than 200 meters thick and probably more than 10 kilometers long, could not have been emplaced unless it were somewhat superheated. The temperature of its magma would be raised by

large plagioclase individuals which seem to have crystallized from a hybrid magma, formed by the solution of the gabbro in the invading red-rock magma. This contact phase of the red rock is specially dark in color because of the abundance of a femic mineral, now completely chloritized. Thus the red-rock magma was capable of performing some assimilation, even at a late stage in its history. If that deduction is correct, it tends to fortify the assumption that hydrous, feldspathic quartzite, related to red rock in composition could be wholly dissolved by the initial, hot, gabbroid magma.

\*The "gabbro" (really a coarse porphyrite) shown in fig. 3 of Bayley's paper belongs to a thick dike, which is certainly older than the red rock and probably older than the main gabbro. The cross-cutting quality of the red rock at this point may be explained either by stoping or by local upfaulting of the sill roof along the contact of the massive, strong dike. In any case the section does not invalidate the conclusion that the main eruptive is a sill.

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friction in the very act of injection, if that magma were initially nearly frozen and therefore highly viscous. Superheat to the extent of 100° or perhaps 200° C. can be safely assumed for the melt when the main injection took place. On any hypothesis of origins this original magma was gabbroid in composition. Its temperature at the time of emplacement was probably at 1100° C. or higher. The freezing temperature of the red rock is not known; but, on account of its richness in water, was doubtless well below 1000° C., if not as low as 800°. Taking the masses of the gabbro and red rock as seven to one, and assuming fair values for the latent and specific heats involved, one may roughly calculate the initial superheat required for the assimilation of the sediments in volume sufficient to furnish the observed amount of red rock. The result is to show that the thermal problem is not so portentous as it is thought to be, in such cases, by certain petrologists.

Assimilation in the Sill Conduit.—But there is no necessity of assuming all the solution or fusion of the Animikie sediments, corresponding to the volume of the red rock, to have taken place in the visible sill chamber itself. The Pigeon Point eruptive rose through nearly the whole thickness of the great Animikie series. Those rocks are quartities and metargillites like those exposed in the peninsula. Some solution of the sediments during the uprise of the initial, hot magma must be regarded as not impossible. The sill injection may have been a single act, the magma rising, through one or more simple dike-passages, from the earth's deep interior. Or the magma may have occupied one or more temporary sill chambers before reaching the horizon of the visible sill. The two modes of injection may be briefly described as respectively *legato* and staccato. If the injection were staccato in quality, some assimilation in the temporarily occupied chambers might have been brought about. Material then dissolved would tend to be mixed through the original gabbroid magma, because of the later movements; the final separation of the solute occurring in the chamber finally occupied.

Whether the eruption was legato or staccato, the rising gabbroid magma doubtless received an accession of water, which was thermally expelled from the Animikie sediments, then possibly wetter than now. Such resurgent water, added to that absorbed from xenoliths and main contacts in the visible sill chamber, would become concentrated at the sill roof. Through the consequent depression of its freezing temperature, the magma at the roof was not quickly chilled, as was that at the floor; but was able to continue stoping and also some marginal solution of country rock. Stoping and vertical currents incidental to differentiation must have stirred the upper layer of magma and prevented rapid chilling at the roof.

To this rather bold sketch of the probable events, objection may be urged that the magmatic gas, so clearly forming an original part of the magma of the drusy red rock, may have been purely juvenile and in no degree resurgent. Such a speculation is founded on a difficult thesis, for it denies the efficiency of gas tension to drive connate water into the initial magma from the hot walls of the conduit. Some petrologists will have it that gas can move centrifugally from an intrusive body, but never in the reverse direction, into the intrusive They think of the contact surface of the magma as a magma. one-way gate. This remarkable conception surely needs critical examination. The gas moves because of differential pressure. In contact aureoles developed in relatively impervious, hydrous sediments, the steam pressure must, in very many cases, rise enormously. If the pores of the sediments were originally full of water, such pressure might be very much greater than that of the initial magma at the level concerned. To explain dehydration in such contact aureoles, it is quite gratuitous to assume that all the water moves centrifugally. The certainty of pegmatitic emanation in the late magmatic stage proves nothing at all regarding the direction of migration for gases during the long preceding stage of higher temperatures and gas pressures. In the present case the conditions, including the existence of many horizons of impervious shales in the Animikie series, seem to imply the necessity of expulsion of much water-gas from the wall-rocks into the gabbroid magma.

Further, no good reason is in sight for crediting this particular body of magma with a much higher proportion of juvenile gas than that fairly attributable to many Keweenawan injections in Minnesota. On the other side, no one can doubt that the Animikie sediments, especially the shaly beds, were during Keweenawan time rich in water. So true is this that it would not be utterly absurd to regard the abundance of gas, probably water-gas, in the red rock as another suggestion of consanguinity between that formation and the Animikie sediments.

Again, the heat producing gas tension in the wall-rocks of the conduit, and also aiding in the preparation of the temperature suitable for solution of their solid material in the magma, was not merely magmatic heat. Before the gabbro eruption, the lower beds of the Animikie series and the unconformably underlying rocks had been heated because of their burial under the thick, upper part of the Animikie series, perhaps already covered by early-Keweenawan lava flows. General earth heat had thus begun the process of superheating the connate water, with the final development of steam pressure which tended to expel the water from the wall-rock into the conduit magma. How great this effect was cannot be estimated without a knowledge of the geothermal gradient in the Keweenawan period. That it was steeper than now is indicated by the efficiency of static metamorphism in pre-Cambrian time. Possibly the conduit walls of the Pigeon Point eruptive, where passing through the wet sediments, had a general temperature of 200° C. or higher. Experiments have shown the ample power of water, at temperatures little above 200°, to promote the solution of siliceous materials.

Herein, perhaps, is an explanation of the fact that very many of the known gabbroid sills and laccoliths bearing acid, granophyric differentiates, have pre-Ordovician, if not pre-Cambrian, dates of intrusion.\*

Before leaving this subject, one other speculative point may be noticed. The Pigeon Point eruptive is precisely *en axe* with the Duluth laccolith, which in its essential petrography, in its gravitative differentiation, and in its general structural relations is a colossal replica of the sill under discussion. The known outcrops of the two bodies are separated by little more than 30 kilometers. Is the sill an apophysis from the 200-kilometer laccolith? Was some syntexis accomplished in the vaster chamber before the offshooting sill forced a way eastward as far as Pigeon Point? In the face of this possibility, is it safe to deny the efficiency of magmatic assimilation simply because of facts observed at the visible contacts of the sill ?†

Summary on the Origin of the Red Rock.—Assimilation of the Animikie or underlying rocks had three possible loci: in the sill conduit, including one or more dikes and perhaps laccolithic or sill enlargements; at the main contacts of the visible sill chamber; and in the heart of the sill, where downstoped blocks are concerned.

Differentiation of the syntectic material had two possible loci: in the conduit, and in the visible sill chamber. The actual differentiation, implied by the existing rock types in the sill, had two phases: that controlled directly by gravity, and that controlled by gas tension.

\* Compare list in the writer's "Igneous Rocks and Their Origin," New York, 1914, pages 230 and 344 ff.

† Elsewhere (Memoir 38, Geological Survey of Canada, 1912, page 250) the writer has described a mechanism by which syntectic magma, formed in one sill chamber, may be injected into a new, higher sill or dike chamber, where differentiation unaccompanied by further assimilation of country rock is possible. The country rocks of the second chamber may be chemically little related to those of the chamber where the assimilation occurred, or to any differentiate in the second chamber. The origin of the red rock in the Duluth laccolith is not here specially considered, but the size of that body warrants a sympathetic reception for the syntectic theory when applied to its red rock. The observed characters and geological relations of the sill were established *after* both assimilation and differentiation had been completed.

In view of so many complexities, it is not astonishing that the problem of the red rock still awaits definitive solution. The solution must, of course, depend on a patient application of the principle of inference from known facts. Of these the most significant, in the writer's opinion, is the development of indigenous granophyric intergrowths of quartz and feldspar in the contact-metamorphosed sediments. The typical intergrowth has properties identical with those of the abundant micropegmatite of the red rock. That the red-rock material was derived from dissolved or fused sediments is further suggested : by the thorough reddening of the Animikie strata where strongly metamorphosed; by the discovery of isolated druses, like the druses of the red rock, in the same strata; and by the unusual abundance of gas, presumably water-gas, in the red rock. Some genetic, though not easily deduced, relation between red rock and quartzite is implied by the presence of red-rock shells around quartzite xenoliths and their absence at xenoliths of the older gabbro. Supplemented by the principle of differentiation, Bayley's idea of contact fusion seems to give one essential element in a valid explanation of the progressive, and ultimately complete, replacement of quartz xenoliths by red rock.

The principal difficulty with the assimilation fusion hypothesis is the higher alkali, especially potash, content of the red rock, as compared with the Animikie sediments already analyzed. Bayley states that individual strata carry 75 per cent of feldspar, but such beds must be rare, and it is unsafe to assume for the average sediment a percentage of alkalies as large as that characterizing the red rock. The alkalies concentrated in the red rock may, in part, have been derived from the gabbroid Combining with the silica and alumina of the Animagma. mikie shales, these juvenile alkalies may have risen to the sill roof during the general differentiation. The analyzed gabbro has, in fact, proportions of soda and potash which are abnormally low for gabbro. The same feature appears in other instances where granophyric and gabbroid rock have differentiated from each other.\*

As the proximate mode of origin for the red rock, differentiation must be assumed. Both syntexis and mere fusion *in situ*, though probably important, have been masked by differentiation. The mechanism of magmatic separation represents an unsolved problem. Specifically, future investigation may well be devoted to the question as to how the feldspar molecules

\* R. A. Daly, Igneous Rocks and Their Origin," New York, 1914, page 320.

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have been concentrated in the red-rock envelopes surrounding xenoliths and in the red-rock layer, thin or thick, between the main gabbro and the sill roof. Until that mechanism is understood, a final decision concerning the origin of the red rock must be delayed.\* Nevertheless, the facts now in hand seem to show the origin of the red rock to lie in both assimilation and differentiation, rather than in the differentiation of a wholly primary magma. In any case, be the fate of past and present speculation what it may, Pigeon Point will long engage the profound interest of petrologists, for its mysteries are the mysteries of igneous rocks in general and at but few other localities are the rocks representing the two commonest magmas the basaltic and the granitic—better or more suggestively exposed.

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\* While fully believing in fractional crystallization as a cause for the diversity of igneous rocks (see Journal of Geology, vol. xvi, 1908, pp. 401-420), the writer finds much difficulty in applying that principle as the sole explanation of the Pigeon Point differentiation. The matter is not here discussed.

## ART. XL.-On the Temperature Coefficient of a Heterogeneous Reaction; by R. G. VAN NAME.

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

In the course of a series of studies on the rates of solution of metals, the results of which have been published in four previous papers,\* the writer has found that certain of these reactions are exceptionally well adapted for accurate measurements of reaction velocity, having distinct advantages in this respect over most other types of heterogeneous reactions.

Since our knowledge of the effect of temperature on the velocity of heterogeneous reactions is rather limited, it has seemed desirable to utilize the experience gained through the work above mentioned, in the careful measurement of the temperature coefficient of the velocity of a single reaction of this type over a considerable range of temperature. For this purpose the reaction between cadmium and a water solution of iodine in potassium iodide has been selected, and the velocity determined at seven temperatures covering the range from 0° to 65°.

The choice of this reaction was due not only to the exceptional convenience and accuracy with which iodine can be titrated, but also to the fact that cadmium can easily be obtained practically free from objectionable impurities, can readily be rolled out into sheets, and when so rolled has a very finely crystalline structure, so that it dissolves in the iodine solution without any appreciable roughening of the surface, thus preserving a constant surface area.

The procedure employed did not differ in any essential respect from that described in an earlier paper, + and therefore calls for no general description. A few points, however, which are only very briefly or incompletely treated in the previous articles, will be taken up in detail here. The following data apply to all the experiments: Reaction vessel, a thin beaker 11<sup>cm</sup> in internal diameter. Diameter of cadmium disk 38.3<sup>mm</sup>, thickness 0.5mm. Composition of liquid: KI, 0.5 molar;  $H_2SO_4$ , 0.01 molar;  $I_2$  (at start) about 0.02 molar. Volume of liquid, 600 cm<sup>3</sup> at start, 20 cm<sup>3</sup> taken for each titration. Thiosulphate used in titrations, 0.02 normal. Rate of stirring 200 revolutions per minute.

Experiments were conducted at 0°, 15°, 25°, 35°, 45°, 55°, and 65°. Only at 25° was the temperature found to be prac-

\*Van Name and Edgar. this Journal (4), xxix, 237, 1910; Van Name and Bosworth, ibid. (4), xxxii, 207, 1911; Van Name and Hill, ibid. (4), xxxvi, 543, 1913, and (4), xlii, 301, 1916. †The second of the articles cited in the preceding foot-note.

tically the same in the reaction beaker as in the water of the thermostat. At 15°, and at 35° and above, the thermostat was regulated to that temperature which would give the desired temperature in the beaker. Even this was not sufficient in cases where the difference in temperature was large, since the difference was then found to increase with decrease in the surface of contact between the beaker and the reaction liquid, that is, with the depth of the liquid in the beaker, which decreased about one-fourth during the course of the experiment. In such cases the temperature of the thermostat was gradually varied as the volume of the liquid diminished. Thus, to maintain the temperature of the liquid in the beaker at 65° it was found necessary to set the thermostat to 67.7° at the start and gradually raise its temperature during the experiment to  $68.2^{\circ}$  at the end. By careful use of this expedient the temperature, even at  $65^{\circ}$ , where the error was largest, was maintained for the most part within 0.2° of the correct value, greater variations occurring but rarely, and then only for very brief periods.

For the experiments at 0° the thermostat was kept at that temperature by the frequent addition of liberal quantities of fine snow. The temperature in the beaker, directly measured, was always between one and two-tenths of a degree higher, averaging  $+ 0.15^{\circ}$ .

The rate of the reaction follows the equation

$$K = 2.3 \frac{v}{\Delta t} \log \frac{c_1}{c_2} \tag{I}$$

The reaction velocities were calculated by substituting the observed values of c in this equation,  $\Delta t$  being the duration of a single reaction period, i.e. the time interval between the removal of two consecutive samples of the solution. These intervals were generally ten minutes in length, but somewhat shorter reaction periods were employed at the highest temperatures, and longer periods at the lowest. The velocity constants so obtained were first corrected, as described below, for variations in the rate of stirring. So corrected they represented the apparent rate of the reaction, but not in general its true velocity, since in many cases a further correction was needed to compensate for the effect of evaporation from the solution.

Corrections for Variations in the Rate of Stirring.—The average rate of stirring during each reaction period was determined and a correction, based on the assumption that the reaction velocity varies as the 4/5 power of the rate of stirring,\* was afterward calculated and applied to the observed

<sup>\*</sup> An empirical relation shown in a previous paper (this Journal (4), xxix, 251, 1910) to be approximately true for an apparatus of this type and dimensions.

value of the velocity constant K. The method of determining and controlling the rate of stirring was as follows: To the axle of the stirrer was attached a mechanism which rang a bell at every 100th revolution. A stop-watch was started at the first ring of the bell after the beginning of the reaction period and was stopped at the nearest ring to the end. The elapsed time so recorded was that required for an even multiple of 100 revolutions, from which the average rate for the period and the necessary correction to K were readily calculable. Furthermore, if the rate were exactly 200 revolutions per minute the rings would evidently coincide with the passage of the second hand of the stop-watch over the even minute and half minute on the dial.\* Any variation in the speed was immediately shown by the failure of this coincidence, and was promptly corrected by adjusting a rheostat in series with the stirring motor. In this way the average rate was kept, in the great majority of cases, within 0.2 per cent of the correct value, and only in rare cases did the correction to be applied reach 0.5 per cent. In most of the experiments, therefore, the effect of these corrections, sometimes positive and sometimes negative, upon the final result (i. e. the average value of K for the whole experiment), was nearly or wholly negligible.

Corrections for Evaporation.—Except at the lower temperatures the effects of evaporation had to be taken into account, since the liquid in each experiment was stirred in an open vessel for a period varying from 40 to 90 minutes. Such evaporation may affect the apparent reaction velocity, as calculated from equation (I), in two ways: first by decreasing the volume v, and second by altering the values of the concentrasions of iodine.

The first error drops out if we use the actual value of v in calculating K, which has been done in the present work. Since the rate of evaporation is proportional to the area of the free surface of the liquid, which remains nearly constant,<sup>†</sup> the decrease in volume per minute may be regarded as constant. In the experiments of the writer this rate of evaporation was determined either by special blank experiments made under like conditions, or by determining the actual loss during the experiment itself, by carefully measuring the volume remaining at the end. Since the rate of evaporation depends somewhat on the external conditions the latter procedure is preferable, and was employed in most cases, especially when the rate of evaporation was large. The total change in volume up to the middle of each reaction period was then calculated, and the

\*Another watch was of course needed to fix the beginning and end of the reaction period.

† In reality the concavity of the surface produced by the stirring increases slightly as the volume of liquid diminishes.

value of v so found, i. e. its mean value,  $\frac{1}{2}(v_1+v_2)$ , for the given interval, was used in the calculation of K. This method was followed in all cases at 35° and higher temperatures. At 25° a simpler procedure, equivalent in effect, was employed instead. (See p. 453.) Below 25° corrections to v were found to be negligibly small and were therefore not applied.

The second error resulting from evaporation, namely, change in the iodine concentration, might conceivably be practically zero if iodine and water evaporated in nearly the same ratio as that in which they were present in the solution. Under the conditions obtaining in the present investigation, however, evaporation of iodine predominated, blank experiments without a cadmium disk giving always a positive value of the velocity constant. The problem of correcting for errors so introduced was encountered in one of the previous investigations<sup>\*</sup> and is briefly discussed in the published paper. Although the corrections needed in that work were rightly calculated and properly applied, the discussion as printed unfortunately contains a rather obvious error. The following is a corrected and more detailed statement of the case :†

Evaporation of the solute, iodine, (assuming constancy of the liquid surface) obeys the equation  $-\frac{dm}{dt} = K'c$  in which m is the mass of iodine and K' a constant. Simply transformed this becomes

$$-\frac{dc}{dt} = K'\frac{c}{v} \tag{II}$$

Evaporation of the solvent, water, follows the equation  $-\frac{dv}{dt} = K''$  which is equivalent to

$$+\frac{dc}{dt} = K'' \frac{c}{v}$$
(III)

In equation (III) v is a variable, though a constant in (II). As an approximation, however, equation (III) may safely be integrated upon the assumption that v is constant and equal to  $\frac{1}{2}(v_1-v_2)$ , the arithmetical mean of its limits, provided that these limits are close together.<sup>‡</sup> In the integrated

<sup>\*</sup> This Journal (4), xxxvi, 543, 1913.

<sup>&</sup>lt;sup>†</sup>To replace, on page 545 of the article just cited, the second paragraph and the first nine lines of the third paragraph. The error referred to occurs in the 11th line from the bottom of this page, where the word "added" should appear in place of "subtracted."

<sup>&</sup>lt;sup>‡</sup>The error introduced by this approximation when  $v_1$  and  $v_2$  differ by 2 per cent is only 0.19 per cent of the value of K", which is itself only a correction term. In the present series of experiments the effect of this error upon the final result was in all cases wholly negligible.

Integrated for constant v, equations (II) and (III) yield, respectively,  $K' = \frac{v}{\Delta t} \ln \frac{c_1}{c_2}$ , and  $-K'' = \frac{v}{\Delta t} \ln \frac{c_1}{c_2}$ , both identical in form with the velocity equation for the main reaction. Hence when the three processes, reaction of iodine with the metal, evaporation of iodine, and evaporation of water, all occur at once, the reaction velocity as calculated by equation (I) from the change in the iodine concentration, will be equal to K + K' - K''. To calculate K we have only to subtract (K' - K'') which is evidently the reaction velocity as observed in a blank experiment (without cadmium disk) under like conditions.

This was the method used here. Table I gives the values of  $-\frac{dv}{dt}$  (in cm<sup>3</sup> per minute), and of K' - K'', as actually observed and used in applying the corrections for evaporation.

	TABLE I.						
25°	35°	$45^{\circ}$	55°	65°			
$-\frac{dv}{dt} = 0.03$	0.16	0.36	0.63 to 0.66	1·14 to 1·33			
K' - K'' = 0.05	0.13	0.18	0.36	0.64			

At 0° and 15° no corrections were required. At 25° the value of  $-\frac{dv}{dt}$  was so small that the individual values of v were not corrected, but instead a correction, calculated to be equivalent in effect, was applied to the observed average value of K. This called for a decrease in K of less than two units in the second decimal place.

Results of Reaction Velocity Measurements.—Table II gives the results of the whole series of reaction velocity measurements. The numbers in the first column show the order in which the experiments were performed. Determinations were begun at 25° and then repeated from time to time, particularly after any prolonged interruption, so as to detect any accidental changes in the adjustments of the apparatus. In this way, during the course of investigation, fifteen duplicate experiments were made at 25°, of which, however, only eight—those which on consideration of the sources of error appeared to be most trustworthy—are included in the table as representative of the whole series. The mean value of K (corrected) for the eight is 7.62. For the whole fifteen it was 7.64, a compara-

			~		TABI	LE II.				
No.				Te	mpera	ature	$0.15^{\circ}$			K
									Average	corr.
19	K = K	$\frac{3.87}{2.00}$	3.75	3.75	3.75	3.86	3 3.6	7	3.78	
20	$K \equiv K =$	3.88	3.77 3.74	3.00	5.07 3.67	3.60	5 3.6 3 3.7	0 5	3.68	
~1	<u> </u>	0.00	011		0.01	0.06	G	onorolov	3.74	2.79
							u	enerar av.	0 14	$(at 0^{\circ})$
				$T\epsilon$	mper	ature	$15^{\circ}$			(
8	K =	5.98	5.94	5.99	6.02	5.93	5 5.9	1 5.91	5.96	
9	K =	5.80	5.90	5.79	5.79	5.86	3 5.6	9	5.81	
10	K =	5.93	5.79	2.80	5.73	5.84	1 5.7	4 5.86	5 85	
							G	eneral av.	5.87	5.87
				Te	mper	ature	$25^{\circ}$			
1	K =	7.77	7.66	7.58	7.67	7.66	3 7.6	1	7.66	
7	K = K	7.76	7.77	7.73	7.67	7.75	5 7.70	6	7.74	
12	K = K -	7.40	7.80	7.44	7.00	1.02	8 7.0		7.60	
17	K = K	7.59	7.75	7.69	7.66	7.67	7.5	9 7.67	7.66	
18	K =	7.73	7.73	7.79	7.76	7.60	) 7.80	0 7.77	7.74	
22	K =	7.73	7.63	7.65	7.67	7.65	5 7.6	7	7.67	
23	K =	7.63	7.82	7.73	7.63	7.75	5 7.60	3	7.70	
							G	eneral av.	7.67*	
							Corr.	for evap.	02	7.62
				Te	mpera	ature	35°			
2	K =	9.75	9.82	9.70	9.58	9.67	9.60	)	9.69	
3	K =	9.74	9.77	9.59	9.56	9.52	8 9.28	3 9.58	9.58	
4	K = 1	10.00	9.99	974	9.90	9.05	9.00 0	5 9°00	9.77	
							Corr	for evan	9.08	9.55
				Ла			450	ior ovap.	10	0.00
5 1	$\overline{V} = 1$	0.94	19.40	19.14	mpera	ature	40	10.04	10.00	
6	K = 1 K = 1	2·19	12.06	12.14	11.	20 57	$12^{\circ}24$ 11.58	$13^{\circ}24^{\circ}11^{\circ}38^{\circ}$	12.28 11.78	
13	K = 1 K = 1	2.03	12.04	12.19	12	07	11.91	11.54	11.96	
14	K = 1	1.98	11.90	11.93	11.	82	11.99	11.93	11.93	
							Ge	oneral av.	11.99	
							Corr.	for evap.	– ·18	11.81
				Te	mpera	ature	55°			
27	K = 1	4.93	14.53	14.63	14	52	14.48	14.70	14.63	
28	K = 1	4.88	15.00	14.95	14·	94	14.74	14.71	14.87+	
29	K = 1	4.61	14.48	14.50	14	22	14.30	14.12	14.37+	
							Ge	eneral av.	14.62	1100
							Corr.	for evap.	36	14.26
				Te	mpera	ture	$65^{\circ}$			
15	K = 1	7.45	17.78	17.81	17.	65	17.70	18.16	17.76	
16	K = 1	7.96	17.91	18.06	18.	12	18.11	17.97	18.02	
24	K = 1 V = 1	0.08	17.03	17.27	17.	19 68	17.30	17.11	17.44	
$\frac{26}{26}$	K = 1 K = 1	7.17	17.34	17.04	17	18	16.81	17.00	17.09	
			1.01	1.01			G	eneral av	17:57	
							Corr	for evap.	64	16.93
								1		

\* Actual average 7.687. Reduced to 7.67 by application of the correction for the effect of evaporation on the volume. † Observed values in these two experiments have been multiplied through-out by the ratio 7.62/7.23, for reasons given on p. 455.

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tively insignificant difference. At the other temperatures this procedure has not been followed, but all experiments not evidently faulty have been included in the table.

While working at 55°, the last temperature to be studied, the beaker used as reaction vessel was unfortunately broken, after only one experiment (No. 27) had been made. Although a new beaker was procured which had very nearly the same dimensions it was found by a series of careful determinations at 25° that the value of K (corrected) was 7.23 for the new beaker as compared with 7.62 for the old one. Experiments 28 and 29, at 55°, were carried out with the new beaker, and the observed velocity constants have therefore been multiplied

FIG. 1.

# 

throughout by the ratio 7.62/7.23 to make them comparable with the rest of the table.

The value of K for 0°, 3.72, was derived by a short extrapolation from the observed value for  $+0.15^{\circ}$ , (3.74).

The observed relation between reaction velocity and temperature is shown graphically in fig. 1.

Fluidity.—The above results derive much of their interest from their bearing on the diffusion theory of heterogeneous reactions, and for this reason the change in the fluidity of the solution with the temperature was also measured, on account of its possible influence on the thickness of the diffusion layer. The solution used was made up to approximate to the composition of the reaction liquid near the middle of an average experiment of Table II. It contained, per liter, 83.3 grm. KI, 2.8 grm. I<sub>2</sub>, 4 grm. CdI<sub>2</sub>, and 0.1 mol H<sub>2</sub>SO<sub>4</sub>.

Table III gives the values of the density d, the absolute viscosity  $\eta$ , and the fluidity  $\phi$ , for this solution at the different temperatures in question, together with the values of the ratio

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 $K/\phi T$ , the reaction velocity divided by the product of the fluidity and the absolute temperature. It will be observed that this ratio is very nearly constant, its maximum variation being only about three per cent. The possible significance of this fact will be considered later.

#### TABLE III.

Density, Viscosity and Fluidity.

	0°	$15^{\circ}$	$25^{\circ}$	35°	45°	$55^{\circ}$	$65^{\circ}$
d	1.0683	1.0663	1.0633	1.0594	1.0551	1.0499	1.0444
η	.01659	$\cdot 01095$	·00868	.00709	.00598	.00510	·00438
$\phi$	60.3	91.3	115.2	141.1	167.4	196.2	228.3
$\frac{K}{\phi T}.10^{\circ}$	22.6	22.3	22.2	22.0	22.2	22.2	21.9

The fluidity when plotted against the temperature gives a curve of the same general form as that for the reaction velocity (fig. 1), but its rate of increase with the temperature is relatively slower. This fact is shown in a different way in Table IV, which gives the temperature coefficients of each expressed as the ratio of increase for every 10° temperature rise. For the interval 0° to 15° the value of this coefficient was calculated for K (and similarly for  $\phi$ ) on the assumption that within this interval  $d \ln K/dT = \text{constant}$ . Integrated, this gives  $log_{10}K_2 - log_{10}K_1 = A (T_2 - T_1)$  (in which A is a constant whose value is found from the experimental data), and hence

$$\log \frac{K_{t+10^\circ}}{K_t} = 10 A.$$

#### TABLE IV.

Temperature Coefficients of Reaction Velocity and of Fluidity.

**	$0^{\circ}$ - $15^{\circ}$	$15^{\circ}$ - $25^{\circ}$	25°-35°	35°-45°	$45^{\circ}$ - $55^{\circ}$	55°-65°
$\frac{K_{t+10^{\circ}}}{K} =$	= 1.350	1.298	1.252	1.237	1.208	1.192
$\frac{\phi_{t+10^\circ}}{\phi_t} =$	= 1.319	1.261	1.225	1.186	1.172	1.163

#### DISCUSSION OF RESULTS.

The absence of any noticeable irregularity in the graph of the reaction velocity in fig. 1 is an indication of the consistency of the values of K, and their probable freedom from large errors. A similar series of measurements has been made by Meyer Wildermann<sup>\*</sup> of the rate of solution of benzoic acid in water, which was determined at five temperatures covering the range between 1.5° and 60°.

\* Zeitschr. phys. Chem. lxvi, 445, 1909.

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Wildermann's velocity constants, K, are given in Table V, together with the values of  $\frac{K_{t+10^{\circ}}}{K_t}$  as calculated for the various intervals by the method described above.

#### TABLE V.

Results of Wildermann.

		$1.5^{\circ}$	17·5°	31°	40°	$60^{\circ}$
K	=	1.587	2.851	4.524	5.756	9.946
$\frac{K_{t+10^{\circ}}}{K_{t}}$	=	1.443	1.408	1.307	1.314	ł
A	=	2920	3020	2550	2850	)

This reaction is not as well adapted for accurate measurement as the one between cadmium and dissolved iodine, and Wildermann's duplicate results show a rather poor agreement. The values of A given in the last line of the table are those

calculated from the equation  $lnK_2 - lnK_1 = A \frac{T_2 - T_1}{T_2T_1}$ , the integrated form of the van't Hoff equation,  $d \ln K/dT = A/T^2$ , for the effect of temperature on the velocity of a homogeneous reaction.

Wildermann, whose article is throughout an attack on the diffusion theory, regards the apparent constancy of A as an argument against that theory. The soundness of this argument, however, is very doubtful, since there is nothing to show that an approximate agreement with an equation of this form is in any way incompatible with the mechanism of the reaction postulated by the diffusion theory.

Upon calculating the constant A from the reaction velocities measured by the author, as given in Table II, we obtain the following values, which show a distinct progression and a total variation of over 20 per cent:

	0°–15°	15°–5°	25°-35°	$35^{\circ}-45^{\circ}$	$45^{\circ}$ – $55^{\circ}$	$55^{\circ}$ – $65^{\circ}$
$\mathbf{A} =$	2388	2239	2069	2079	1962	1902

It is evident that in this case, at least, the experimental results do not conform to the van't Hoff equation.

A question of special interest and importance from the standpoint of the diffusion theory, is the nature of the relation between the observed temperature coefficient of the reaction velocity and that of the rate of diffusion of dissolved substances. Unfortunately our knowledge of the effect of temperature on rates of diffusion is very imperfect, since but few direct meas urements have been made at temperatures above  $25^{\circ}$ . Nernst<sup>\*</sup> gives the equation  $D_t = D_o (1 + 0.026 (t - 18^{\circ}))$  as approximately expressing the experimental results in the case of salts. For acids and bases the numerical coefficient is 0.024 instead of

0.026. Calculating from this equation the value of  $\frac{D_{t+10^{\circ}}}{D_t}$  for the different intervals in the range covered by the reaction velocity measurements we obtain the following results:

 $\frac{2 \cdot 5^{\circ} - 12 \cdot 5^{\circ}}{D_{t}} \frac{15^{\circ} - 25^{\circ}}{D_{t}} \frac{25^{\circ} - 35^{\circ}}{25^{\circ} - 35^{\circ}} \frac{35^{\circ} - 45^{\circ}}{35^{\circ} - 45^{\circ}} \frac{45^{\circ} - 55^{\circ}}{55^{\circ} - 65^{\circ}} \frac{D_{t}}{1220} \frac{1100}{1180} \frac{1153}{1132}$ 

These figures can only be regarded as rough approximations, since the change in D with the temperature is not, in reality, strictly linear as the equation assumes. Moreover Öholm<sup>+</sup> has shown that the numerical coefficient is not the same for all salts, but varies between the limits 0.023 and 0.027.

On comparing these results with corresponding ratios for the reaction velocity, as given in Table IV, we see that with the exception of the lowest value the increase in the reaction velocity with the temperature is throughout slightly more rapid than that of the rate of diffusion. This appears to be at least a partial confirmation of the predictions of the diffusion theory, since the increase in the fluidity with the temperature probably causes some decrease in the thickness of the diffusion layer.<sup>‡</sup> No great significance can be ascribed to this result, however, because of the above mentioned uncertainty in the calculated values of the diffusion coefficients, and because the case of iodine diffusing in an iodide solution is not wholly analogous to that of the diffusion of a simple electrolyte. Although the iodine is largely in the form of tri-iodide ion a probability of complications is introduced by the fact that this ion is itself in dissociation equilibrium with free iodine. It has been proved, for example, that the rate of diffusion of iodine in potassium iodide solutions increases with the concentration of the salt,§ while the reverse would be expected if the case were normal.

\* Zeitschr. phys. Chem. ii, 625, 1888.

† Zeitschr. phys. Chem. 1, 309, 1905.

 $\ddagger$  That the effect would be in this direction is practically certain, but nothing definite is known about its magnitude. The results of Van Name and Hill (this Journal (4) xxxvi, 543, 1913) would seem to show, however, that the effect of viscosity changes upon the thickness of the diffusion layer is relatively small.

§ Édgar and Diggs, Jour. Amer. Chem. Soc., xxxviii, 253, 1916.

This follows from the fact that the velocity of the tri-iodide ion is considerably lower than that of the potassium ion, together with the rule (Abegg and Bose, Zeitschr. phys. Chem., xxx, 551, 1899), that the presence of an excess of a common ion tends to impart to a diffusing salt the velocity characteristic of its other ion. • In short, no adequate comparison between reaction velocities and rates of diffusion can be made in the present case without a knowledge of the value of the diffusion coefficient of iodine in 0.5-normal potassium iodide at several of the temperatures involved. The value of this coefficient at 25° has already been measured by Edgar and Diggs,\* but at other temperatures its value is unknown. The most that can be said at the present time is that the observed changes in the reaction velocity with the temperature are of very nearly the order of magnitude which would be expected from the usual value of the temperature coefficient of diffusion.

We have still to consider the significance of the observed proportionality between the reaction velocity and the product of the fluidity by the absolute temperature, which is indicated by the constancy of  $K/\phi T$ . No doubt in many cases the diffusion coefficient of a dissolved substance is proportional, over a fairly wide range of temperature, to the product  $\phi T$ . This should be at least approximately true in cases in which the diffusion formula of Einstein

$$D = \frac{RT}{N} \frac{1}{6\pi\eta P}$$

is applicable, since in this formula R and N are constants, and the value of P, the molecular radius, can generally be considered as constant for the same kind of molecule at different and not too widely separated temperatures. Hence, D must be proportional to the absolute temperature divided by the viscosity  $\eta$ , or  $D \propto \phi T$ .

The Einstein formula is strictly valid only when the molecules of the solute are not dissociated and are large compared with those of the solvent,  $\dagger$  but dissociation, if nearly complete, would not necessarily interfere with the proportionality between D and  $\phi T$ . There is, however, one limitation which may be important. P is the radius, not of the molecule of solute itself, but of the diffusing particle, which in many cases includes an attached or entrained group of molecules of the solvent. Whether P in such a case would vary with the temperature or not, would depend upon the nature of this attachment, but its variation might often be appreciable, especially over wide temperature intervals.

If we assume that the rate of diffusion of iodine, under the conditions of the experiments in Table II, is proportional to the product  $\phi T$ , it follows from the constancy of  $K/\phi T$  that the reaction velocity is closely proportional to the diffusion

\* Loc. cit.

† Einstein, Ann. der Physik (4), xix, 289, 1906.

coefficient. This, regarded from the standpoint of the diffusion theory, would mean that the change in fluidity between  $0^{\circ}$  and  $65^{\circ}$  C. (an increase in the ratio 1:4) has no appreciable effect upon the thickness of the diffusion layer.

On the other hand, it is at least equally probable that in reality D for iodine in potassium iodide solution increases somewhat slower than  $\phi T$ , for the disturbing effect of the thermal dissociation of the tri-iodide ion would act in this direction, as is evident from the fact that iodine diffuses slower in pure water than in aqueous solutions of potassium iodide. If so, the rate of diffusion must increase with the temperature somewhat more slowly than the reaction velocity, in complete agreement with the predictions of the diffusion theory.

The truth or falsity of this inference can and must be decided by direct measurement of the diffusion coefficient of iodine at the different temperatures, upon the values of which, as already stated, the settlement of the whole question turns.

#### Summary.

1. The velocity of the reaction between metallic cadmium and iodine, dissolved in a 0.5 normal solution of potassium iodide, has been measured at  $0^{\circ}$ ,  $15^{\circ}$ ,  $25^{\circ}$ , 35,  $45^{\circ}$ ,  $55^{\circ}$ , and  $65^{\circ}$ , together with the fluidity of the solution at each of these temperatures.

2. The temperature coefficient of the reaction velocity for a  $10^{\circ}$  rise varies from 1.35 for the lowest, to 1.19 for the highest temperature interval, and is therefore of about the same order of magnitude as the temperature coefficient of diffusion of a binary electrolyte.

3. The reaction velocity is proportional to the product of the fluidity of the solution by the absolute temperature.

### ART. XLI.—A Sail Fish from the Virginia Miocene; by Edward W. Berry.

THE Paleontological collections of the Johns Hopkins University contain two specimens of vertebrate fossils collected many years ago from Tar Bay in Virginia and without other record than "presented by Mr. Dew." At this locality a few feet of Eocene glauconitic marl of the Aquia formation is overlain by a considerable thickness of argillaceous beds of the lower part of the Calvert formation. The fossils represent a well-preserved tooth of *Physeter vetus* (Leidy) and a rostrum of a new species of Istiophorus. The former is a well-known Miocene type and the latter is also considered as coming from the same horizon as the tooth, although this is not conclusive.

The genus Istiophorus of Lacépède (numerous authors, as for example Smith Woodward, use Histiophorus) comprises several existing species of large, elongate, compressed, pelagic fishes of warm seas—chiefly Indo-Pacific, but also represented in the Atlantic. They are popularly known as Sail fishes because of the height of the undivided dorsal fin and have the premaxillæ vomer and ethmoid united and produced forward to form a rostrum, bony muzzle or sword, which is shorter and rounder than that of the closely related more recent and more specialized true sword fishes (Xiphias).

Istiophorus is a convenient name for the rather numerous fossil rostra of Istiophorus—or Tetrapturus-like forms, of which a number of different types have been recorded from strata ranging in age from the Éocene to the Pliocene.

The rostrum, which is more complete and better preserved than is usually the case, may be described as follows:

#### Istiophorus calvertensis, sp. nov.

Rostrum subcylindrical, tapering distad. This tapering is gradual when the rostrum is viewed from the side, and confined to the distal one-third from the dorsal or ventral aspect. Bluntly pointed, 31<sup>cm</sup> in length, in general elliptical in transverse outline. Surface of anastomosing striæ. Dorsal surface distinctly less convex than the ventral surface for its anterior twothirds. The anterior third shows scarcely any trace of the lateral dorsal furrows which about half way to the base are pronounced but not sufficiently emphasized to break the even contour of the surface. From the median region backward these furrows increase in depth and width, flanking a more arched median region, at length becoming toward the base an open lateral gutter, the inner limb of which is flattened and

#### 462Berry—A Sail Fish from the Virginia Miocene.

with an open obtuse sinus. This sinus becomes more angular as it is traced forward until at one-third of the distance forward it is acutely angular, from which point forward its sides gradually become confluent. The ventral surface is convex, showing traces of a lateral suture separating the marginal  $\frac{1}{4}$  from the median  $\frac{1}{2}$  of the lateral diameter. There is a pronounced median suture more or less distinct for the whole length of This broadens out in the proximal third of the the rostrum. rostrum to form a broad shallow palatine sinus. There are no traces of dentigerous surfaces. Each premaxillary is traversed by a nutrient canal which at the base are large and elliptical with their longer diameters oblique and forming an angle of about 40 degrees. Ventrally they approach within about 2<sup>mm</sup> of one another and their maximum and minimum diameters are 12<sup>mm</sup> and 6.5<sup>mm</sup> respectively. Medianly and lying above the premaxillary canals is a central oblanceolate foramina about 7<sup>mm</sup> in height and with a maximum transverse diameter of  $1^{mm}$  dorsad.

The component elements of the rostrum are completely coössified and indicate a fish of considerable size.

		Vertical	Transverse
Diameter of rostrum -	1/4 distance from ba	se 26 <sup>mm</sup>	$36^{mm}$
	1/2	23·5 <sup>mm</sup>	$33^{mm}$
	3/4	18·5 <sup>mm</sup>	$28^{mm}$

The accompanying text figures 1/3 natural size show the dorsal (fig. 1) and ventral (fig. 2) aspects of the rostrum and transverse sections (figs. 1a, 1b, 1c, 1d) at the points indicated. Occurrence.—Calvert Formation. Tar Bay, James River,

Prince George County, Virginia.

The fragments from the Ashley River marls which Leidy\* described as *Xiphias robustus* and appears to have considered as Eocene in age, and which Hayt referred to Istiophorus and considered Post-pliocene in age is similar in general form but smaller and with two dentigerous bands separated by a groove. The age of the South Carolina form is, of course, uncertain since the Ashley marls contain so many mechanically mixed fossils of various ages. As I have remarked elsewhere, this may be true of the Virginia specimen since the Calvert is underlain by the Aquia Eocene. In both cases, however, the Istiophorus rostra are associated with teeth of the Miocene *Physeter vetus* (Leidy).

*I. antiquus* (Leidy<sup>‡</sup>) from the Eocene of New Jersey is \* Leidy, J., in Holmes' Post-pliocene Fossils of South Carolina, p. 119, pl. 27, figs. 3-5, 1869. † Hay. O. P., U. S. Geol. Survey Bull. 179, p. 402, 1902. ‡ Leidy, J., Proc. Acad. Nat. Sci. Phila., vii, p. 397, 1855.

smaller and more flattened. I. parvulus (Marsh\*) from the Upper Cretaceous or Eocene of New Jersey is a much smaller, more slender, more pointed, and more compressed form. I. homalorhamphus (Cope<sup>†</sup>) is more nearly like the Virginia form, but is considerably smaller, somewhat different in form, being more tapering and more nearly elliptical in transverse



section. The premaxillary canals are much smaller and the dentigerous area is well developed. This last species is of uncertain age and may be either Upper Cretaceous, Eocene or Miocene. *I. eocaenicus* (Smith Woodward<sup>‡</sup>) from the middle Eccene of southern England is much smaller with straight

\* Marsh, O. C., Proc. Am. Assn. Adv. Sci., p. 227, 1869. † Cope, E. D., Proc. Bost. Soc. Nat. Hist., xii, p. 310, 1869. ‡ Smith Woodward, A., Cat. of Fossil Fishes in the British Museum, Pt. 4, 1901, p. 495, fig. 18, No. 2.

converging sides and *I. rotundus* (Smith Woodward<sup>\*</sup>) from the Phosphate beds of South Carolina is a very much shorter, wider and more rapidly pointed form.

In addition to the foregoing Van Benedent has described a number of rostra under different generic names including a somewhat similar but larger and otherwise different form which he calls Brachyrhynchus teretrirostris (Rütimeyer) and which occurs in the Mio-Pliocene of Belgium, France and Italy. B. solidus (Van Beneden) from the middle Eocene of Belgium is somewhat similar to the Virginia form but more depressed and with much smaller and more widely separated nutrient canals. Xiphiorhynchus elegans (Van Beneden) from the Middle Eocene of Belgium is also somewhat similar, but shows five nutrient canals. These embrace all the forms with which the present fossil has been compared.

Johns Hopkins University, Baltimore.

### ART. XLII.—Eakleite, a New Mineral from California; by ESPER S. LARSEN.<sup>‡</sup>

WHILE making a microscopic study of minerals the author found in the Museum of the University of California a speci-men labelled "Wollastonite, St. Inez, Calif.," whose optical properties are different from those of wollastonite, pectolite, and all other known minerals. The mineral proved to be a new species and the name eakleite (pronounced aké-el-ite) is proposed for it, after the mineralogist Prof. Arthur S. Eakle.

The largest piece of eakleite in the collection is about three centimeters across; it is free from foreign material and is made up of successive, irregular layers of fibers, some of these layers several millimeters across. It is compact, very tough, and has a hardness of about  $6\frac{1}{2}$ . A specific gravity measurement on a large fragment with a balance gave 2.705 and one made by suspending in Thoulet solution gave 2.685. Eakleite fuses at about 2.5 with slight boiling to a glassy, somewhat vesicular globule; it loses its water only at a high heat. It is easily soluble in acid with separation of flaky silica but without gelatinization.

\* Idem, fig. 18, No. 3.

† Van Beneden, P. J., Recherches sur quelques poissons fossiles de Belgique, Bull. Acad. Roy. Belg., xxxi, pp. 495-518, pl. 1-4, 1871.
‡ Published with permission of the Director of the U. S. Geological

Survey.
The optical properties of eakleite are characteristic. It is pale pink with vitreous to silky luster. Under the microscope fibers give parallel extinction and are seen to be elongated parallel to Z. It is optically positive and the axial angle is very small.

The indices of refraction as measured in sodium light by the immersion method are:

 $a = 1.583 \pm 0.001.$   $\beta = 1.583 \pm 0.001.$  $\gamma = 1.593 \pm 0.001.$ 

Chemical analyses.—Two chemical analyses of a sample of the mineral, which a microscopic examination showed to be free from impurities and homogeneous, were kindly made for the author by Professor Eakle, and are given in columns 1 and 2 of the table. Column 3 gives the average of the two analyses, column 4 gives the molecular ratios, and column 5 the theoretical composition of a mineral with the formula  $5CaO.5SiO_2.H_2O.$ 

Analyses	and	ratios	of	Eakleite.
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	1	2	3	4		5
SiO <sub>2</sub>	50.43	49.90	50.17	832	5  imes 166	50.16
Fe <sub>2</sub> O <sub>3</sub> CaO	0.98 45.51	$1.11 \\ 45.39$	1.04 45.45	6 812	$5 \times 168$	46.82
$\begin{array}{c} MgO \\ Na_{2}O \& K_{2}O \end{array}$	tr. none	tr. none	tr. none			
H <sub>2</sub> O	3.25	3.11	3.18	177	$1 \times 177$	3.02
	100.17	99 <sup>.</sup> 5 l				100.00

The relation of eakleite to other minerals is not clear, but it may be a calcium pectolite, as some analyses of pectolite show an excess of water over that commonly assigned to the species. Its fibrous structure and general appearance are those of pectolite.

## ART. XLIII.—Rensselærina, a New Genus of Lower Devonian Brachiopods; by CARL O. DUNBAR. With Plate II.

[Contributions from the Paleontological Laboratory, Peabody Museum, Yale University.]

In the Linden shale of western Tennessee, which is the equivalent formation to the New Scotland of New York, the stout dorsal beaks of an undescribed *Rensselæria*-like brachiopod are among the most conspicuous fossils, although the rest of the shell, which is quite thin, is far less often preserved. It is a very characteristic species in the southwestern development of the New Scotland fauna, but seems not to have reached the Appalachian trough. Its elongate form and partially plicated surface, combined with its specialized, septate brachidium, preclude its reception in any described genus. It is therefore proposed to give to the new genus which it represents the name *Rensselærina*, because of its nearer approach to *Rensselæria* than to any other genus of the Centronellidæ, to which family it belongs. The genotype is *Rensselærina medioplicata*, n. sp.

It is a pleasure to acknowledge the writer's obligation to Professor Charles Schuchert of Yale University for advice and criticism in describing the new genus.

#### Order TELOTREMATA Beecher

# Superfamily TEREBRATULACEA Waagen

Family CENTRONELLIDÆ Hall and Clarke

RENSSELÆRINA, new genus

Diagnosis.-Shell decidedly elongate oval, often nearly cylindrical, but otherwise having the general form of the later Rensselærias, though always less broad-shouldered. Shell substance very finely punctate. Of the exterior surface, the posterior half and the lateral slopes of the shell are entirely smooth; but anteriorly the median portion of both valves bears a few simple, rounded, conspicuous plications which become obsolete about half-way to the beaks. The plications are separated by well-defined concave interspaces that are at least as wide as the plications themselves. There is no cardinal area and the cardinal and lateral slopes are rounded. The sides of the shell are not incurved as in Beachia, nor steeply angulated as is commonly the case in Rensselaria. The minute beak of the dorsal valve is concealed by that of the ventral valve, which is strongly incurved and closely appressed; the pedicle foramen is minute and neither resorbed nor abraded through the umbo.

The ventral interior differs from that of *Rensselwria* in having very small vertical dental plates that do not attain the bottom of the valve, while the pedicle or rostral cavity between them is very deep and narrow. The muscle scar is limited to the posterior half of the shell. The diductor scars are elongate and slender. Between their more deeply impressed posterior portions are embraced the narrow imprints of the adductor muscles. The dorsal interior has a thick and conspicuous triangular hinge-plate, supported by two thickened crural lamellæ. This plate is highly variable. Most commonly it is thickened medially into a slight triangular elevation, the actual cardinal process (see Plate II, figs. 14-18), on which are the scars of the cardinal muscles; but all gradations occur from such an elevation to a decided triangular pit (Plate II, figs. 14, 15) for the insertion of these muscles, or to the other extreme where a distinct median process arises (Plate II, fig. 18), at the sides of which lie the muscle scars. This tendency toward an elevation of the center of the hinge-plate is in marked contrast with *Rensselæria*, wherein the plate is primitively flat but in later forms always has a depressed cardinal pit. As in most Lower Devonian terebratulids, the hingeplate is traversed by a well defined visceral foramen, which, beginning dorsad of the anterior edge of the plate, emerges on its surface just below the beak. The adductor muscle scars are narrow, separate, and distinctly impressed.

The brachium is distinctive and may be described as follows : The thin, slightly divergent, descending lamellæ are broad and stand nearly vertical dorso-ventrally as they leave the wide and conspicuous crural processes; then, diverging more rapidly, the lamellæ become narrower and rotate into a horizontal position as the loop attains its greatest width, and by a regular curvature begins to converge (Plate II, figs. 1, 3). Approaching the median line, just in front of the middle of the shell, the loop broadens into a spoon-like plate, drawn out anteriorly into a long acumination which curves gently downward. The edge of the loop, which was ventral when it left the cruræ, is now anterior and forms the outer margin of this plate, dipping outward at about 40° below the horizontal. From its concave ventral surface arises a vertical median lamella (Plate II, fig. 2) which extends forward beyond this plate, just in front of which it reaches its greatest height. It continues anteriorly to near the front of the shell, where it approaches the ventral valve.

Relationships.—This genus is one of the several divergent lines or phyla of the Centronellidæ. While in general the external aspect resembles most Amphigenia and Rensselæria, it presents essential differences. Amphigenia is at once set off by its entirely smooth surface and, especially on the interior, by the incomplete loop, the clearly defined double dorsal septa, and the extremely large rostral cavity which apparently has become a true spondylium and is supported by a high median septum.

*Rensselæria* differs in its uniformly striate surface, in its wide, strong, and recumbent dental lamellæ whose outer sides rest on the bottom of the valve and which unite medially to make a broad and more or less deep rostral cavity; but most especially in its simpler brachidium, which is without the median vertical lamella of the new genus.

Beachia is readily distinguished from Rensselærina by its flat ovate shape, its erect ventral beak which exposes the deltidial plates, its smooth or finely striated surface, and its inverted margins, but particularly by its simpler Rensselæria-like loop, with a median posterior spine instead of an anterior vertical lamella.

Lissopleura is for the time being provisionally placed in the Centronellidæ, although it is not yet clearly understood. At any rate, it differs widely from the new genus under consideration in its rhynchonelloid shape, in its coarse plications which have no interspaces between them, and in its high dorsal septum.

One other genus needs comparison. Romingerina is based on a single species, R. julia, which is a very small, smooth, lenticular shell from the Lower Mississippian of Michigan. The only character which seems to relate this genus to the new one is the presence of a median vertical lamella on the loop. However, this is evidently only a case of parallel development. The lamella in Romingerina is described by Hall and Clarke as follows:\* "The median ridge on the anterior plate of the brachidium is elevated into a conspicuous vertical lamella, extended both anteriorly and posteriorly, being in fact a double plate produced by the abrupt deflection of each lateral branch of the brachidium near the median line; union taking place along the upper edge, which almost reaches the inner surface of the pedicle valve."

It is but a simple step to the development of this type of brachidium out of one of the later Centronellas. Furthermore, the shell of *Romingerina* has a smooth surface, its beak is erect enough to disclose the deltidial plates, and it frequently shows a faint fold and sinus—all centronelloid characters. The lateral branches of the loop in *Centronella* are also sharply deflected before meeting medially, their deflected edges forming a slight ridge. A mere expansion of this character will produce essentially the loop of *Romingerina*.

\* Hall and Clarke, Pal. N. Y., vol. viii, Pt. 2, 1894, p. 271. Winchell's drawings erroneously show the crura directed dorsally.

Such a genus in the early Mississippian, however, can scarcely have evolved from one which in the early Devonian has already reached as great a specialization in another direction as is the case in *Rensselærina*. In the latter genus the vertical median lamella is simple, not double, it has no posterior extension, and it is not formed by a deflection of the descending lamellæ of the loop. On the contrary, the halves of the loop meet medially without any deflection or thickening, and the dorsal side of the median plate is smooth and evenly rounded, while from its ventral side there arises the very thin, simple, vertical lamella.

Summary.—The essential characters of the new genus Rensselærina will be, then, its rensselæroid shape, its medially plicate surface, and, on its interior, the centronelloid brachidium with its high, vertical, anteriorly directed, median lamella.

### Rensselærina medioplicata, new species. Pl. II, Figs. 1-9, 12-18.

Shell with the characters of the genus; length of a mature individual  $24^{mm}$ , width  $14^{mm}$ , thickness  $11^{mm}$ . Six to eight plications on the middle of the ventral valve and one more on the dorsal. About three of these plications in a width of  $5^{mm}$  on the anterior margin. Hinge-plate extremely variable, being in some specimens excavate, in others raised into a median process.

Horizon and locality.—Linden formation; western Tennessee. The cotypes are in the Peabody Museum, Yale University.

### Rensselærina medioplicata var. latior, new variety. Pl. II, Figs. 10, 11.

In Professor Schuchert's collection there is a shell like R. medioplicata but proportionally much broader and shorter, and with the plications finer and somewhat more restricted to the anterior part of the shell. The length of a fully grown specimen is  $20^{\text{mm}}$ , breadth  $16^{\text{num}}$ , thickness  $11^{\text{mm}}$ . There are four plications in about the width of three in R. medioplicata.

Horizon and locality.--Linden formation; Henry County, Tennessee. Holotype in Professor Schuchert's collection.

#### EXPLANATION OF PLATE II.

#### Rensselærina medioplicata, n. sp.

FIGS. 1, 2, 3. Dorsal, side, and ventral views of the loop, restored. In figs. 2 and 3 the visceral foramen which traverses the hinge-plate is indicated.

FIG. 4, Dorsal view of the posterior portion of a specimen.

FIG. 5. Cardinal view of a very obese specimen which is almost cylindrical. The beak is abraded off.

FIG. 6. Cardinal view of a normal specimen.

FIGS. 7, 8. Lateral and ventral views of a specimen which shows the normal shape of the species. Fig. 7 is slightly enlarged. The shell is exfoliated, so the plications do not appear clearly.

foliated, so the plications do not appear clearly. FIG. 9. Ventral view of another specimen, to show that the posterior portion and lateral slopes are smooth and only the median portion is plicated.

FIG. 12. Interior of a ventral valve, to show the deep pedicle cavity, the hinge-teeth supported by small dental lamellæ, and the narrow adductor muscle scars embraced in the posterior portion of the diductor muscle scars,  $\times 2$ .

scars.  $\times 2$ . FIG. 13. Interior of the posterior portion of a dorsal value which shows most of the slender adductor muscle scars.  $\times 2$ .

FIGS. 14, 15, 16. 17, 18. A series of individuals showing the extreme variability of the diductor muscular area of the hinge-plate. In figs. 14 and 15, this area is excavate, in figs. 16 and 17 slightly raised, and in fig. 18 a conspicuous process has arisen between the diductor muscles, which are inserted at its sides. Note the perforation of the hinge-plate by the visceral foramen just below the beaks.  $\times 2$ .

From the series of cotypes in the Peabody Museum, Yale University. All figures natural size unless otherwise stated.

#### Rensselærina medioplicata var. latior, n. var.

FIGS. 10, 11. Dorsal and lateral view, to show the broad and short outline and nearly obsolete plications. Fig. 10 natural size, fig, 11 slightly enlarged.

From the cotypes in Professor Schuchert's collection, Peabody Museum, Yale University.

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## ART. XLIV.—Local Versus Regional Distribution of Isostatic Compensation; by WILLIAM BOWIE.

ONE of the most important phases of the subject of isostasy is that of the distribution of the compensation of the topography, in a horizontal direction. As is well known, the compensation is assumed, in the computations made by the U. S. Coast and Geodetic Survey, to be directly under the topographic features. While this is not held to be strictly or even probably true, it facilitates the reductions which, under the most favorable circumstances, require much time and labor.

In the latest investigation by the Survey on the subject of gravity and isostasy\* certain tests were made to discover, if possible, the horizontal distribution of the compensation.

Three tests were made, with the data from 124 stations in the United States. First, the compensation was distributed uniformly from the station out to the limit of zone K, which has a radius of 18.8 kilometers (11.7 miles). At each station the average elevation of the topography within this area was read from maps, and then the compensation of this topography was distributed uniformly throughout the circle with the given radius. It was assumed to extend uniformly to a depth of 113.7 kilometers. Second, similar computations were made for the average elevation of the topography from the station to the outer limit of zone M, 58.8 kilometers (36.5 miles). Third, this was done for the average elevation of the topography to the outer limit of zone O, 166.7 kilometers (103.6 miles) from the station.

In order to make the regional method of reduction logical, the compensation of each topographic feature should be computed separately to the limits of the zone having the topographic feature at its center. The method of computation actually adopted may give erroneous results. For instance, let us assume that the compensation is distributed regionally within zone O, with the station at its center. It may happen that the station is in a broad valley or on a plain with mountains surrounding it at a distance of about 167 kilometers. None of the compensation under the mountains would be taken into account in making the regional reductions and the computed value of gravity would be too great. On the other hand, if the station were in the mountains with valleys or plains just beyond the limits of zone O, then none of the compensation of the mountains would be distributed to the valleys or plains, and the computed value of gravity at the station would be too small. Therefore, in making the reductions by

\* Investigations of Gravity and Isostasy, Special Publication No. 40 of the Coast and Geodetic Survey.

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 258.—JUNE, 1917. 32 the regional method the compensation for each topographic feature should be distributed separately before making the computations to obtain its effect. This, of course, would be possible, but it would be such a laborious process that it would not be practicable. While the method of making the computations for the regional distribution of the compensation is somewhat illogical, yet it is probable that none of the conclusions reached in the study of the question would be materially changed if the ideal method had been employed.

The compensation of the topography, beyond the areas selected for the regional distribution, was assumed to be directly under the topographic features, as is the case with the local distribution computations.

In each test the gravity anomaly was computed for each of the 124 stations. An anomaly is the difference between the observed value of gravity and the computed value. The computed value is the theoretical value, at sea-level, for the latitude of the station, corrected for the elevation of the station, for the attraction of the topography of the whole world (this is nearly always positive for land areas and is always negative for ocean areas), and for the attraction of the isostatic compensation (this is negative for land areas and positive for ocean areas).

The value of gravity at the base station in Washington is 980.112 dynes per gram as a force or centimeters per second per second as an acceleration. The anomaly is given in the third place of decimals of dynes. Thus the anomaly of .001 dyne is about one millionth of the force of gravity.

A disc of material 2.67 in density, 100 feet thick, and 20 kilometers in diameter, has an attractive effect of .0034 dyne on a gram mass located on the surface of the disc at its center. We may therefore interpret the average anomaly (0.020) as equivalent to an excess or deficiency of mass of average density which is 20 kilometers in diameter and 600 feet thick.\*

There are given in the following table the mean anomalies with and without regard to sign for all of the 124 stations used in the tests.

	negional Anomalies			
	Local			
	Anomaly	Zone K	Zone M	Zone O
Mean with regard to sign	-0.005	-0.001	-0.001	-0.005
Mean without regard to sign	0.050	0.019	0.050	0.050

The mean anomalies for the various methods of distribution of the compensation are practically the same. This is no doubt due to the fact that most of the stations are on topography with little relief.

 $^{\ast}$  A table of attractions for various masses is given on page 73 of Special Publication No. 40.

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It is readily seen that the compensation would be the same under the several methods of distribution at a station located on a coastal plain or on an extensive plateau. But if the area about a station has varied topography as in mountainous regions, the effect of the compensation will vary with the method of distribution employed. If the station is on a mountain peak the regional distribution will place some of the compensation at a distance, horizontally, and its effect at the station will be lessened. On the other hand, if the station is in a valley, the regional distribution will place under the station some of the compensation of the mountain mass, and the compensation will have a greater effect on the gravity at the station than is the case with local distribution.

If we assume, as we must in these tests, that the anomalies are due entirely to the departures from the truth in the method of horizontal distribution of the compensation, then we are justified in concluding that that method of distribution is nearest the truth which shows the least effect of systematic errors, in the anomalies for the various classes of topography.

The stations were therefore arranged in five groups according to the topography. The mean local and regional anomalies for these groups are given in the following table:

#### LOCAL AND REGIONAL ANOMALIES.

For 18 coast stations.

	Local Regional Anoma		lies	
•	Anomalies	Zone K	Zone M	Zone O
Mean with regard to sign	-0.004	-0.004	-0.004	-0.006
Mean without regard to sign	0.018	0.018	0.018	0.050

For 25 stations near coast.

Mean	with regard to sign	-0.005	-0.001	-0.001	-0.001
Mean	without regard to sign	0.022	0.051	0.021	0.022

For 39 stations in the interior, not in mountainous regions.

Mean	with regard to sig	gn + 0.001	+0.002	+0.005	+0.003
Mean	without regard to	sign 0.017	0.018	0.018	0.017

For 22 stations, in mountainous regions, below the general level.

Mean with regard to sign	0.000	+0.001	+0.003	+0.006
Mean without regard to sign	0.017	0.012	0.018	0.019

For 18 stations, in mountainous regions, above the general level.

Mean	with regard to sign	+0.003	+0.003	0.000	-0.010
Mean	without regard to sign	0.018	0.018	0.012	0.020

The means without regard to sign for the anomalies by the several methods of distribution are practically the same for the five classes of topography considered. This is a striking confirmation of the theory of isostasy. This is shown when we compare these average anomalies with those by the Bouguer reduction which postulates an entire absence of isostasy. The Bouguer anomalies without regard to sign for 217 stations in the United States are given below for the five classes of topography used in the investigations.

		Bouguer
	Mea	n Anomaly
	with	nout regard
		to sign
		Dyne
27	coast stations	0.021
46	stations near the coast	0.025
88	stations in the interior, not in mountainous regions	0.033
36	stations in mountainous regions, below the general	
	level	0.108
20	stations in mountainous regions, above the general	
	level	0.111
217	stations, all classes of topography	0.049

These mean anomalies show a very decided relation to the topography.

While the isostatic anomalies without regard to sign show no relation to the topography, even for various methods of distributing the compensation, yet there is shown some relation to the character of the topography when we consider the sign of the anomalies. Each method of distribution shows a negative mean anomaly with regard to sign for the 18 coast stations. This can probably be explained by the presence of light Cenozoic material near the coasts.\* This subject need not be discussed here and we may leave these stations out of consideration.

For the remainder of the topographic groups the means with regard to sign show no decided relation to the character of the topography for the local and the regional distribution of compensation out to the limits of zones K (18.8 kms.) and M (58.8 kms.). The ranges in the means are '005, '004 and '004, respectively, for the three methods. But there is a decided relation shown by the means with regard to sign for the regional distribution to the outer limit of zone O (166.7 kms.). For the 22 stations in mountain regions below the general level the mean is  $\pm 0.006$  and for the 18 stations in mountainous regions above the general level, the mean with regard to sign is -0.010. The range in values is therefore '016, which is nearly as great as the average anomaly, without regard to sign, by the various methods of distribution for all stations.

If we make the reasonable assumption, that the method which shows no deviation from normal with changed topographic conditions is nearest the truth, we may conclude that the

\* See page 76 of Special Publication No. 40 of the U.S. Coast and Geodetic Suryey, Investigations of Gravity and Isostasy.

regional distribution of the compensation out from the station to a distance of 166.7 kilometers is farther from the truth than the local distribution or than the regional distribution out to a distance of 18.8 kilometers or 58.8 kilometers. There is little or no evidence to show that any one of these last three methods is nearer the truth than the other two. It may be possible that there is some distance between 58.8 kilometers and 166.7 kilometers which would give a slightly smaller range of the mean anomalies with regard to sign, but it is probable that there is not.

It seems improbable that further computations and additional data can evaluate the true horizontal distribution of the compensation. Therefore in making the computations the local distribution of the compensation (horizontally) may with propriety be continued in use.

The mean anomaly with regard to sign for the various classes of topography by the Bouguer method of reduction has such a wide range of values that the isostatic method by any one of the distributions under consideration appears to be much nearer the truth. The Bouguer anomalies with regard to sign for 217 stations are given below.

	I	Bouguer Mean Anomaly. Dyne
27	coast stations	- +0.017
46	stations near the coast	+0.004
88	stations in the interior not in mountainous region	s — 0.058
36	stations in mountainous regions, below the genera	.1
	level	0.107
20	stations in mountainous regions, above the genera	1
	level	- 0.110
217	stations, all classes of topography	-0.036

The evidence given here in comparison with that given by the anomalies of the isostatic method shows that the Bouguer method has no general application whatever. The range in the means is  $\cdot 127$  dyne, which is 8 times the range of the mean regional (horizontal) isostatic anomalies with compensation uniformly distributed to a distance of 166.7 kilometers, and 25 times the range of the mean anomalies with local distribution of the compensation.

The data given in this paper favor strongly the isostatic method of reduction and also favor the local distribution of the compensation or the regional distribution to a distance much less than 166.7 kilometers.

Division of Geodesy, U. S. Coast and Geodetic Survey. April 20, 1917.

## ART. XLV.-The Constitution of Melilite and Gehlenite;\* by FRANK WIGGLESWORTH CLARKE.

ALTHOUGH many attempts have been made to determine the chemical constitution of melilite and gehlenite, no one of them can be accepted as absolutely conclusive. The analyses of the two minerals vary widely, showing that they are not true species but crystalline mixtures analogous to those found in the feldspar series, the micas, the scapolites, and the garnet group. The problem is, to determine the individual components of melilite and gehlenite, and in such a way as to show their relations to each other, and to all minerals of similar chemical composition or type.

The most recent, and decidedly the most successful attempt to interpret the constitution of these minerals is due to W. T. Schaller.<sup>+</sup> He regards melilite and gehlenite as mixtures of four definite silicates, namely, åkermanite, Mg<sub>4</sub>Ca<sub>8</sub>Si<sub>9</sub>O<sub>30</sub>; sarcolite, Al<sub>2</sub>Ca<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>; soda sarcolite, Al<sub>2</sub>Na<sub>5</sub>Si<sub>3</sub>O<sub>12</sub>, and "velardenite," Al<sub>a</sub>Ca<sub>a</sub>SiO<sub>a</sub>. The last of these silicates is well known as an artificial compound, but not definitely as a natural mineral. All four silicates are tetragonal, and Schaller has shown that their formulæ can be adjusted to the analyses of melilite and gehlenite with a remarkable degree of accuracy. The crystallographic and chemical data are in harmony, but unfortunately, they do not cover the whole ground. The relations of melilite and gehlenite to other minerals, such as anorthite, garnet, zoisite, vesuvianite, and meionite, are not indicated by Schaller's method of formulation, and so the fundamental problem is incompletely solved. A great advance has been made, but much still remains to be done. The present communication represents an effort to find a more general interpretation of the lime-alumina silicates, not only with regard to their chemical composition, but also with reference to their associations in nature, their mode of origin, and their alterations.

To Schaller's formulation of melilite and gehlenite there are obvious objections, which, however, he has shown to be not absolutely insuperable. The four primary compounds of his scheme can be represented by a single type of formula, but to that procedure there are alternatives which seem to be more reasonable. The compounds are not alike chemically; for åkermanite is non-aluminous, "velardeñite" is extremely basic, and sarcolite is most simply formulated as a normal orthosili-The other lime-alumina silicates which have already cate.

\* Published by permission of the Director of the U. S. Geological Survey.  $\dagger$  U. S. Geol. Survey, Bull. 610, pp. 106–126. Schaller gives a good sum-mary of earlier interpretations, which need not be repeated here.

been mentioned are also orthosilicates, and the true components of melilite and gehlenite ought in all probability to follow the same rule. The tetragonal sarcolite, for example, has the same molecular ratios as the isometric garnet, and a probable structural difference between the two species is easy to represent graphically. Including an analogous compound, prehnite, the following constitutional formulæ are at least probable:



Natural sarcolite is a mixture of the lime salt and the soda salt, but the replacement of lime by soda is not necessarily complete. The formulation given here fits best into the general scheme, which will be developed presently. The two sarcolites, however, as Schaller has shown, are probable components of melilite and gehlenite. That is an important step forward.

On comparing the trustworthy analyses of melilite and gehlenite two striking differences appear. In melilite the ratio of oxygen to silicon is slightly lower than that required for the orthosilicate radicle SiO<sub>4</sub>; and for that reason trisilicate molecules may be assumed as possibly present. This assumption is justified by familiar analogies as in the isomorphism of albite and anorthite, and of the scapolitic minerals marialite and meionite. In each of these pairs a trisilicate and an orthosilicate are morphologically equivalent. In gehlenite, on the other hand, the oxygen is largely in excess of the orthosilicate, and basic molecules must be taken into account. This condition is satisfied by assuming the presence in gehlenite of the univalent group  $-Al <_{O}^{O} > Ca$ ; which in Schaller's system is characteristic of his basic silicate, "velardenite." In the present discussion its function will be differently shown. Furthermore, natural melilite always contains soda, presumably as soda sarcolite, while gehlenite contains little or none. Weinschenk's fuggerite is an exceptional mineral, lying near the boundary between melilite and gehlenite, and showing affinities for both species. It is best classified as a sodic variety of gehlenite.

The reported syntheses of melilite are not altogether satisfactory, and need not be discussed here. There are, however, melilites of artificial origin which are very significant as regards chemical composition. For example, the melilite crys-tals obtained by Bodländer\* from Portland cement, have very nearly the composition represented by the formula Al<sub>a</sub>(SiO<sub>4</sub>)<sub>e</sub>  $Ca_sMg_s$ ; which may be written structurally thus:

$$\begin{array}{c} \left / \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 \right \\ \operatorname{Al} - \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 - \operatorname{Al} \\ \left / \operatorname{SiO}_4 \equiv \operatorname{Mg}_3 \equiv \operatorname{SiO}_4 \right \end{array}$$

Another crystalline melilite isolated by Stahl<sup>+</sup> from furnace slag has very nearly the same molecular ratios. In this instance, however, the general formula Al<sub>2</sub>(SiO<sub>4</sub>)<sub>6</sub>R<sub>9</sub>" includes a large proportion of ferrous iron and some zinc among the components of R. With these clues we may write the following series of formulæ:

$Al_{6}$	$(SiO_{a})_{e}Ca_{s}$	Anorthite.	
Al	$(SiO_4)_6Ca_6$	Garnet (and sarcolite)	•
Al	(SiO <sub>4</sub> ) <sub>6</sub> Ca <sub>6</sub> ,	In melilite.	

These expressions are to be qualified by the evident fact that in melilite as in garnet ferric molecules may be commingled with those of alumina, and ferrous or magnesian molecules with those of lime. In natural melilite we have, apparently, a crystalline mixture of the *normal* melilite, as written above, with sarcolite, soda sarcolite, and a small proportion of a trisilicate, Al<sub>4</sub>(Si<sub>3</sub>O<sub>8</sub>)<sub>6</sub>Ca<sub>4</sub>Na<sub>4</sub>, equivalent to sarcolite. A study of the available analyses of melilite will serve to show how closely this scheme fits the facts.

#### Analyses of Melilite

1.	Damour an	alyst.	From	Vesuviu	s.
2.	66	• • •	Capo	di Bove,	yellow.
3.	66	"	<u>دة</u>	66	brown.
4.	Bodländer	66	"	66	
5.	Zambonini	"	"	66	yellow.
6.	66	"	66	۴۴ .	brown.
7.	Schaller	"	Iron	Hill, Un	compangre
	rang	le, Colo	orado.‡		. 0

quad-

\* Neues Jahrb., 1892, vol. i, p. 53. † Berg-u.-Hüttenmännische Zeitung, lxiii, 273, 1904. Discussed by Zam-bonini in Zeitschr. Kryst., xli, 226, 1906. ‡ See Larsen and Schaller, Journ. Wash. Acad., iv, 473, 1914.

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	1	2	3	4	5	6	7
SiO <sub>a</sub>	40.69	39.27	38.34	41.09	40.14	39.20	42.07
TiO					trace	trace	•20
Al <sub>Q</sub> O <sub>2</sub>	10.88	6.42	8.61	10.93	6.47	7.56	10.20
Fe <sub>2</sub> O <sub>3</sub>	4.43	10.17	10.02	3.40	9.95	11.34	•30
FeO					•53		2.18
MnO					trace	trace	.16
CaO	31.81	32.47	32.02	34.78	32.98	32.18	35.41
MgO	5.75	6.44	6.71	5.87	6.33	6.41	4.15
Na <sub>o</sub> O	4.43	1.95	2.12	3.40	2.18	2.21	3.24
K Õ	$\cdot 36$	1.46	1.51	·68	1.49	1.45	trace
H O				•24	•27	$\cdot 21$	•47
$P_0$							•82
$\dot{\rm CO}_2$							•90
	00.25	0.0.10	00.26	100.20	100.24	100.56	100.40
	90.30	90.10	99.30	100.39	100.34	100.90	100.40

Reducing these analyses to standard form, by computing Fe<sub>2</sub>O<sub>3</sub> into its equivalent of  $Al_2O_3$ ; FeO, MnO, and MgO into CaO; K<sub>2</sub>O into Na<sub>2</sub>O, and recalculating to 100 per cent, the data become comparable as shown in the next table. The P<sub>2</sub>O<sub>5</sub> and CO<sub>2</sub> of the Colorado mineral are reckoned as representing calcium phosphate and carbonate, and rejected.

### Reduced analyses of melilite.

	1	2	3	4	5	6	17
SiO	41.13	40.67	39.16	40.76	40.84	39.88	43.41
$Al_2O_3$	13.85	$13\ 36$	15.32	13.01	13.03	15.05	10.92
CaO	40.31	42.96	42.33	42.41	42.98	41.86	42.34
Na <sub>2</sub> O	4.71	3.01	3.19	3.82	3.12	3.21	3.33
	100.00	100.00	100.00	100.00	100 00	100.00	100.00

From these reduced analyses the following formulæ are derived:

- 1.
- 2.
- $7 \text{Al}_{4}(\text{Si}_{3}\text{O}_{8})_{6}\text{Ca}_{4}\text{Na}_{4} + 31 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{4}\text{Na}_{4} + 62 \text{Al}_{2}(\text{SiO}_{4})_{6}\text{Ca}_{9}.$   $6 \text{Al}_{4}(\text{Si}_{3}\text{O}_{8})_{6}\text{Ca}_{4}\text{Na}_{4} + 18 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{4}\text{Na}_{4} + 6 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{6}.$   $+ 70 \text{Al}_{2}(\text{SiO}_{4})_{6}\text{Ca}_{9}.$   $2 \text{Al}_{4}(\text{Si}_{3}\text{O}_{8})_{6}\text{Ca}_{4}\text{Na}_{4} + 24 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{4}\text{Na}_{4} + 19 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{6}.$   $+ 60 \text{Al}_{2}(\text{SiO}_{4})_{6}\text{Ca}_{9}.$   $7 \text{Al}_{4}(\text{Si}_{3}\text{O}_{8})_{6}\text{Ca}_{4}\text{Na}_{4} + 21 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{4}\text{Na}_{4} + 72 \text{Al}_{2}(\text{SiO}_{4})_{6}\text{Ca}_{9}.$   $7 \text{Al}_{4}(\text{Si}_{3}\text{O}_{8})_{6}\text{Ca}_{4}\text{Na}_{4} + 21 \text{Al}_{4}(\text{SiO}_{4})_{6}\text{Ca}_{4}\text{Na}_{4} + 72 \text{Al}_{2}(\text{SiO}_{4})_{6}\text{Ca}_{9}.$ 3.
- 4. 5.
- $7 \operatorname{Al}_{4}(\operatorname{Si}_{3}\operatorname{O}_{8})_{6}^{*}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{*} + 19 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{*} + 1 \operatorname{Al}_{4}^{2}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{6}^{*} + 73 \operatorname{Al}_{2}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{9}^{*} + 22 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{*} + 19 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{6}^{*} + 4 \operatorname{Al}_{4}(\operatorname{Si}_{3}\operatorname{O}_{8})_{6}^{*}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{*} + 22 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{*} + 19 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{*}\operatorname{Ca}_{6}^{*} + 19 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{*} + 10 \operatorname{A}_{4}(\operatorname{SiO}_{4})_{6}^{*} + 10 \operatorname{A}_{4}(\operatorname{A}_{4}(\operatorname{SiO}_{4})_{6}^{*} + 10 \operatorname{A}_{4}(\operatorname{A}_{4})_{6}^{*} + 10 \operatorname{A}_{4})_{6}^{*} + 10 \operatorname{A}_{4}(\operatorname{A}_{4})_{6}$ 6. +  $60 \text{Al}_{2}(\text{SiO}_{4})_{6} \text{Ca}_{9}$ .
- 7.  $13 \operatorname{Al}_{4}(\operatorname{Si}_{3}\operatorname{O}_{8})_{6}^{2}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{2} + 14 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}\operatorname{Ca}_{4}\operatorname{Na}_{4}^{2} + 67 \operatorname{Al}_{2}(\operatorname{SiO}_{4})_{6}\operatorname{Ca}_{9}^{2}$

These correspond to the following calculated analyses :

				-			
	1	2	3	4	5	6	7
SiO,	41.21	40.64	-39.16	40.99	40.97	40.15	43.36
Al <sub>2</sub> Õ <sub>3</sub>	14.13	13.36	15.26	13.04	12.93	15.11	10.96
CaO	39.93	43.00	42.36	42.50	42.88	41.56	42.32
Na <sub>2</sub> O	4.73	3.00	3.22	3.47	3.22	3.18	3.36
						<u> </u>	
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Calculated analyses of melilite.

The agreement between the reduced and calculated analyses is very close. In many cases the normal melilite silicate Al<sub>2</sub>(SiO<sub>4</sub>)<sub>6</sub>Ca<sub>6</sub> predominates, forming from 60 to 70 per cent of the mixed crystals. The two sarcolites come next, with the hypothetical trisilicate molecule in subordinate amount. The existence of the trisilicate, however, is subject to some doubt. Melilite is prone to contain impurities, inclusions of other minerals, and the excess of silica shown by the analyses may perhaps be due to their presence. The melilite of Capo di Bove, for example, commonly contains inclusions of leucite,\* and it is possible that dissolved silica may sometime be present also. The largest proportion of trisilicate appears in the massive melilite from Colorado, which is more likely to contain impurities than the crystallized mineral. If the excess of silica is really dissolved silica, then the trisilicate molecule would be replaced by an equivalent amount of soda sarcolite, and the formulæ of natural melilite would be simplified. It would then be represented as a crystalline mixture of the two sarcolites with the compound  $Al_{a}(SiO_{a})_{a}Ca_{a}$  in varying proportions.

It has already been pointed out that gehlenite differs from melilite in its ratio of silicon to oxygen; and that the difference may be accounted for by assuming the presence in it of the univalent groups— Al  $\bigcirc O$  Ca. That is, gehlenite is a basic silicate, and the basic group may be combined in one of several ways. The compound containing it may have the formula Al(SiO<sub>4</sub>)<sub>3</sub>(AlO<sub>2</sub>Ca)<sub>9</sub>, or, more probably, a formula derived from that of the melilite silicate, thus:

$$\begin{array}{c} {\color{black} \textstyle / \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 \setminus {\color{black} / } \\ \operatorname{Al} - \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 - \operatorname{Al} \\ {\color{black} \textstyle \setminus \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 / } \end{array}$$

Melilite silicate

 $\begin{array}{c} \left / \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 \right \\ \operatorname{Al} - \operatorname{SiO}_4 \equiv \operatorname{Ca}_3 \equiv \operatorname{SiO}_4 - \operatorname{Al} \\ \left / \operatorname{SiO}_4 \right \\ \left / \operatorname{SiO}_4 \right \\ \left (\operatorname{AlO}_2\operatorname{Ca})_3 \right$ 

\* See Stelzner, Neues Jahrb., Beil. Bd. ii, 369, 1883.

With these formulæ the two minerals become similar in structure, and, as will be shown later, simply related to many other species. As for natural gehlenite, its analyses are easily re-ducible to mixtures of the two silicates just given, with sarco-In fuggerite a little soda sarcolite also appears. lite.

### Analyses of gehlenite.

	1.	Damour	analyst.	From	Monzoni,	Tyrol.	
	2.	Lemberg	دد م	66	٢٠ - ١	້ເເ	
	3.	Rammelsk	perg "	66	66	66	
	4.	Janovsky	° ((	Orowi	itza. Banat	t	
	5.	Allen	66	Velard	eñamining	r district. I	Mexico.*
	6.	Mayr	"	Monzo	oni. Fugg	gerite.†	
		1	2	3	4	5	6
D_		31.60	30.01	29.78	30.73	26.33	34.04
Ů,					~ ~	•03	·
Ů.		19.80	21.33	22.02	22.24	27.82	17.97
$^{2}O^{3}$		5.97	3.56	3.22	•41	1.43	3.49
Û Ů				1.63	3.01	•50	
nO				$\cdot 19$		.01	trace
$_{\rm gO}$		2.20	3.77	3.88	6.10	2.44	4.99
O		38.11	36.74	37.90	37.93	39.55	37.65
a O		.33				·21	2.04
Ú						•10	trace
0						1.85	
n.		1.53	4.72	[1.38]	•37		
solul	ble						.12
		99.54	100.13	100.00	100.79		100.20

Si Ti Al Fe Fe M M Ca Na K H Ig In

The iron oxides in the Mexican gehlenite are due to inclusions of magnetite, and should therefore be rejected. With . this qualification the reduced analyses are as follows :

### Reduced analyses of gehlenite.

	1	2	3	4	5	6
SiO <sub>2</sub>	33.03	31.36	30.52	30.10	27.06	33.65
Al Ô	23.61	24.73	23.64	22.08	28.56	20.35
CaO	43.36	43.91	45.84	47.82	44.38	43.98
Na <sub>2</sub> O						2.02
	100.00	100.00	100.00	100.00	100.00	100.00

\* See Wright, this Journal (4), xxvi, 575, 1908. † See Weinschenk, Zeitschr. Kryst, xxvii, 577, 1896. The other analyses are from Dana's System of Mineralogy.

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These analyses correspond to the following formulæ:

1.	$3 \operatorname{Al}_4(\operatorname{SiO}_4)_{\mathfrak{s}} \operatorname{Ca}_{\mathfrak{s}} + 1 \operatorname{Al}_2(\operatorname{SiO}_4)_{\mathfrak{s}} \operatorname{Ca}_{\mathfrak{s}} + 2 \operatorname{Al}_2(\operatorname{SiO}_4)_{\mathfrak{s}} \operatorname{Ca}_{\mathfrak{s}}(\operatorname{AlO}_2 \operatorname{Ca})_{\mathfrak{s}}.$
2.	$4 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{5} \operatorname{Ca}_{5} + 1 \operatorname{Al}_{2}(\operatorname{SiO}_{4})_{5} \operatorname{Ca}_{5} + 4 \operatorname{Al}_{2}(\operatorname{SiO}_{4})_{5} \operatorname{Ca}_{5}(\operatorname{AlO}_{5} \operatorname{Ca}_{5})_{5}$
3.	$1 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{6}^{\circ} \operatorname{Ca}_{6}^{\circ} + 1 \operatorname{Al}_{6}^{\circ}(\operatorname{SiO}_{4})_{6}^{\circ} \operatorname{Ca}_{6}^{\circ} + 2 \operatorname{Al}_{6}^{\circ}(\operatorname{SiO}_{4})_{6}^{\circ} \operatorname{Ca}_{6}^{\circ}(\operatorname{AlO}_{2}^{\circ} \operatorname{Ca}_{6})_{6}^{\circ}$
4.	$1 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{s} \operatorname{Ca}_{s} + 9 \operatorname{Al}_{s}(\operatorname{SiO}_{4})_{s} \operatorname{Ca}_{s} + 11 \operatorname{Al}_{s}(\operatorname{SiO}_{4})_{s} \operatorname{Ca}_{s}(\operatorname{AlO}_{4}\operatorname{Ca})_{s}$
5.	$1 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{s} \operatorname{Ca}_{s} + 4 \operatorname{Al}_{5}(\operatorname{SiO}_{4})_{s} \operatorname{Ca}_{s}(\operatorname{AlO}_{s} \operatorname{Ca})_{s}$ approximately.
6.	$17 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{s}^{*} \operatorname{Ca}_{s}^{*} + 16 \operatorname{Al}_{4}(\operatorname{SiO}_{4})_{s}^{*} \operatorname{Ca}_{4}^{*} \operatorname{Na}_{4}^{*} + 36 \operatorname{Al}_{5}^{*}(\operatorname{SiO}_{4})_{s}^{*} \operatorname{Ca}_{6}^{*}$
	$+ 25 \text{Al}_{2}(\text{SiO}_{4})_{6} \text{Ca}_{6}(\text{AlO}_{2}\text{Ca})_{6}$

To these formulæ the following calculated analyses correspond:

						•
	1	2	3	4	5	6
SiO <sub>2</sub>	33.00	31.37	30.32	29.72	27.03	33.51
Al <sub>2</sub> Õ <sub>3</sub>	23.37	24.70	23.62	22.06	27.57	20.40
CaO	43.63	43.93	46.06	48.22	45.40	44.13
$Na_{2}O$						1.96
	100.00	100.00	100.00	100.00	100.00	100.00

Calculated analyses of gehlenite.

The agreement between the reduced and the calculated analyses is satisfactory, except in the case of the Mexican mineral, which seems to have a small excess of alumina.

It has now been shown that melilite and gehlenite can be represented as mixed crystals of a few compounds of precisely similar chemical type. Sarcolite and the melilite silicate are known compounds; the basic gehlenite silicate is hypothetical, and not yet found in the free state. So far the argument is weak, but it is strengthened by other evidence of the most valid kind. The garnets and prehnite have, as we have seen, the same type of structure, and several other lime-alumina silicates can be compared with these. The following formulæ may be taken as illustrative of this fact :

$\angle { m SiO}_4 \equiv { m Al}_2 \equiv { m SiO}_4 \setminus$	$ ightarrow { m SiO}_4 \equiv { m Al}_2 \equiv { m SiO}_4 \setminus$
$Al - SiO_4 \equiv Al_2 \equiv SiO_4 - Al$	$Al - SiO_4 \equiv Ca_3 \equiv SiO_4 - Al$
$\searrow \mathrm{SiO}_{4} \equiv \mathrm{Ca}_{3} \equiv \mathrm{SiO}_{4}$	$\searrow SiO_4 - Ca - SiO_4 /$
Anorthite	AIOH AIOH
	Zoisite
$/\operatorname{SiO}_{4} \equiv \operatorname{Ca}_{3} \equiv \operatorname{SiO}_{4} \setminus$	$/\operatorname{SiO}_{4} \equiv \operatorname{Al}_{2} \equiv \operatorname{SiO}_{4} \setminus$
$Al - SiO_4 \equiv Ca_3 \equiv SiO_4 - Al$	$Al - SiO_4 \equiv Al_2 \equiv SiO_4 - Al$
$\langle SiO_4 - Ca - SiO_4 \rangle$	$\searrow \operatorname{SiO}_4 = \operatorname{Ca}_2 = \operatorname{SiO}_4 \checkmark$
Aloh Aloh	Ca - O - Ca

Meionite

Vesuvianite

Epidote and its congeners, piedmontite, allanite and hancockite, are of course analogous to zoisite. As for meionite, the carbonate-meionite and sulphate-meionite of Borgström\* contain the atomic groups -Ca-CO<sub>3</sub>-Ca- and -Ca-SO<sub>4</sub>-Careplacing the groups -Ca-O-Ca- of the formula given here. Possibly a similar group -Ca-SiO<sub>3</sub>-Ca- may account for the excesses of silica shown in some analyses of meionite, which are not always ascribable to marialite.

We now see that melilite and gehlenite fall into place as members of a well-defined group of silicates of similar chemical constitution. Furthermore, they frequently occur in nature as products of contact metamorphism in limestones. That is. they have a common origin. Garnet, epidote, vesuvianite, and scapolites are well-known as associates in such rocks, and anorthite is sometimes found with them. Sarcolite and also vesuvianite are found in the ejected limestone blocks of Monte Somma; but prehnite, presumably a derivative of garnet, is exceptional. I do not find it recorded as an associate of the other species.

At Orawitza gehlenite is found in rolled pebbles containing grains of vesuvianite; and the Colorado melilite is associated with both garnet and vesuvianite, which are products of its alteration. The garnet is probably derived from its isomer, sarcolite; and the vesuvianite appears to be a basic derivative of the melilite silicate,  $Al_{a}(SiO_{a})_{a}Ca_{a}$ .

Anorthite alters into scapolite; vesuvianite and gehlenite to garnet; and garnet to epidote and scapolite. All of these minerals alter into micas, and the magnesian varieties into chlorites also. These facts all strengthen the argument that the several silicates which are considered here are intimately related both structurally and chemically. Their relations, moreover, can be clearly expressed in terms of a general theory.

In a considerable number of publications<sup>+</sup> issued during the past thirty years, I have shown that many of the aluminous silicates can be regarded constitutionally as substitution derivatives of the normal orthosilicate,  $Al_4(SiO_4)_3$ . This conception may be modified in form, but not in principle, by treating the silicates in question as salts of these alumosilicic acids,

> $Al_{a}(SiO_{a})_{3}H_{a}$ , trialic acid.  $Al_{3}(SiO_{4})_{3}H_{6}$ , dialic acid.  $Al_{i}(SiO_{i})$ ,  $H_{i}$ , unalic acid.

the numeral prefixes indicating the number of aluminum atoms in each compound. The names are proposed, not as positive contributions to nomenclature, but as devices to avoid circum-

\* Zeitschr. Kryst., liv, 238, 1914.
† For a summary of the whole subject see U. S. Geol. Survey, Bull. 588, 1916. The conclusions there given as to melilite and gehlenite are modified in this communication.

location in the following paragraphs. The acids themselves are not definitely known; but the first of the series may be represented by kryptotile, although that is not certain.

In the present discussion we have three fundamental compounds, corresponding with the three acids.

Anorthite is normal calcium trialate, and from it the basic silicate meionite is derived.

Garnet is normal calcium dialate, with sarcolite as an isomeric form. Prehnite is an acid, and zoisite a basic derivative of garnet.

The melilite silicate is normal calcium unalate, with vesuvianite and the gehlenite silicate as basic derivatives.

These three fundamental silicates seem to undergo alteration along parallel lines. Anorthite is altered to muscovite, a trialate, garnet into other dialates, such as biotite and the corresponding chlorites; and melilite *probably* follows the same rule. In short, nearly all of the orthosilicates which are characterized as aluminous can be represented as normal, acid, or basic salts of the three alumo-silicic acids. This rule has been sufficiently discussed in my previous publications, and needs no farther development here.

It is interesting to note that in abundance and stability the trialates outrank the other two series. Anorthite is the most abundant of the three calcium salts, and is the only one which can be recrystallized from fusion. Its corresponding mica, muscovite, is also the most abundant and the least alterable. Garnet, upon fusion, breaks down into a mixture of silicates, and anorthite is commonly one of them. The dialate mica, moreover, is easily alterable. As for the pure melilite silicate, its behavior as regards stability is not known, but it is the least abundant of the three calcium compounds. Nephelite, the sodium trialate, is very stable, easily synthesized, and alterable into muscovite. The normal sodium salts of the other alumosilicic acids are not known. Their high proportion of sodium would probably render them too easily alterable for permanence under geochemical conditions. The commonest unalates seem to be among the chloritic minerals, which are basic salts and easily decomposable.

In conclusion a word of caution is necessary. Formulæ such as have been developed in this paper are not to be taken as absolute representations of molecular structure. They are merely graphic expressions of known relations, and as such are legitimate and useful. They show the elementary atoms, moreover, as arranged upon a plane surface, but the true arrangement, the real molecular structure, should be tridimensional. Such an arrangement, which might correlate chemical relations with crystalline form, does not seem to be as yet possible. It may be developed in the future.

### SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. The Extraction of Potash from Silicate Rocks.-WILLIAM H. Ross of the U. S. Bureau of Soils found several years ago that when 1 part of feldspar and 3 parts of calcium carbonate were ignited for about an hour at a temperature of 1300-1400°, the potash was completely volatilized and the clinker which remained had a composition within the limits required for Portland cement. He observed also that when the lime was partly replaced by a quantity of calcium chloride equivalent to the alkalies in the feldspar the volatilization was completed in about onehalf of the time. From these results it was concluded that potash could be set free from feldspar by substituting it for clay in the manufacture of cement, and that it might be collected from the flue-dust. Moreover, since the ordinary materials used for cement manufacture contain some potash it was expected that its volatilization would take place in the usual process. This has been found to be the case, although the volatilization has been found to be only partial in most cases on account of the short time to which the clinker is exposed to the proper temperature, but in several plants the potash is now being collected with the flue-dust by electrical precipitation. The importance of this matter has led the author to study the various methods that have been proposed for the extraction of potash from feldspar, and to make further experiments. The patented processes relating to this subject now exceed 100 in number, and it is concluded that no process can be economically successful unless there is recovered at the same time some other product of value in addition to the potash. The most promising use of the by-product is for cement, since a vast quantity of this product is manufactured. The new experiments consisted in the first place of an attempt to decompose feldspar by means of water at high temperature and pressure, but at a temperature of 500° C. in a bomb at an estimated pressure of 1,450 atmospheres there was no decomposition. However, when the powdered feldspar was digested with water and 1.7 parts of lime at a steam pressure of 10-15 atmospheres about 90 per cent of the potash passed into solution in the form of hydroxide and the residue had the composition required for Portland cement clinker. Since the pressure here required can be safely produced in an ordinary boiler, the process is regarded as a promising one.-Jour. Indust. and Eng. Chem., is, 467.

H. L. W.

2. Preparation of Uranium Dioxide.—CHARLES L. PARSONS of the U. S. Bureau of Mines has devised a simple method for the manufacture of the black oxide of uranium from the sodium uranate obtained from carnotite ore at the Denver plant of the National Radium Institute. When uranium is extracted from its ores it is almost invariably obtained by precipitation in the form of sodium uranate, Na2U2O2. The process consists in melting at a red heat in an iron pot a mixture of 20 parts of the sodium uranate, 35 parts of common salt and one part of ground charcoal. After cooling, the material is treated with water which leaves the black oxide in the form of a powder while the salt dissolves. together with some sodium vanadate, as the sodium uranate obtained from carnotite contains this salt. The vanadium is saved by precipitation with iron sulphate. Several tons of the uranium oxide have been prepared in this way with the expectation that it will be useful in the manufacture of steel. Professor Parsons states that there appears to be no doubt that uranium steel is being used in Germany in some of the larger cannon, in which it is said to give improved rigidity at the high temperatures occasioned by rapid firing. Also that uranium has been proposed and, indeed, used to replace tungsten in tool steel, in which it is claimed that one per cent of uranium can successfully take the place of from 6 to 12 per cent of tungsten.-Jour. Indust. and Eng. Chem., ix, 456. H. L. W.

3. Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics; by WALTER NERNST. Fourth English Edition, Revised by H. T. TIZARD. 8vo, pp. 853. London, 1916 (The Macmillan Company, New York).-The first edition of this important work on physical chemistry appeared in 1893. The present English edition is based upon the seventh German issue. The translator says that the character of the work is slowly changing, since it is no longer possible in a book of this size to describe fully all the modern developments of theoretical chemistry, and that the new matter in this edition is concerned mainly with Dr. Nernst's own researches. These inevitable restrictions, however, will detract but little from the value of the book. The work is so well known in its many editions that no detailed description of it need be given here, but it may be stated that the work is very comprehensive in regard to theory, and that the treatment of the subject is extremely mathematical, so that it is particularly suited for the use of advanced students of physical chemistry. H. L. W.

4. A Text Book of Thermochemistry and Thermodynamics; by OTTO SACKUR; Translated and Revised by G. E. GIBSON. 8vo, pp. 439. London, 1917 (The Macmillan Company, New York).—There is no doubt that a thorough understanding of thermodynamics is of great importance in the study of physical chemistry, and this book gives a very well-arranged and able presentation of the subject in connection with thermochemistry. The student using it is expected to be a master of the fundamental principles of physics and chemistry, and to have some knowledge of the differential and integral calculus, but the more important chapters of the book will probably be intelligible without the mathematical knowledge. It appears that the translator has produced a very satisfactory English edition, and that he has made some desirable changes and additions in the text. H. L. W.

5. X-Ray Band Spectra.—Several years before Laue made the very important discovery that solid crystals may be used as threedimensional gratings for X-rays, the investigations of Barkla, Sadler, Whiddington and Kaye brought out the following facts. The coefficient of absorption of a given element for the characteristic *X*-radiations emitted by a series of elements, taken in the order of increasing atomic numbers, showed an abrupt and great increase when the incident radiation passed through the wavelength corresponding to the characteristic emission of the absorbing element. The coefficient maintained a high value for a certain interval and then decreased, as the frequency of the incident radiation increased. After Laue's discovery de Broglie showed (in 1914) that the photographic method could be most advantageously and conveniently applied to the study of the X-ray absorption bands of the chemical elements. It was only necessary to interpose a screen, made of a few decigrams of the absorbing medium, in the path of the direct rays from the anticathode, between the bulb and the slowly rotating crystal grating.

In two more recent papers DE BROGLIE gives the results obtained by applying this method to the K and L series, respectively. The incident radiations were produced by the tungsten target of a Coolidge tube, and a crystal of rock-salt  $(2d = 5.63 \times 10^{-8} \text{cm.})$  was used to analyze the rays transmitted by the screen. For the K series seventeen elements, from bromine to cerium, having smaller atomic numbers than tungsten, were investigated. The glancing angles for the edges of the bands are all tabulated, the values for the extreme elements, bromine and cerium, are given as 9° 20.5' and 3° 2', respectively. Six elements having greater atomic numbers than tungsten (platinum to bismuth) gave angles decreasing from 1° 31.5' to 1° 20'. The corresponding wave-length for bismuth was calculated to be  $1.3 \times 10^{-9}$  cm.

In the case of the L series one angle is given for each of the elements platinum and thorium, while two angles are recorded for gold, lead, and uranium. The glancing angles for "band I" were found to be 10° 55.5′ and 7° 20′ for platinum and uranium, in the order named. It is stated that each of these five elements has a third absorption band which is weaker and of slightly inferior wave-length to "band II." It thus appears that the L series involves a group of, at least, three bands. For the edges of homologous bands both in the K and in the L series Moseley's linear law was found to represent the experimental data satisfacfactorily.— Comptes rendus, clxii, pp. 87, 352, July and October, 1916.

6. Finite Collineation Groups; by H. F. BLICHFELDT. Pp. xi, 194. Chicago, 1917 (The Univ. of Chicago Press).—The theory of finite collineation groups (or linear groups) as developed so far is to be found mainly in scattered articles in mathematical journals and in a few texts on group theory. In the present volume the author has endeavored to give an outline of the different

AM. JOUR. SCI.—FOURTH SERIES, VOL. XLIII, NO. 258.—JUNE, 1917. 33 principles set forth in these publications while making use of a minimum of abstract group theory.

The elementary properties of linear transformations and linear groups are developed in the first chapter in such a manner as to require no previous knowledge of the technique of group theory. An introduction to the theory of groups of operators and substitution groups is given in the second chapter. The third, fifth, and seventh chapters deal with linear groups in two, three, and four variables, respectively. Chapter IV is entitled "Advanced Theory of Linear Groups" and it prepares the reader for a proper appreciation of the material presented in the later chapters. The theory of group characteristics (chapter vi) is developed in a very simple form by means of explicit definitions and easy proofs which avoid complicated sigma-constructions. The eighth and last chapter pertains to the history of linear groups, to Klein's extension of the Galois theory of equations, and to the connection between linear groups and linear differential equations having algebraic solutions. The value of the text is enhanced both by the appendix, which contains statements in explicit form of certain definitions and theorems from advanced algebra needed throughout the book, and by the inclusion of 115 exercises for solution by the student.

H. S. U.

#### II. GEOLOGY AND MINERALOGY.

1. Thirty-seventh Annual Report of the Director of the United States Geological Survey; by GEORGE OTIS SMITH. Director. Pp. 185, 2 pls., 1916.—The United States Geological Survey ranks first among geologic organizations as an agency in developing the nation's resources, as a body of instructors and students, and as a research institution. The Director's annual report is therefore of large interest. During the year 1915-1916 geologic investigations were made in 47 states, Alaska, the Canal Zone, and the West Indies, covering 54,000 square miles; 33,000 square miles were mapped by topographers, and 32,000,000 acres of land were classified. The total number of pages in publica-tions for the year was 19,722 and included 210 new books and pamphlets, 33 reprinted books, 6 new geologic folios, and 230 topographic maps. The demand for the Survey publications is shown by the record of distribution for the year: 603,575 books, 23,534 folios, and 597,149 maps. Nearly 400,000 maps were sold. In addition to its regular work the Survey prepared and published maps for more than 40 government bureaus and departments. The widespread influence of the Survey is indicated by the work of the division of mails which received 255,504 letters and sent out 436,806 pieces of mail during the year-an increase of 12 per cent over 1915. The roll of secretary's appointees numbered 872, and the chief items of expenditure in the appropriation of \$1,355,000 were geologic surveys and geologic maps, \$460,000; topographic surveys, \$350,000; water resources, \$150,000; resources of Alaska, \$100,000; mineral resources of the United States, \$75,000. Special features of the Survey's activity are the discovery and development of new oil fields, the zealous search for potash-particularly in the "Red Beds" of the Southwest-, the completion of fundamental studies by G. K. Gilbert on erosion and sedimentation involved in the problem of California mining debris, and the enlargement of the scope of the committee on physiography. H. E. G.

2. Publications of the United States Geological Survey, GEORGE OTIS SMITH, Director.—Further publications of the Survey (see also pp. 418, 419 of the May number) are noted below:

GEOLOGIC ATLAS, FOLIOS.-No. 202. Eureka Springs-Harrison Folio, Arkansas-Missouri; by A. H. PURDUE and H. D. MISER. Pp. 21; 2 pls. topography, 2 pls. areal geology, 1 pl. structure sections, 13 text figs.

No. 204. Tolchester Folio, Maryland; by B. L. MILLER, E. B. MATHEWS, A. B. BIBBINS and H. P. LITTLE. In coöperation with the State of Maryland. Pp. 14; 1 pl. topography, 1 pl. areal geology, 1 pl. columnar sections, 1 page of illustrations, 3 text figs.

PROFESSIONAL PAPERS.-No. 98. Shorter Contributions to General Geology, 1916, Parts Q-T, pp. 279-395.

The Inorganic Constituents of Marine Invertebrates; No. 102. F. W. CLARKE and W. C. WHEELER. Pp. 56 (noticed on p. 419).

No. 103. Brachyceratops: A Ceratopsian Dinosaur from the Two Medicine Formation of Montana; with notes on associated Fossil Reptiles; by C. W. GILMORE. Pp. 45; 4 pls., 57 figs.

No. 108. Shorter Contributions to General Geology, 1917, parts A, B, pp. 1–29.

MINERAL RESOURCES. 1915, Parts I, II. Numerous advance chapters.

BULLETINS.-No. 624. Useful Minerals of the United States; compiled by FRANK C. SCHRADER, RALPH W. STONE, and SAMUEL SANFORD. Revision of Bulletin 585. Pp. 412.

Nos. 640, 641. Contributions to Economic Geology, 1916. 640, Part I. J, K, L; 641, Part II. F, I, J, K, L.

Triangulation and Primary Traverse, 1913-1915; No. 644. R. B. MARSHALL, Chief Geographer. Pp. 655; 2 pls. No. 650. Geographic Tables and Formulas. Fourth edition;

compiled by SAMUEL S. GANNETT. Pp. 388, 8 figs.

No. 661. Contributions to Economic Geology, 1917, Part II. A. WATER SUPPLY PAPERS.—Surface Water Supply of the United States; NATHAN C. GROVER, Chief Hydraulic Engineer. No. 361. 1913, Part XI. Pacific Slope Basins in California. Pp. 514, 2 pls., 1 fig.-No. 392. 1914, Part XII. North Pacific Drainage Basins: A. Pacific Drainage Basins in Washington and upper Columbia River Basin. Pp. 200.-No. 402. 1915, Part II. South Atlantic and Eastern Gulf of Mexico Basins. Pp. 51 with appendix; 2 pls.-No. 407, 1915, Part VII. Lower Mississippi River Basin. Pp. 43 and appendix; 2 pls.

No. 380. The Navajo Country: A Geographic and Hydrographic Reconnaissance of parts of Arizona, New Mexico, and Utah; by HERBERT E. GREGORY. Pp. 208; 29 pls., 29 figs.

Profile Surveys, prepared under the direction of W. H. HERRON, acting Chief Geographer. No. 398, Colorado River Basins in Wyoming, Utah, Colorado and New Mexico. Pp. 6; pls. 43.— No. 417, Rivers in Wisconsin. Pp. 16; 32 pls.—No. 419, Skagit River Basin, Washington. Pp. 8, 12 pls.—No. 420, Henry's Fork, Idaho, and Logan River and Blacksmith Fork, Utah. Pp. 8, 10 pls.—No. 421, Rio Grande, Peco River and Mora River, New Mexico. Pp. 11; 11 pls.

No. 415. Surface Waters of Massachusetts; by C. H. PIERCE and H. J. DEAN. Pp. 433; 12 pls., 6 figs.

No. 416. The Divining Rod: A History of Water Witching; with a bibliography; by ARTHUR J. ELLIS. Pp. 53; 4 figs.

3. Report of the State Geologist on the Mineral Industries and Geology of Vermont, 1915-1916; G. H. PERKINS, State Geologist. Pp. xii, 333, 9 figs., 74 pls.—Papers chiefly of local and economic interest are: The Geology of Western Vermont, List of Altitudes in Vermont, by G. H. Perkins; The Lime Plant of the Vermont Marble Company, by H. L. Smith; Copper Mining in Vermont, The Talc and Serpentine Deposits of Vermont, by E. C. Jacobs; The Physiography of Greensboro, Hardwick and Woodbury, by Daniel P. Jones; The Serpentines of Vermont, by E. Wigglesworth (previously published in Proc. Boston Soc. Nat. Hist., vol. 35, pp. 95-107, 1915); and Mineral Resources, by G. H. Perkins. Prof. H. L. Fairchild contributes a paper on Post Glacial Marine Waters in Vermont, in which the uplifted marine plane and other marine features are discussed, and detailed areal description given of eleven districts in the Champlain-St. Lawrence area.

The map of the uplifted marine plane is extended southward across New England and westward into New York. In Vermont "the initial or summit water-plane now lies between 400 and 800 feet above tide." The relation of the marine invasion to the terraces in Connecticut Valley and to the ancient glacial lakes of central and northern Vermont is also pointed out. In a paper, "Evidence for and against the Former Existence of Local Glaciers" in Vermont, J. W. Goldthwait reaches the conclusion that "it is very unlikely that local glaciers ever existed " in the Green Moun-Prof. C. H. Richardson, who has been making a study of tains. the eastern flanks of the Green Mountains, contributes a paper on the geology of Calais, East Montpelier, Montpelier and Berlin. An erosional unconformity separating Cambrian and Ordovician metamorphosed sediments, discovered at Irasburg in 1904, has been traced from Northfield into Canada. The discovery of 33 beds of graptolites in sediments heretofore considered unfossiliferous fixes the age of certain limestones and slates in eastern Vermont as Ordovician (Deepkill to Lower Trenton). H. E. G.

4. Illinois Geological Survey; FRANK W. DEWOLF, Director. Bulletin 33, pp. 180, 15 figs., 10 pls, 1916.—The Administrative Report of the State Geological Survey for the fiscal year 1915, Bulletin 33, gives an account of a large amount of work on coal, oil and gas, clay, ground water, drainage, topographic mapping, and educational bulletins. Coöperation with the Federal Geological Survey, the Bureau of Mines, the State University, and various coal and oil companies is an important phase of the State Survey's activities, and has resulted in extensive stratigraphic studies by Professor Weller, Professor Savage, and Mr. Rich, and economic studies by Fred H. Kay, G. H. Cady, Professor Parr, Professor Stull, C. B. Anderson, and others. The Year Book for 1915 includes papers on Mineral Resources of Illinois, by H. J. Skewes; Petroleum in 1914 and 1915, by Fred H. Kay; Geologic Structure of Canton and Avon quadrangles, by T. E. Savage; Notes on Bremen Anticline, by Fred H. Kay; Oil and Gas in Birds and Vincennes quadrangles, by John L. Rich.

The Survey has recently issued : Oil Investigations in Illinois in 1916, by Fred H. Kay, Albert D. Brokaw, Stuart St. Clair, and Charles Butts, Bulletin No. 35, 1917, 80 pp., 12 figs., 9 pls.; Clay Deposits near Mountain Glen, Union County, Illinois, by Stuart St. Clair, extract from Bulletin 36, 1917, 15 pp., 2 figs. Four reports of the Coöperative Coal Mining Series have also appeared : Surface Subsidence in Illinois resulting from Coal Mining, by Lewis E. Young, Bulletin 17, 1916, pp. 112, 56 figs., 4 pls. Tests on Clay Materials available in Illinois Coal Mines, by R. T. Stull and R. K. Hursh, Bulletin 18, 1917, pp. 130, 62 figs. Chemical Study of Illinois Coals, by S. W. Parr, pp. 86, 10 pls. Coal Resources of District VI, by G. H. Cady, pp. 94, 7 pls., 25 figs. H. E. G.

5. Geology and Economic Deposits of a Portion of Eastern Montana; by J. P. RowE and R. A. WILSON. State Univ. Montana Studies, Series No. 1. Pp. 61, 27 figs., 4 pls.—The stratigraphic and economic geology of 6,800 square miles on the eastern border of Montana has been described in detail. The groups of sedimentary rocks present are the Fort Union formation (Tertiary) 300 to 1200 feet, with the Lebo shale 0 to 340 feet; the Lance formation (Cretaceous or Tertiary) 450 to 550 feet, including the Colgate sandstone 90 to 175 feet; and 300 feet of the Pierre shale (Upper Cretaceous). The lignites in the Fort Union and Lance beds of the area studied reached the enormous total of 75,600,632,820 tons, an estimate which takes into account only beds 36 inches or more in thickness. H. E. G.

6. A Preliminary Report on the Alkali Resources of Nebraska; by ERWIN H. BARBOUR. Nebraska Geol. Survey, vol. 4, pt. 28, pp. 405-438, 21 figs.—A few of the many alkali lakes of northwestern Nebraska carry important amounts of potash in addition to soda. Practically all of these lakes have been mapped and their water analyzed. The source of the potash now being obtained from Jess Lake, near Alliance, is ascribed to the local vegetation. H. E. G.

7. Recent and Fossil Ripple-Marks; by E. M. KINDLE, Canada Dept. Mines, Geol. Survey, Mus. Bull. 25, 1917, pp. vi, 56, 64 pls., 7 figs.—During three field seasons Dr. Kindle has studied and mapped and measured ripple-marks in shallow water, deep water in lakes and rivers and ocean bays, and in wind-laid materials. These ripple-marks are classified and the origin of the various types is explained. The results constitute a contribution of high value for the interpretation of the physiography of ancient sedimentary formations. The significance of fossil ripples in different geologic formations, the distinction between ripples in marine and lacustrine sediments, and the relation of ripples to ancient shore lines are discussed. Numerous references to the literature and the 64 photographic figures increase the value of this helpful study. H. E. G.

8. The State of the Ice in the Arctic Seas; by C. I. H. SPEERSCHNEIDER.—Two special prints, Nautical Meteorological Annual, Danish Meteorological Institute, 1916, 1917. Pp. 16, 5 maps and pp. 25, 5 maps, resp.—The position and character of ice in the arctic seas during the months April, May, June, July, August, 1916, have been described and mapped by Commander C. I. H. Speerschneider. In a separate publication the records of observations for the period 1898-1913 are summarized and charts constructed to show the average position of the ice, the outer limit of the ice drift, and the relation of the inner edge to The maximum and minimum ice limits for the the shore. months are indicated. The period 1898-1904 records the least ice, and the ice-covered area in 1904 was the smallest since 1877. For Barents Sea the lowest figures are those for 1898, 1904, and 1905. It is worthy of note that 1903-5 was a period of maximum sun spots. H. E. G.

9. Annual Report of the Government Geologist of South Australia for 1915; by L. KEITH WARD, Government Geologist. Pp. 18, 2 figs.—During 1915 the two geologists constituting the staff of the South Australian Survey were engaged chiefly in reporting on mineral deposits and water supplies in many and widely separated localities. The Government Geologist calls attention to the need of a comprehensive study of the mineral resources of the State and of the appointment of an officer charged with investigation of water supplies. The discovery of precious opal at Stuart's Range is announced, and short papers on drainage of Dismal Swamp by natural underground channels, on subartesian water at Mallala, on ground water at Payneham, aud on building stones are presented. H. E. G.

10. The Efficient Purchase and Utilization of Mine Supplies; by HUBERT N. STRONCK and JOHN R. BILLYARD. Pp. 97. New York (John Wiley & Sons, Inc.).—In this time when economy and efficiency are being demanded, it is well that the stores department of the industries devoted to mining and smelting should be especially discussed. The expense involved is necessarily large, and as those trained for mining have often no special business knowledge, considerable waste may occur. This brief but careful presentation of the subject with many useful and practical suggestions, should be of value to those concerned. 11. The Ordovician and Silurian Brachiopoda of the Girvan District; by F. R. C. REED. Trans. Royal Soc. Edinburgh, vol. li, Pt. IV, 1917, pp. 795–998, pls. 1–24.—In this good and up-todate revision of the brachiopods of the Girvan district of Scotland 230 species and varieties are treated, and of these 70 are new. Of new genera there are the orthids Schizophorella, Nicolella, and Harknessella; of strophomenids Playfairia; of pentamerids Metacamarella; and of chonetids Eochonetes.

Even though the species are predominantly peculiar to Girvan, the brachiopod development of the Stinchar (has 60 forms) and Balclatchie (70) divisions correlates best with that of the Mohawkian series of the Appalachian Mountains. No significant forms, however, are common to these two widely separated areas and entire groups of shells are absent in America. The Whitehouse (34) and Drummuck (40) divisions correlate with the Richmondian of eastern North America, and this is best seen in the introduction here of *Rhipidomella*, *Bilobites*, *Schuchertella*, *Eochonetes*, *Triplecia insularis*, *Dayia* and *Atrypa*. There is therefore in the Girvan area, as elsewhere in Europe, a great break between the Balclatchie and Whitehouse formations.

The Silurian in the Mulloch Hill (29) and Saugh Hill (42) divisions appears to correlate best with the earliest American division, the Medina-Cataract series. On the other hand, these two Girvan faunas have of American Clinton forms *Stricklandinia* lens and lirata, Streptis, Rhynchotreta cuneata, Atrypa reticularis, Rhynchospira and Eichwaldia. The highest divisions, Camregan (27) and Penkill (25), appear to be of the age of the Clinton because of the presence of Cælospira hemispherica. C. S.

12. Notes on Cincinnatian Fossils; by AUG. F. FOERSTE. Bull. Sci. Lab. Denison Univ., vol. xviii, 1916, pp. 285-355, pls. 1-7.—Here are described and illustrated the type specimens of 48 species, of which 4 are new to paleontology. Of new genera there are *Caliculospongia*, *Carneyella* and *Isorophus*; the first is a sponge and the others are agelacrinids. C. S.

13. New Mineral Names; by W. E. FORD (communicatedcontinued from vol. xlii, pp. 504-505, December, 1916):-

**Craudallite.** G. F. Loughlin and W. T. Schaller, this Journal, xliii, 69, 1917.—In compact to cleavable masses without distinct crystal outline. Microscopically fibrous. Apparently an alteration from a non-fibrous mineral similar to goyazite, to which the platy structure belonged. Color white to light gray with shadings into yellow or brown. Luster dull to pearly. Nearly opaque in hand specimen but transparent in small fragments. Refractive indices 1.585 to 1.595. Birefringence from 0 to 0.01. B. B. decrepitates somewhat, exfoliates slightly and fuses to a white enamel. In C. T. decrepitates and gives water. Sol. in acids. Comp.—2CaO.4Al<sub>2</sub>O<sub>3</sub>.2P<sub>2</sub>O<sub>5</sub>.10H<sub>2</sub>O (similar to gorceixite). Found at the Brooklyn mine,  $1\frac{1}{4}$  miles east of Silver City, Utah, associated with quartz, barite and tenorite. Named after Mr. M. L. Crandall of Provo, Utah.

Ferroludwigite. See under Magnesioludwigite.

**Griffithite.** E. S. Larsen and George Steiger, J. Wash. Ac. Sc., vii, 11, 1917.—A member of the Chlorite Group. Color, dark green. H. = 1. Sectile. G = 2.309. Fusible at 4 with intumescence to a black magnetic slag. Has usual cleavage of chlorites. Occurs in basal plates and shreds up to 1<sup>mm</sup> across. Optically —. 2V from 0° to 40°. a  $\perp$  to cleavage. Strong birefringence. Pleochroic; a pale yellow, b olive-green, c browngreen.  $a = 1.485 \pm .01$ ,  $\beta = 1.569 \pm .005$ ,  $\gamma = 1.572$ ,  $\pm .005$ . Comp.  $-4(Mg,Fe,Ca)O.(Al,Fe)_2O_3.5SiO_2.7H_2O.$  Occurs filling amygdaloidal cavities in a basalt from Cahuenga Pass, Griffith Park, Los Angeles, Cal.

**Lorettoite.** R. C. Wells and E. S. Larsen, J. Wash. Ac. Sc., vi, 669, 1916.—Tetragonal? Occurs in masses made up of coarse fibers or blades. Perfect basal cleavage. G. = 7.6. H. = 3. Fusible at 1 to a yellow crystalline bead. Easily soluble in hot dilute nitric acid. Color honey-yellow. Adamantine luster. Streak pure yellow. Uniaxial, —.  $\omega_{Li} = 2.40$ ,  $\epsilon_{Li} = 2.37$ . Comp. —Probably 6PbO.PbCl<sub>2</sub>. Found in flat, compact pieces up to an inch thick, apparently occurring in thin seams. From Loretto, Tenn. A specimen in the collection of the University of California from an unknown locality has similar characters.

**Magnesioludwigite.** B. S. Butler and W. T. Schaller, J. Wash. Ac. Sc., viii, 29, 1917.—A preliminary announcement. Color, ivy-green. Comp., MgO.Fe<sub>2</sub>O<sub>3</sub>.3MgO.B<sub>2</sub>O<sub>3</sub> with a small amount of ferrous oxide (2.55 per cent) replacing some of the magnesia. Differs from ordinary ludwigite in having a duller luster, lighter color, weaker pleochroism and absorption and greater translucency. Found associated with ludwigite, forsterite and magnetite at the Mountain Lake mine at the head of Big Cottonwood Canyon, south of Brighton, Utah.

Suggestion is made that the name ludwigite be used as the name of a group, having the following members:

Ferroludwigite,	FeO.Fe <sub>2</sub> O <sub>3</sub> .3MgO.B <sub>2</sub> O <sub>3</sub>
Magnesioludwigite,	MgO.Fe,O,.3MgO.B,O
Pinakiolite,	MnO.MnO.3MgO.BO

**Spencerite.** A brief extract from the description by A. H. Phillips was given in the previous list. The original description, not at that time available, was by W. T. L. Walker, Min. Mag., xviii, 76, 1916. Additional facts to be noted are as follows: Probably monoclinic. Cleavage, 100 perfect, 010 and 001 good.  $\beta_{\text{Na}} = 1.6092$ .  $2V = 47^{\circ} 54'$ . Optically —.  $Bx_{\text{ac}} \perp 100$ . Low birefringence. Dispersion  $\rho > v$ . In thin section shows polysynthetic twinning on 100 with extinction of about 6°. Named after Mr. L. J. Spencer of London.

#### III MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. National Academy of Sciences.-The annual meeting of the National Academy was held at the Smithsonian Institution in Washington on April 16, 17, and 18, and was highly successful in all respects. The names of gentlemen elected to membership and the titles of papers presented are given below. Dr. William H. Welch having retired as president, Dr. Charles D. Walcott was elected to fill this office for a term of six years; Prof. A. A. Michelson was also elected Vice President for a like period. At the annual dinner of the Academy on the 17th, the Henry Draper gold medal was presented to Professor Michelson and the Public Welfare medal to Dr. S. W. Stratton. Two public lectures on the William Ellery Hale foundation were delivered by Prof. E. G. CONKLIN; the subject of these lectures was "Methods and Causes of Organic Evolution."

The following gentlemen were elected to membership: Edward Kasner, of Columbia University, Wallace C. Sabine, of Harvard University, Edward O. Ulrich, of the U.S. Geological Survey, Washington, William F. Durand, of Stanford University, Samuel W. Stratton, of the Bureau of Standards, Washington, Theodore Lyman, of Harvard University, Edward L. Thorndike, of Columbia University, William S. Halsted, of the Johns Hopkins Medical School, Baltimore.

The titles of papers presented are as follows:

J. P. IDDINGS and E. W. MORLEY: Report of progress in the study of igneous rocks from the East Indies and Islands of the South Pacific.

W. M. DAVIS: The Great Barrier Reef of Queensland, Australia.

CHARLES D. WALCOTT: Searching for a doubtful geological zone in the Canadian Rockies.

ARTHUR L. DAY: The rôle of the gases in volcanic activity. W. A. NOYES: A kinetic hypothesis to explain the function of electrons in the chemical combination of atoms.

A. A. MICHELSON: Some recent work in physics.

W. B. CANNON: Some considerations regarding the nature of thirst.

ERWIN F. SMITH: On resemblances of Crown Gall to Cancer: A synopsis of work done in the United States Department of Agriculture.

R. J. ANDERSON and GRAHAM LUSK: The influence of diet upon the heat production during mechanical work in the dog.

JACQUES LOEB and J. H. NORTHROP: What determines the natural duration of life?

SIMON FLEXNER: Mechanisms that defend the body from poliomyelitic infection. (a) external or extranervous, (b) internal or nervous. T. S. GITHENS and S. J. MELTZER: The difference in the action of anti-

pyretics according to the species of animals subjected to this action, the state of health of the animals, the height of their normal temperature and the substance employed.

CHARLES B. DAVENPORT: Heredity and juvenile promise of eminent naval men.

HENRY FAIRFIELD OSBORN: The causes of the evolution of proportions by mammals.

W. V. KING: Sporogony of malaria parasites. Photomicrographs of infected anopheles.

FRANK R. LILLIE: Sex-determination and sex-differentiation in mammals. HERBERT J. SPENDEN: Economic contributions of ancient America.

SYLVANUS G. MORLEY: The Maya hieroglyphic writing.

E. E. BARNARD: (1) The star in Ophiuchus with great proper motion. (2) Total lunar eclipse of January 7, 1917. (3) Measures of the position of the nucleus of the great nebula of Andromeda.

EDWIN B. FROST: Recent remarkable changes in a nebula.

A. G. MAYER: Biographical memoir of William Stimpson.

BENJAMIN Boss: Biographical memoir of Lewis Boss.

2. State Sanitation, A Review of the Work of the Massachusetts State Board of Health; by GEORGE CHANDLER WHIPPLE. Vol. I. Pp. xi, 377. Cambridge, 1917 (Harvard University Press).—The development of public health in America is closely bound up with the history of the State Board of Health of Massachusetts. The report of the Massachusetts Sanitary Commission of 1850 and the report of the Massachusetts Drainage Commission of 1885 are classic documents in the literature of sanitation. The researches on water purification and sewage purification begun at the Lawrence Experiment Station in 1887 underlie modern practice in these arts all over the world. The services of the unpaid Board which has directed the work has been as inspiring from the standpoint of good citizenship as the scientific work of the staff has been fruitful in practical results.

Prof. G. C. Whipple, Professor of Sanitary Engineering in Harvard University and the Massachusetts Institute of Technology and a member of the present Public Health Council of Massachusetts, has told the story of this development in the present volume and duly commemorated the services of Lemuel Shattuck, Henry I. Bowditch, Henry P. Walcott, Hiram F. Mills, X. H. Goodnough, William Ripley Nichols, Ellen H. Richards, Thomas M. Drown, William T. Sedgwick and its other leaders. He has at the same time given us an illuminating discussion of most of the fundamental principles of "state sanitation" as they are involved in and suggested by the historical review.

The present volume includes a full reprint of the memorable Report of the Massachusetts Sanitary Commission of 1850. Volume II will consist of reprints and abstracts of articles published in the Annual Reports and special bulletins and reports of the State Board of Health between 1870 and 1914; while Volume III will contain an exhaustive Index-guide to the forty-six annual reports of the Board and a series of biographical sketches of the distinguished members of its scientific staff.

#### C.-E. A. WINSLOW.

The American Year Book: A Record of Events and 3. Progress, 1916; edited by FRANCIS G. WICKWARE. Pp. xviii, 862. New York (D. Appleton and Company), 1917.-This is the seventh volume of the American Year Book and it appears under the auspices of a Supervisory Board of some forty members, all men of prominence; the list of contributions includes about one hundred and twenty names. Unlike most annual publications, it is not statistical or personal in character, but gives a summary of the important steps of the progress in the

different lines of public interest. About half the volume is given to topics relating to history, to Government relations abroad and at home, to finance, and to social and economic problems, including labor and labor legislation. The latter part of the volume takes up different branches of science, art and literature, also religious and educational matters. A full index covering thirty pages, and conveniently printed on tinted paper, makes the numerous topics discussed, many of them very briefly, easily accessible to the reader.

4. Explorations and Field-Work of the Smithsonian Institution in 1916. Pp. 134 with a folded plate as frontispiece and many text figures. Washington, 1917 (Smithsonian Miscellaneous Collections, vol. 66, No. 17).—This recent publication is made particularly attractive by a wealth of beautiful illustrations. It goes over the entire field of the explorations carried on by the Smithsonian in the past year, the lines of which are so numerous that each topic can be treated only briefly. The opening chapter by Dr. Walcott, with its large number of beautiful mountain views taken by him in the Canadian Rockies, is particularly interesting; this is also true of the account of the botanical exploration of the Hawaiian Islands, and indeed of many other sections of the volume.

Other publications received from the Smithsonian include the following:

Thirty-first Annual Report of the Bureau of American Ethnology to the Secretary of the Smithsonian Institution, 1909– 1910. F. W. Hodge, Ethnologist-in charge. Pp. 1037. The administrative report (pp. 1-26) is followed by an exhaustive monograph of a thousand quarto pages on Tsimshian Mythology by FRANZ BOAS, based on texts recorded by Henry W. Tate. Pp. 27-1037, pls. 3, figs. 10.

Pp. 27-1037, pls. 3, figs. 10. Bureau of American Ethnology Bulletin 55. Ethnobotany of the Tewa Indians; by WILFRED W. ROBBINS, JOHN P. HARRING-TON, and BARBARA FREISE-MARRECO. Pp. xii, 124; 9 pls., 7 figs.

The Determination of Meteor-Orbits in the Solar System; by G. von NIESSE (translation by the late Cleveland Abbe). Pp. 35. (Misc. Collections, vol. 66, No. 16.)

#### **OBITUARY.**

ARNOLD HAGUE, the geologist, one of the staff of the U.S. Geological Survey since 1879 and earlier (1867–1877) a member of the Survey of the 40th Parallel, died at his home in Washington on May 14th in his seventy-seventh year. A notice is deferred to a later number.

GEORGE MASSEE, the English mycologist, died on February 17 at the age of sixty-six years.

JEAN GASTON DARBOUX, the eminent French mathematician and professor in the Sorbonne, died in February at the age of seventy-five years.

R. H. TIDDEMAN, of the Geological Survey of Great Britain, died on February 20 at the age of seventy-five years. Α

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