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FOURTH SERIES

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WITH PLATE I.

NEW HAVEN, CONNECTICUT.

1917.

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THE
AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. I.—*The Motion of Ions and Electrons through Gases;* by E. M. Wellisch, Lecturer in Applied Mathematics at the University of Sydney.

1. Introduction.

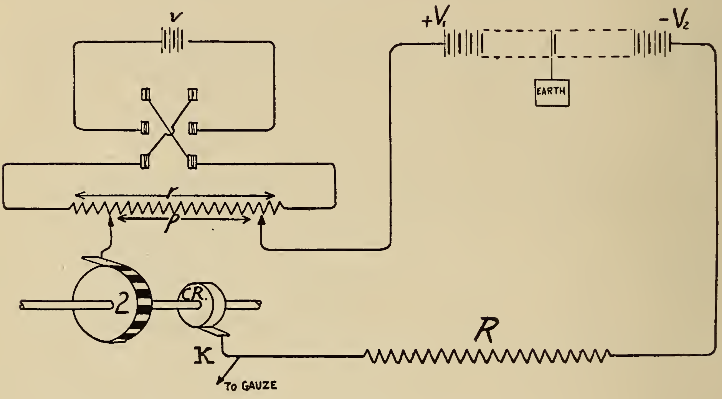
The experiments described in the present paper were carried out in the Sloane Laboratory of Yale University and are a continuation of those which have already been described in this Journal (May, 1915). In determining the mobility (k) of the ion as a function of the pressure (p) of the gas, previous investigators had found that the product pk showed an abnormal increase as the pressure of the gas was reduced. This result had been interpreted as indicating a diminution in the size and mass of the ion at relatively low pressures; for the negative ion in air this diminution appeared to set in at pressures below 10^{cm} while for the positive ion it did not occur till the pressure was reduced below 1^{mm}.

The investigation to which reference has already been made provided experimental and theoretical indications which were entirely different from the foregoing. For the positive ion in air no anomalous results were found; the law $pk =$ const. held good to the lowest pressure employed ($\cdot 05^{mm}$). The negative carriers were found to consist of two distinct kinds, electrons and ions, the former coming more and more into evidence as the pressure of the gas was reduced. When once this separation had been effected all the preceding anomalies disappeared; the law $pk =$ const. was verified for the negative ion in air from 1 atmosphere down to $\cdot 15^{mm}$, indicating that the ion remains unaltered in character over this range of pressures. The electrons appeared to travel freely through the gas without attaching themselves to molecules. No indication was found of any intermediate stage in the nature of the negative carrier, the separation between the ions and the electrons remaining throughout clearly marked.

In the present experiments these results have been extended to other gases; in accordance with expectation the abnormal mobility values found by previous investigators for the negative ions in hydrogen and carbon dioxide were shown to be capable of a similar explanation, all anomalies disappearing as soon as the resolution of the carriers into ions and electrons was effected.

A brief study has been made of the motion of free electrons through carbon dioxide at relatively high pressures; in addition, the motion of ions through a number of vapors has been investigated.

Fig. 1.



A few discussions bearing upon the physical interpretation of the results have been included; in particular, certain outstanding problems of ionic theory have been specially considered.

2. Experimental Method and Arrangement.

A description of the experimental method and apparatus has already been published; on this account it seems advisable to repeat here only the essential features, reference being made to the previous paper for further details. Moreover advantage will be taken here to enter into greater detail in connection with certain features of the method to which only a brief allusion was previously made.

The method employed in the determination of the mobilities was that devised by Franck and Pohl.* The ionization vessel

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* Franck and Pohl, Verh. Deutsch. Phys. Ges., ix, p. 69, 1907.

(*v.* fig. 2) consisted of a brass cylinder divided into two compartments by a brass partition containing a circular aperture. In the upper compartment was a copper plug on which a layer of polonium had been deposited; great care was taken that the radiation from the polonium was confined to the upper compartment. A circular electrode A was situated about 3^{cm} above the aperture and was in metallic communication with the case of the vessel. The lower compartment contained a gauze electrode insulated by a thin ebonite ring from the partition. Two cm. below the gauze was the electrode e connected to the electrometer; this electrode was surrounded by a guard screen (W) connected to earth by means of a guard tube.

Fig. 1 illustrates the method employed to effect the commutation of potential. The commutating discs were of brass with a number of fiber segments of equal width placed at regular intervals along the periphery. The two potentials V_1 and $-V_2$ were connected across the terminals of a large metal resistance R in series with the commutator; it was not in general convenient to alter the potential V_1 except in steps of 40 volts each, and on this account the potentiometer device (v, r, ρ) was employed to effect finer gradations of potential.

When the commutator is in action the potential of K (fig. 1) should alternate between x and $-V_2$ where

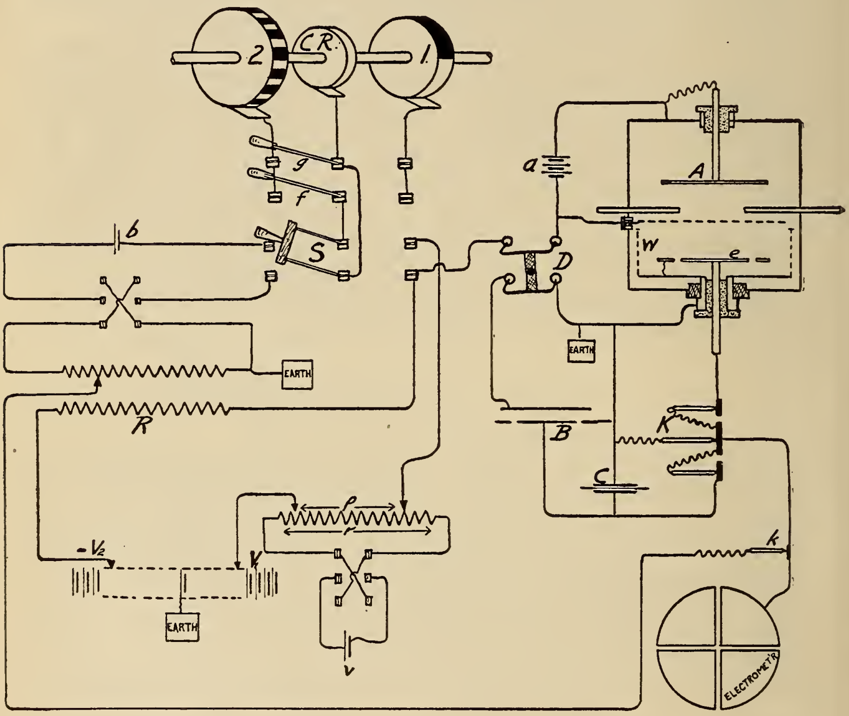
$$x = -V_2 + R\frac{v\rho + r(V_1 + V_2)}{\rho r + Rr - \rho^2} \qquad (1)$$

Owing, however, to the time involved in the establishment of potential this formula will be sufficiently valid only if care be taken to maintain a satisfactory relation between the frequency of commutation and the resistance R. This was effected by an experimental method described later. We shall assume here that the potential of the gauze is given by x and $-V_2$ alternately, the former potential lasting for a fraction f of the total time; this fraction can be determined experimentally. Under these conditions the mobility k of the ion under consideration is given by $k = \frac{d^2 n}{f V_0}$, where n is the number of complete alternations per second, d is the distance between the gauze and the electrode e, and V_0 is the critical potential, *i. e.* the value of x which is just sufficient to enable the ions to reach the electrode e before the field is reversed.

The diagram of connections is exhibited in fig. 2. As in the previous experiments two commutating discs were employed; one of these had 20 fiber segments while the circumference of the other was half fiber and half metal. The motor was worked generally on 110 volts which afforded approximately 42 revolutions per second.

The double-pole, double-throw switch S, when thrown to the right, completed the connections as exhibited graphically in fig. 1. When thrown to the left, connection was made with a subsidiary potentiometer system (*b*); in this position the quadrants of the electrometer could be commutated in potential between zero and any convenient potential read off on the potentiometer. The use of this device in testing the contact at the brushes, in estimating the value of *f*, the fractional duration of contact, and in adjusting the position of the electrometer needle for observations, has been described in the previous paper.

Fig. 2.



For large current values readings were taken with the capacities B and C added to the electrometer system; the capacity of the system was then increased $17\frac{1}{2}$ times.

3. Experimental Procedure.

For convenience in manipulation a table was prepared of the potentials assumed by the gauze for different values of ρ,

V_1, V_2 and R. This was effected by means of formula (1) which for the purpose was put in the following form:—

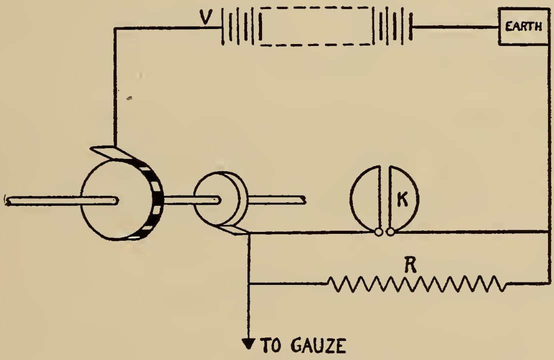
$$\begin{aligned} x &= V_1 + \left[\frac{\rho v}{r} - \left(V_1 + V_2 + \frac{\rho v}{r} \right) \left\{ \frac{\rho (r-\rho)}{\rho (r-\rho) + R r} \right\} \right] \\ &= V_1 + c \text{ (say).} \qquad (2) \end{aligned}$$

v was always chosen equal to 40 volts and r was always 15,000 ohms. The calculated values of c for various values of ρ and $V_1 + V_2$ were then tabulated and the value of x under any desired conditions could be quickly obtained.

Establishment of Potential.

It was important to ascertain that the experimental conditions admitted of an effectively instantaneous establishment of the withdrawing potential $-V_2$ through the resistance R; in other words, the ions must commence to retire as soon as the commutator brushes make contact with the fiber segments. This point was tested experimentally in the following manner: the commutator and resistance R were put in series with a battery V (fig. 3) of which one terminal was earthed; K represents a Kelvin multicellular electrostatic voltmeter which was included in the manner shown in the diagram. The commutator was set in motion at its highest speed and readings were taken on the voltmeter corresponding to different values of R. If the values of R were excessively large there would not be sufficient time during an alternation to admit of the earth connection with the gauze being fully established and in consequence the steady reading of the voltmeter would be too large. It was found that when the small frequency comutator was employed this steady reading remained constant for values of R up to 1,000,000 ohms; for the high

FIG. 3.



frequency commutator the value R = 200,000 afforded a reading greater than the normal by less than 2 per cent. Inasmuch as the potential (V_2) was always chosen considerably greater numerically than the advancing potential (x) the value R = 200,000 was sufficient to ensure the realization of the desired conditions. In the present series of experiments this value of R was chosen in preference to a smaller value because in the determination of electron velocities V_1 is often small and it is advisable to have c in formula (2) small compared with V_1.

Manipulation of Switches.

In general, when the gauze is raised to any potential, the electrode e is raised by induction to a potential which has to be taken into consideration when the electric field is estimated. It was found possible, however, by a suitable manipulation of the switches S, f and g to arrange that the electrode e was practically at zero potential when the potential (x) had been established on the gauze, so that no correction for induction was necessary. The series of operations involved in taking a single reading was as follows :—

(i) potentiometer (b) fixed at a convenient value so that the electrometer needle should have a suitable range of deflection : k closed : S closed on b side : f and g both closed : earth key K open : motor and commutator running but not operating on account of the short-circuit at g : capacities B and C included in the system.
(ii) k opened : S switched to the right.
(iii) g opened, if it is desired to work with added capacity.
or
(iii) capacities B and C cut out and g then opened, if it is desired to work without added capacity.

It will be seen from the foregoing that the effect of induction was to alter only the reversed field whose value had not to be known at all accurately. The electrometer needle experienced always a small kick when the switch g was opened but this quickly subsided and the current was measured with the needle in steady motion, the midpoint of the range of deflections being so chosen as to coincide with the zero of the instrument.

4. EXPERIMENTAL RESULTS.

(A). *Electrons in Gases.*

In fig. 4 of the previous paper typical curves were given showing the relation between the current due either to positive or negative ions and the potential (x) for various pressures; from such curves the critical potential V_0 could be deduced and the ionic mobility determined. In figs. 5 and 7 of the same paper there were given the curves corresponding to the negative carriers in air at relatively low pressures; the characteristic feature of these curves is their compound nature resulting from the independent passage through the gas of electrons and ions. It is convenient to designate as I curves the former type which is due solely to ions, while the latter type may be referred to as EI curves; moreover, those curves or parts of curves which arise solely from the motion of electrons will be called E curves.

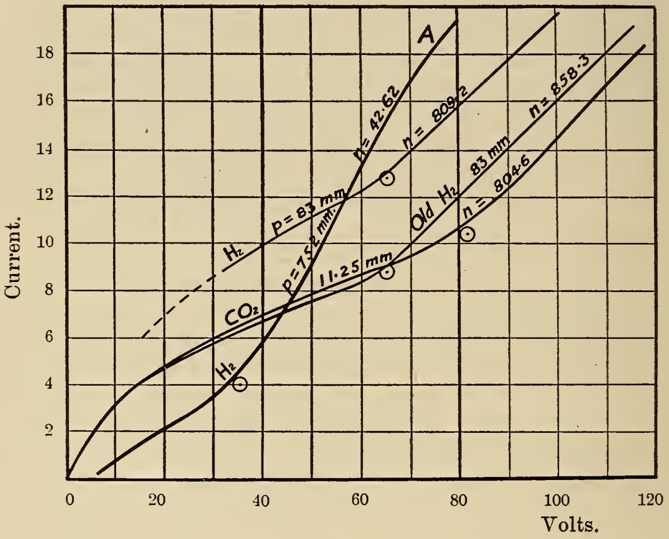
On resuming the experiment an investigation was made of the gases CO_2 and H_2. The CO_2 was prepared in a Kipp's apparatus by means of the action of dilute HCl on marble and was passed through $NaHCO_3$ Aq. in order to remove acid fumes; the H_2 was obtained by the action of dilute HCl on zinc and was passed through KOH Aq. In each case the gas was passed through a series of tubes of $CaCl_2$ and P_2O_5 in order to remove traces of moisture. A series of I and EI curves was obtained for these gases under various conditions, a few examples of the latter type being given in fig. 4. The free electrons were more numerous in each of these gases than in air at the corresponding pressure; this point is brought out by the fact that with the same frequency of commutation the electrons appeared at much higher pressures than in air, e. g. it was just possible to detect electrons in air at 8^{cm} pressure whereas in CO_2 they appeared in large numbers at a pressure of 14^{cm} and in H_2 they were readily observable at atmospheric pressure (*v.* Curve A fig. 4 which was obtained with a frequency of only 42·6; also curve in fig. 5). This result was to be expected from the conclusions of previous experimenters who had found that the abnormal increase in the ionic mobility set in for these gases at higher pressures than for air. It should be remembered that we cannot form any definite inference as to the relative number of electrons by comparing the ionization currents in the E curves for different gases at the same pressure because these currents are due to the electrons which have passed through the meshes of the gauze electrode and the fraction of electrons which accomplish this depends upon the gas concerned.

When the pressure of the CO_2 or H_2 was relatively high the free electrons appeared to be extremely sensitive to the presence of impurities in the gas under consideration; the number of free electrons was greatly decreased if the gas were allowed to stand undisturbed for a few hours in the measuring vessel which was presumably air-tight. This effect is illustrated in the curves of fig. 5; curve A refers to CO_2 at 79^{mm} pressure, the readings being taken quickly after the introduction of the gas; curve B exhibits the values after the gas had been allowed to remain 2½ hours in the closed vessel.

For lower pressures of the gas this effect practically vanishes; with CO_2 at a pressure of $4\frac{1}{2}^{mm}$ the EI curve obtained after the gas had remained undisturbed in the vessel for 2 days was identical with that obtained immediately after the introduction of the gas.

It is probable that the above effect arose from a very slow leak of oxygen into the vessel from the outside atmosphere; actual experiments were performed to test this point and it was found that traces of air added to CO_2 or H_2 at relatively high pressures resulted in a marked decrease of the number of free electrons whereas when these gases were at low pressures the number of electrons was not appreciably affected by the admixture.

Fig. 4.



It should, however, be mentioned that a similar though much more intense effect was found in experimenting with the free electrons in the vapor of petroleum ether (*v.* sec. 4 D); in this instance the diminution in the number of electrons was very rapid and could not reasonably be ascribed to a small leak of air into the apparatus. All the indications pointed to the appearance in the vapor of a constituent capable of absorbing electrons at ordinary temperatures. It is convenient to refer to nuclei, whether molecules or aggregations, which possess this property, as 'electron sinks'; the electrons cannot remain in the free state during their motion through a gas which contains these sinks other than in excessively small quantity. All the experimental evidence indicates that the molecules of oxygen do not belong to this class of impurities and that the larger electron velocities attendant upon the act of ionization are necessary for the formation of negative oxygen ions.

It is of course possible that the decay of the electrons in CO_2 and H_2 does not arise from an air leak but is due to an ageing effect similar to that in petroleum ether. In this connection several unsuccessful attempts were made to remove possible nuclei from CO_2 which had been allowed to remain for several hours at a pressure of 81^{mm} in the measuring vessel. In one experiment the gauze electrode was maintained for several hours at a potential of –160 volts in the hope that the electrons which were being continually produced would ultimately remove the nuclei from the gas; however the current measurements failed to indicate any tendency to restore the original condition of the gas under which permanently free electrons were in evidence.

The same gas was subsequently passed several times through P_2O_5 by means of a mercury reservoir attachment in order to remove any trace of water vapor which might have arisen from the metal walls: the free electrons, however, did not reappear and the possibility of the existence of nuclei consisting of molecules of water vapor was thus excluded.

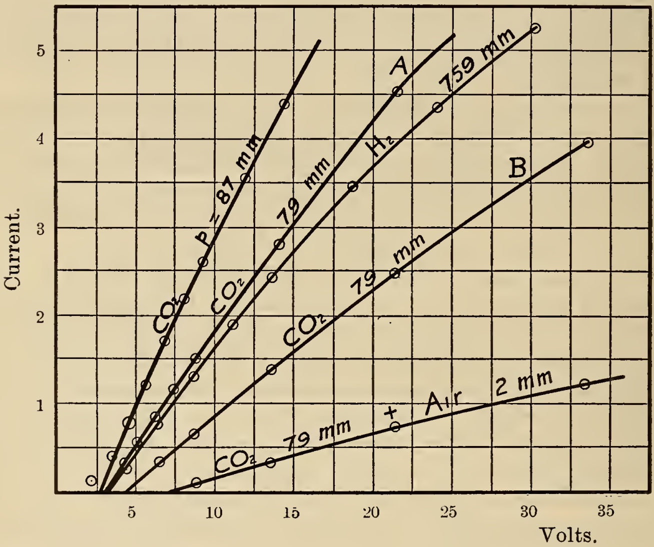
A few experiments were made to ascertain whether free electrons are present in carbon monoxide. This gas was liberated by the action of concentrated sulphuric acid on potassium ferrocyanide and was passed through solid caustic potash, calcium chloride and phosphorus pentoxide before admission into the measuring vessel. A typical EI curve was obtained for CO at a pressure of 13^{mm}, demonstrating thus the existence of free electrons; these were, however, not nearly so numerous as in air at the same pressure and, as the manipulation with this gas presented difficulties, it was not considered expedient to extend the investigation.

It seems fitting to refer here to an apparent difficulty in connection with the existence of free electrons in gases. The electrons were shown to appear in measurable amount in dry air at pressures as high as 8^{cm} and yet it has been mentioned in this section that a trace of oxygen is sufficient to cause them to disappear from CO_2 or H_2 at relatively high pressures. Reference is made later (sec. 5) to this apparent discrepancy; the difficulty is in large measure removed by a consideration of the experimental fact that the sensitivity to oxygen decreases rapidly as the pressure of the original gas is reduced. To take actual figures, it was found that a trace of air would rob H_2 at 1 atmosphere of its free electrons and yet in a mixture of H_2 at $82\frac{1}{2}^{mm}$ and air at $2\frac{1}{2}^{mm}$ the electrons appeared in considerable numbers.

(B) *Motion of Free Electrons.*

A number of experiments were undertaken to determine the velocity with which the free electrons moved in an electric field through CO_2 and H_2. Mobility values have already been assigned by Franck* for the electrons in argon, helium and nitrogen at atmospheric pressure; the values given were respectively 209, ca. 500, and 120^{cm} per sec. per volt per cm. The mobility values were found to be extremely sensitive to the presence of impurities in the gas under consideration, the slightest trace of oxygen, for example, causing a considerable reduction in the value. Recently Haines† has investigated the motion of free electrons in pure nitrogen at atmospheric pressure and has obtained a mean value of 367 for the mobility.

Fig. 5.



Carbon dioxide appeared especially suitable for experiments in this connection because the electrons were relatively numerous in it and at the same time the density of the gas was sufficiently great to justify the belief that the velocities would not be inordinately large and thus incapable of measurement with the apparatus at disposal. Even with the high frequency of 800 alternations per second and at the highest practicable pressures of the CO_2 it was found that the values of the critical potential (V_0) were considerably less than 10 volts, so that the observa-

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* Franck, Verh. Deutsch. Phys. Ges., xii, pp. 291, 613, 1910.

† Haines, Phil. Mag., vol. xxx, p. 503, 1915.

tion error in the determination of the electron mobility was of necessity considerable. Moreover there was also the difficulty connected with the presence of the ageing effect which, as mentioned above, occurs at the higher pressures; it was of course not feasible to attempt determinations at the lower pressures where this effect is absent because the electron velocities become excessively large.

It was in every instance found that the effect of age (i. e. of allowing the CO_2 to remain for any length of time in the apparatus) was to reduce considerably the velocity of the electrons. On this account great care was taken to exclude impurities, the gas being in all cases swept several times through the measuring vessel, and the observations quickly made after the final introduction.

In figs. 5 and 6 there are given a few typical E curves which were obtained in the determination of V_0 for the free electrons; the ions do not make their appearance until much higher potentials are employed. Reference will be made later to the fact that the experimental results rendered doubtful the assumption that the velocity of the electron is proportional to the applied field, so that the use of the term 'mobility' is not certainly justified; however it was thought useful to make the calculations on the assumption that there exists a distinct mobility for the electron just as for the ion. In the following table there are given the results of the mobility determinations for freshly prepared CO_2 together with some of the results for CO_2 in various degrees of impurity; the symbol K denotes the mobility reduced to atmospheric pressure on the assumption of the validity of the law pk = const.

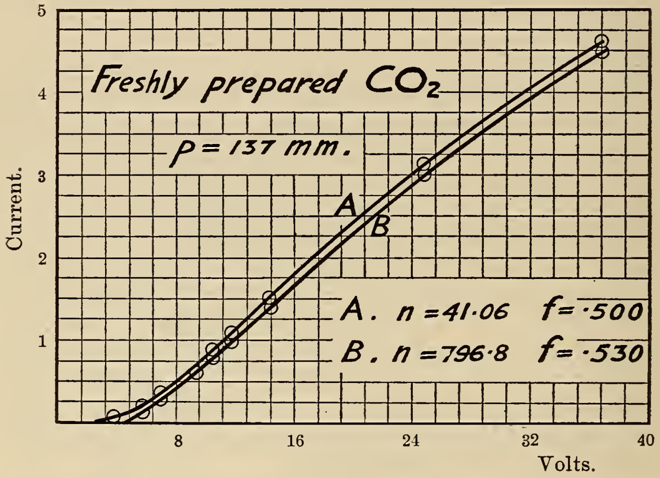
Freq.	f	p mm.	V_0	k	K	Remarks.
807·9	·545	35·5	1·4	4232	197·6	Fresh
820·6	·518	54	2·45	2587	183·8	
824·5	·527	87	2·8	2233	255·6	
796·8	·530	137	4·5	1336	241·0	
833·3	·540	79	3·0	2056	214·0	
830·1	·545	54	8	761·7	54·1	2 days old
834·2	·550	25	2·2	2757	83·4	do.
833·3	·540	79	4·6	1341	139·4	2½ hrs. old
828·2	·540	81	7·35	834		79^{mm} CO_2 + 2^{mm} air

In fig. 5 there is given an E curve for freshly-prepared hydrogen at atmospheric pressure; the value of K deduced from this curve was 1700^{cm} per sec.

The values of K for freshly prepared CO_2 are scarcely in sufficient agreement to justify the assignment of an average value. It is evident from the table that the electron velocities are very sensitive to the presence of impurities; the highest value of K obtained was 255^{cm} per sec., but even this cannot be regarded as a maximum as a greater degree of purification would probably result in still higher values.

There is some evidence of an indirect character that the electron does not move with a velocity which is strictly proportional to the applied field but traverses with an accelerated motion distances comparable with the distance between the electrodes. The close approach for small potentials of the E curves in fig. 6 which refer to CO_2 at the same pressure (137^{mm}) but with different alternation frequencies suggests very large values for the velocities of the electrons; this is more readily understood if we apply the formula $i'=i\,(f-\frac{d^2n}{k\mathrm{V}})$ where i' is the current for potential V when the alternating field is employed and i is the current for potential V directly applied. If we take the velocity calculated from V_0 at the higher frequency, viz. $k=1336$ at 137^{mm}, the above formula (with $d=2$) gives $i'_1/i'_2=4{\cdot}1$ for $V=5{\cdot}78$ volts where the suffixes 1 and 2 refer to the low and high frequency respectively; the value obtained from the experimental curves is only 1·3. Similarly for $V=6{\cdot}96$ volts we obtain a calculated ratio of 2·6 whereas that obtained experimentally is 1·2. These considerations would seem to imply that the value $k=1336$ is too small

Fig. 6.



and that the critical potential is really smaller than the value ($V_0=4·5$) apparently obtained.

In this connection it is a significant fact that several of the E curves, especially those obtained at the highest pressures, showed a distinct curvature in the neighborhood of the potential axis, the tendency being to shift the point of intersection towards the origin. This shape of the current-potential curves in the vicinity of the origin suggests accelerated motion of the electron or a slow acquisition of a terminal velocity.

Further experimental data are of course necessary before the nature of the motion of the electron is definitely ascertained; the suggestion here given is that the electron may traverse a considerable distance with accelerated motion before its terminal velocity is acquired. It should be remembered that Franck and Hertz* have already shown that the collisions of electrons with the molecules of the inert gases are practically perfectly elastic so that the drift motion of the electron would under these circumstances be accelerated. The experiments with regard to the effect of impurities upon the number of free electrons in CO_2 or H_2 strongly suggest that the collisions of electrons with the molecules of these gases have a high degree of elasticity, although naturally not so high as with the inert gases. The effect of this high but imperfect elasticity would be to cause the electrons when moving under an electric field in CO_2 or H_2 to move with an accelerated motion until their terminal velocity is acquired.

On this view the effect of traces of impurities in the gas in diminishing the velocity of the electron is readily explained; the impact of the electron with the molecule of the impurity is in all probability either inelastic or considerably less elastic than the collision with the gas molecule, and, in consequence, the electron is unable to acquire as great a velocity as in the pure gas.

(C) *Electrons in Vapors.*

The demonstration of the existence of free electrons in air, CO_2 and H_2, at relatively high pressures rendered it fairly obvious that all permanent gases were able to contain electrons in the free state. Franck's experiments had shown previously that the inert gases were especially conspicuous in this respect, the negative carriers appearing to consist entirely of free electrons. It became of interest to extend the investigation to the case of vapors, especially as these are liable to occur as impurities in gases. It was thought extremely improbable that the electrons, if they were present in the free state, would occur in large numbers except at very low pressures; preliminary

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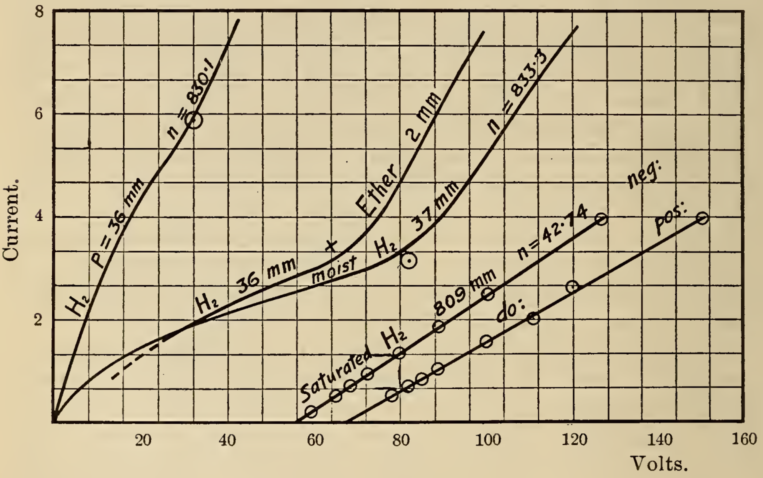
* Franck and Hertz, Verh. Deutsch. Phys. Ges., xv, pp. 373, 613, 1913.

trials with a few vapors justified this conclusion. With the high frequency commutator there was not the slightest indication of the presence of free electrons either in dry SO_2 at a pressure of 7^{mm} or in CH_3I at a pressure of 28^{mm}. It was however quite possible that lower pressures would bring the electrons into evidence, but as the apparatus did not readily lend itself to securing low vapor pressures the investigation was resumed in a slightly different manner. A small quantity of the vapor under consideration was mixed with a permanent gas and experiments were made to ascertain whether free electrons could continue to exist in this mixture; if the vapor molecules behaved as electron sinks and were present in appreciable amount then the number of collisions and subsequent attachments between electrons and vapor molecules would be sufficiently great to prevent the existence of free electrons. This information was of importance in view of the experimental results with regard to the effect of impurities on the number of free electrons in a gas. Three vapors were tried in this connection, viz.: ether, alcohol and water; these were chosen because they were deemed to be the most probable absorbers of electrons. In each of these instances hydrogen at a reduced pressure was chosen as the gas with which the vapor was mixed because of the copious supply of free electrons which it affords.

Fig. 7.



An EI curve was first obtained for dry hydrogen at a pressure of 36^{mm} (fig. 7); ether vapor was then admitted until the pressure of the mixture was 38^{mm}, and the readings were again taken. It was found that even in the presence of 2^{mm} of ether vapor a considerable number of free electrons were able to traverse the distance between the electrodes. The number was less than in the pure hydrogen, but the EI curve for the mixture (fig. 7) was sufficiently definite to justify the conclusion that the molecules of ether vapor do not behave as electron sinks.

The experiments with alcohol vapor were conducted in a similar manner; an EI curve was obtained for a mixture consisting of hydrogen at 35^{mm} and alcohol at a pressure slightly less than 1^{mm}. The number of electrons was again distinctly smaller than in the pure gas, but was sufficiently great to make it evident that the molecules of alcohol were unable to absorb the free electrons.

In order to experiment with traces of water vapor present in the gas, the tubes containing the drying agents were removed so that the hydrogen passed into the measuring vessel directly after generation in the Kipp's apparatus. The moist hydrogen was introduced at a pressure of 37^{mm} and a current-potential curve (*v.* fig. 7) was obtained in the usual manner; the presence of the moisture caused a reduction in the number of free electrons, but these were in sufficient evidence to show that the water molecules do not behave as electron sinks.

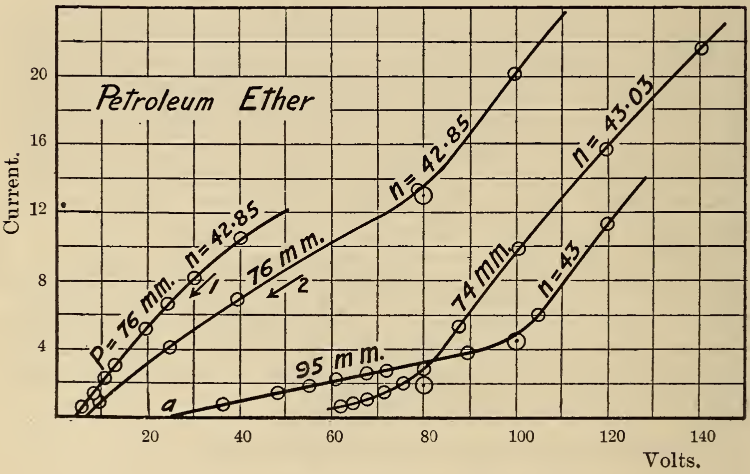
It is of course quite possible that in all these instances a loose attachment may occasionally exist between the electron and the vapor molecule; the experimental results indicate, however, that such an attachment, if it occur at all, persists only for a time which is small in comparison with that during which the electron remains free.

Vapor of Petroleum Ether and the ageing effect.

The previous experiments with CO_2 and H_2 suggested that the atoms of carbon and hydrogen were in great measure responsible for the relatively large number of free electrons in these gases as compared with air. It became of interest to make a special study of some member of the paraffin series whose molecules contain only atoms of carbon and hydrogen or indeed of any vapor which does not contain electro-negative atoms such as those of oxygen or iodine. It was originally proposed to make the experiment with pentane, but as this was not immediately available the vapor of petroleum ether was employed instead. Petroleum ether (sp. gr. ca. ·67) consists of a mixture of pentane (C_5H_{12}) and hexane (C_6H_{14}); its molecules contain, therefore, only atoms of carbon and hydrogen. A number of determinations of ionic mobilities were also made for this vapor; reference is, however, made to these only as far as they concern the motion of electrons, the actual values obtained for the mobilities of the ions being deferred to a later section (4D).

The first experiments with this vapor, which was introduced at a pressure of 95^{mm}, gave a normal value (K = ·41) for the mobility of the positive ion; the current-potential curve for the negative carriers (fig. 8) was distinctly abnormal, as it afforded evidence of two types of carriers; in addition to the normal negative ion (K = ·44) there appeared a carrier (*a*, fig. 8) for which K had the value 1·692, which is about four times as great as one might have reasonably expected for the negative ion and, on the other hand, considerably less than the value corresponding to a free electron. On attempting to repeat the experiment after the vapor had been allowed to remain for about two hours in the vessel, only the normal value was obtained for the mobility of the negative ion.

FIG. 8.



In the next experiment, after a preliminary evacuation of the vessel, streams of vapor were swept through repeatedly in the hope of removing traces of impurities; the vapor was finally admitted at a pressure of 76^{mm} and the readings quickly taken. The curve obtained is given in fig. 8; the direction of the arrow signifies that the current measurements were made in descending order of potential. It will be seen that this curve shows the presence both of ions and of free electrons; the ions enter at 80 volts and possess a normal mobility, viz. K = ·430. The curve marked 1 was obtained only a few minutes before that marked 2 and it will be observed that the electrons have decayed appreciably during this short interval of time. The third curve was obtained 2½ hours after the introduction of the vapor; there is now only the slightest indication of free electrons while the negative ion has still a normal mobility (K=·428).

Subsequent experiments were made with freshly introduced vapor at a pressure of 20^{mm} and gave evidence of a very large percentage of electrons; however, the ageing effect was very pronounced, the free electrons decreasing in number so rapidly that no regular curve was obtained.

The general indications seem to be that in the pure vapor of petroleum ether a large fraction of the negative carriers are free electrons, the negative ions if present at all appearing only in small numbers; the free electrons are, however, extremely sensitive to the presence of some constituent which arises gradually in the vapor, with the result that at the expiration of a few hours the electrons have disappeared and the current of negative electricity is due entirely to ions.

The nature of the constituent which occasions the ageing effect in the vapor can at present only be conjectured; systematic experiments are necessary before a definite conclusion can be reached. There is distinct evidence, however, that we are dealing here with a true electron sink; in other words, this constituent, whatever be its nature, is capable of absorbing an electron during its drift motion through the vapor and in this respect must be carefully distinguished from impurities such as oxygen, which seem to require for the absorption of electrons velocities considerably higher than those which are afforded by thermal agitation at ordinary temperatures. The effect of the latter type of impurity is to reduce the number of free electrons in a gas and at the same time to diminish appreciably the velocity of the electron through the gas; this diminution in velocity has been ascribed (*v.* sec. 4B) to the comparatively inelastic impact between the electron and the molecule of the impurity.

In the experiments with the vapor of petroleum ether the effect of the impurity is to cause likewise a reduction in the number of free electrons and a diminution in the electron velocity; the electron, however, appears now to be capable of acquiring all velocities intermediate between that of a free electron in the pure vapor and that of a negative ion. We seem, therefore, to be dealing with a carrier which changes continuously and progressively from a free electron to a negative ion; the most feasible hypothesis is that the electron as it drifts through the vapor is for part of the time in the free state and for the remainder in attachment with the molecule of the impurity. It is highly probable that this attachment, occurring as it does as a result of ordinary thermal motion, is of a very loose nature and is liable to be broken at molecular encounters; we would thus expect continual alternations of the electron between the free and combined states.

With regard to the nature of the sink which is gradually formed in the vapor of petroleum ether, nothing at all definite can be said. We may imagine that polymers or small aggregates of pentane or hexane are formed gradually under the influence of the radiation from the polonium; such systems would probably be able to form stable negative ions for large electron velocities and unstable ions for small velocities. Initially, when the vapor is pure, the negative carriers are for the most part electrons; as the sinks appear, the velocity of the electrons would be reduced through the formation of unstable ions. The fact that ultimately the carriers consist entirely of negative ions may be explained by ascribing to a polymer the property of being able to effect occasionally a union between an electron and a molecule of the vapor.

(D) *Ions in Gases and Vapors.*

Gases.—The law pk=const. was verified for both the positive and the negative ions in dry air over a wide range of pressures. Some of the values obtained experimentally for K at the lower pressures have been given in the previous paper and should be sufficient to illustrate the unchanging nature of the negative ion. A set of values obtained for the mobility of the positive ion in air at low pressures is given below; the first table refers to values obtained by means of determinations of the critical potential V_0, while the values given in the second table were determined by means of the formula $k = \frac{d^2n}{V} \cdot \frac{i}{fi - i'}$.

Press mm.	V_0 volts	f	Freq.	k_1	K_1
8·31	53·0	·546	864·3	119·5	1·31
1·66	11·5	·540	834·2	537·5	1·17
1·64	10·2	·540	850·9	618·0	1·33*
1·01	6·0	·574	851·7	989·0	1·31
·563	3·0	·574	836·5	1944	1·44
·416	2·5	·584	862·1	2363	1·29
·321	1·75	·585	833·3	3254	1·37

Mean value of K_1: **1·32**

* $a = 8$ volts (*v.* fig. 2); for the other determinations $a = 20$.

Press mm.	V volts	i	i'	f	Freq.	k_1	K_1
1·66	14·3	4·18	·52	·540	829·2	557·4	1·22
1·64	14·3	2·84	·34	·540	851·1	568·2	1·23*
1·01	9·03	2·20	·40	·574	851·7	965	1·28
·563	5·00	1·73	·34	·574	836·5	1781	1·32
·416	6·26	1·506	·46	·584	862·1	1975	1·08
·321	4·17	1·84	·60	·585	833·3	3090	1·31
·151	1·13	1·05	·155	·565	856·0	7265	1·44
·052	·55	·298	·068	·565	842·4	18250	1·25*
·052	1·15	·333	·137	·565	842·4	19130	1·31*

Mean value of K_1 : **1·27**

* $a = 8$ volts (*v.* fig. 2); for the other determinations $a = 20$.

The mean value obtained for K_1 at the higher pressures was 1·23 which is in sufficient agreement with the above values to justify the conclusion that the nature of the positive ion is independent of the pressure.

The mobilities of both the positive and the negative ions in CO_2 and H_2 were determined over a wide range of pressures; there was no evidence in either gas of any systematic alteration in the value of pk_1 or pk_2 as the pressure was reduced. It was deemed unnecessary to extend the determination for these gases down to the low pressures employed in the case of air inasmuch as it was apparent that the processes were entirely similar; for this reason the law $pk=$const. was only verified down to a pressure of 4^{mm} in CO_2 and 12^{mm} in H_2. The mean values of K for air, CO_2 and H_2 were estimated from the results obtained at the higher pressures where the observation error is relatively small although the results at the lower pressures showed good agreement. The values thus obtained are as follows:

	K_1	K_2	K_2/K_1
Air	1·23	1·93	1·57
CO_2	·73	1·07	1·47
H_2	5·11	9·67	1·89

The values of K refer as usual to the dry gas at atmospheric pressures and are expressed in cm./sec. per volt/cm.

For each gas the value of K_1 is less and that of K_2 is greater than the value usually assigned; for the sake of comparison the values of the mobilities obtained by Zeleny* are given below:

	K_1	K_2	K_2/K_1
Air	1·36	1·87	1·375
CO_2	·76	·81	1·07
H_2	6·70	7·95	1·19

Zeleny's values for air and CO_2 are in fair agreement with those obtained by the writer in former experiments and by several other observers. The cause of the discrepancy is not apparent; it is scarcely probable that any defect either in the method employed in the present experiments or in the determination of any of the constants involved would cause the ascertained values of K_1 and K_2 to vary in different directions. It should be mentioned that the present values for CO_2 and H_2 are in fair agreement with those obtained by Blanc† who used Franck and Pohl's method with X-rays as the ionizing agent. Blanc's values are:

	K_1	K_2	K_2/K_1
CO_2	·83	1·027	1·24
H_2	5·33	10·00	1·88

Haines‡ has recently obtained the value 5·4 for the mobility of the positive ion in pure hydrogen; the negative ions did not appear till a trace of impurity was present and under these conditions their mobility was about 8.

Effect of Water Vapor.

A few experiments were performed to ascertain the effect on the ionic mobilities of saturating with water vapor the gas under consideration. In these experiments the water vapor was introduced by ebullition when the gas in the vessel was at a low pressure; after this operation the gas was admitted till the desired pressure was attained. As a result of condensation

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* Zeleny, Phil. Trans., A, cxcv, p. 193, 1900.
† Blanc, Jour. de. Phys., vol. vii, p. 825, 1908.
‡ Haines, loc. cit., also Phil. Mag. xxxi, p. 339, 1916.

of the vapor the insulation was extremely defective and the currents could not be determined by observation of the rate of deflection of the electrometer needle. However it was observed that the spot of light assumed for each value of the potential a definite position on the scale; in this position the ionization current is balanced by the current due to the leak through the condensed vapor and is thus proportional to the steady reading of the electrometer. The conductivity of the condensed vapor remained constant over a sufficient interval to enable the critical potential to be determined in this manner. Typical curves obtained for saturated H_2 are given in fig. 7.* The results of the mobility determinations for saturated H_2 and CO_2 together with the calculated values for the dry gases at the same pressure are given below:

	p mm.	K_1	K_2
H_2 dry	809	4·80	9·09
saturated	809	5·03	6·105
CO_2 dry	769	·72	1·06
saturated	769	·77	·88

In addition, other experiments were performed in which small quantities of water vapor and ether vapor were mixed with hydrogen; in these experiments the mobilities were determined in the ordinary manner. The following results were obtained:

	p mm.	K_1	K_2
H_2 dry	517	7·51	14·21
H_2 with water vapor	517	7·43	10·27
H_2 with ether vapor	766	4·13	7·25

The presence of water vapor appears thus to be without effect on the mobility of the positive ion but occasions a marked diminution in that of the negative ion. This is in accordance with the results obtained by previous investigators.

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* The current scale for these curves is different from that for the other curves in fig. 7.

The diminution in the mobility of the negative ion is too great to be accounted for by the extra resistance to the motion of the ion which arises when the vapor is mixed with the gas. The diminution may be explained in part by assuming that the effect of the water molecules is to cause inelastic impacts with the negative ions and thus prevent them from acquiring the larger terminal velocities which they attain in the dry gas. It seems probable, however, when the gas is saturated with water vapor, that condensation occurs round the negative ion and that the diminution in mobility is to a large extent due to this process. We would thus have the negative ion constituted by a cluster of water molecules round a charged nucleus; it should be carefully noticed that the existence of such a cluster in a moist gas affords no evidence as to the nature of the ion in a dry gas. In a later paper experimental evidence will be given which indicates that the water molecules are not held together in the cluster by the electrostatic forces due to the charge on the ion, the function of the charge being merely to determine the act of condensation.

Vapors.

A number of measurements were made of the mobilities of the positive and negative ions in a few vapors; this was of interest as affording a comparison with the results obtained by the different method employed in a previous investigation.* The mobilities were determined in the usual manner; the average values estimated from a number of determinations in good agreement are recorded below together with the corresponding values taken from the previous research. The figures in the second column give the minimum and maximum pressures employed; the mobilities given correspond as usual to a pressure of 1 atmosphere.

Vapor	Pressure range mm.	1915		1909	
		K_1	K_2	K_1	K_2
Ethyl ether	67—126	·27	·346	·29	·31
Ethyl alcohol	23— 39	·39	·412	·34	·27
do (saturated†)	38— 42	·365	·392		
Petroleum ether	73—115	·370	·440	·36‡	·35‡
Sulphur dioxide	74— 94	·415	·414	·44	·41
Methyl iodide	63— 65	·24	·233	·21	·22

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* Phil. Trans., ser. A, vol. ccix, p. 249, 1909.

† Measured by the method employed with saturated water vapor.

‡ Pentane.

The agreement in the case of the positive ion is as good as could reasonably be expected in view of the difficulties attendant upon experimenting with vapors; we can say with a high degree of certainty that to each vapor there corresponds a definite value of the mobility of the positive ion. The mobilities of the negative ions in alcohol and petroleum ether are, however, in greater disagreement than can be accounted for by experimental error. We have seen (sec. 4C) that in the pure vapor of petroleum ether the negative carriers are practically all electrons and that the negative ions come into evidence only when the vapor is allowed to remain for some time in a closed vessel. We are therefore constrained to associate the negative ions in this vapor with impurities; and it is of course not improbable that there are other vapors in which the existence of negative ions is conditioned by the presence of some impurity. Refined experiments on ionic mobilities in vapors are necessary before the nature of the negative carriers can be determined.

5. DISCUSSION OF RESULTS.

It is proposed to discuss briefly in this section the significance of the results of the present experiments in connection with the theory of electric conduction in gases. Several of the points brought forward have already received attention in the previous paper; reference is made here to these only for the sake of continuity.

The experiments with air showed that the mobility (k) of the positive ion varied inversely as the pressure (p) of the gas down to the lowest pressure which it was convenient to employ ($\cdot 05^{\mathrm{mm}}$). It was not thought necessary to proceed to very low pressures in the case of carbon dioxide and hydrogen but all the indications were that the law $pk=$const. would continue to be valid. The validity of this law over a wide pressure range signifies that the nature of the positive ion remains unchanged throughout this range.

The same law was found to be valid for the negative gas ion but only after care had been taken to separate the negative carriers into the two components, *electrons* and *ions*. It was found that the apparently anomalous increase at reduced pressures of the mobility of the negative ion to which many observers had previously drawn attention was occasioned by this dual nature of the negative carrier; when the ions were considered apart from electrons all the anomalies disappeared, the velocity being expressible in the form $v=k_0\dfrac{X}{p}$.

It is instructive in this connection to consider the difference between the present and the older point of view. It has long been known that in air at very low pressures the current of negative electricity is due practically entirely to free electrons; at the higher pressures, however, the current is due to the motion of negative ions. What is the nature of the negative carrier at intermediate pressures? The answer hitherto given to this question was that the carrier altered in nature during its motion between the electrodes but in such a manner that for a given pressure it possessed an 'average' mass. If, for instance, we regard the ion as being constituted at high pressures by a cluster of molecules, then we would have to assume that as the pressure was reduced the average number of molecules in the cluster decreased; as the pressure was still further reduced, any individual negative carrier would be for part of the time in the ionic state (say now as a single molecule) and for the remainder would exist as a free electron; at this pressure we would have at any given instant a number of free electrons and a certain number of ions, but if we were to follow one electron throughout its motion we would find it associated on the average with a mass intermediate between that of an electron and that of a molecule. Ultimately at very low pressures the carriers would be all free electrons. Prof. Townsend's* point of view differed only slightly from this in that he regarded the average nature of the carrier to be determined by electric force as well as gas pressure.

The answer afforded by the present experiments is fundamentally different. We now regard the electrons and ions as passing independently through the gas, each kind of carrier remaining constant in nature throughout. The transition from the ionic conduction at high pressures to the electronic conduction at low pressures is effected by means of an increase in the number of free electrons relative to the number of negative ions without any alteration in the nature of either kind of carrier. The appearance of the phenomenon of ionization by collision would further affect the relative numbers of carriers but would not influence the nature of the conduction.

Looked at from this point of view it seems clear that, as far as the so-called permanent gases are concerned, we must regard the free electrons as occurring theoretically at all pressures. These gases differ, of course, considerably in the relative number of free electrons and ions for any given pressure, and, practically speaking, there is for each gas a pressure at which the number of free electrons is negligibly small but the general rule is in no way invalidated on this account.

In the above illustration we considered the electric current passing through air. It was shown, however, by Franck† that

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* Townsend, Electricity in Gases, Oxford (1915), Chap. IV, VIII. Cf. also Pidduck, Electricity, Cambridge (1916), Arts. 214–215.

† Franck, loc. cit.

for certain gases, viz. the inert gases and nitrogen (which behaves often as an inert gas), the negative carriers consist entirely of electrons even when the gas under consideration is at atmospheric pressure. Chattock and Tyndall* gave good reasons for believing that hydrogen possessed similar characteristics; more recently Haines† has shown independently that the negative carriers in hydrogen consist practically entirely of electrons. In all these instances a slight trace of impurity (especially oxygen) was sufficient to convert the carriers into ions.

The older point of view was to regard these gases as possessing, by virtue of their inert character or otherwise, the exceptional property of being able at high pressures to contain electrons in the free state: on this account they had to be clearly distinguished from gases, such as oxygen, chlorine, &c., which were regarded as being unable to contain free electrons except at very low pressures. The present experiments indicate that the difference is merely one of degree inasmuch as the electrons are capable of existing in the free state even in air at considerable pressure. We may now regard at any rate the so-called permanent gases as being able to contain both negative ions and free electrons, each kind of carrier maintaining its identity throughout its motion. The inert gases and hydrogen are now regarded as being exceptional not in their power of containing free electrons but rather by reason of their great reluctance to form negative ions, *i. e.* by reason of the exceptionally large proportion of electrons to ions.

It was shown in sec. 4C that the vapor of petroleum ether is able to afford a copious supply of electrons and to maintain them in the free state provided we reduce the contamination to a minimum. As the molecules of this vapor contain only atoms of carbon and hydrogen this result suggests strongly that the negative ions in air, CO, CO_2, etc., are due almost entirely to the presence of the atoms of oxygen. Franck‡ has arranged gases in the following order of increasing electron affinity: helium, argon, nitrogen, hydrogen, oxygen, nitric oxide, chlorine. This list was obtained by considering the relative power of the different gases, when present as impurities, to deprive helium of its free electrons. If, in accordance with the views embodied in this section, we regard this series of gases as affording a relative idea of the proportion of electrons and ions which results from the process of ionization, it would seem probable that in order to supply an appreciable number of negative ions the molecules of a gas must contain atoms either of oxygen or chlorine; we may by analogy include other elec-

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* Chattock and Tyndall, Phil. Mag., xxi, p 585, 1911.

† Haines, loc. cit. ‡ Franck, loc. cit.

tro-negative atoms such as bromine, iodine, etc. This statement is to be regarded merely as a suggestion for further experiments; a study of the ionization in pure ammonia might prove of interest in this connection.

It is known that the presence of a trace of oxygen in an inert gas or in hydrogen at atmospheric pressure will reduce considerably the number of free electrons. The present experiments showed that in hydrogen the sensitivity of the free electrons to traces of oxygen was greatly decreased if the gas pressure was reduced so that, for instance, a considerable number of free electrons was obtained in a mixture of hydrogen at $82\frac{1}{2}^{mm}$ pressure and air at $2\frac{1}{2}^{mm}$. In a previous communication* a definite theory in explanation of these results has been given; the underlying idea is that an electron cannot effect a permanent union with an uncharged molecule to form a negative ion unless the relative velocity at collision exceed a critical value characteristic of the molecule concerned. We have seen that in a large number of gases the electrons persist in the free state so that it would appear that the negative ions in these gases must in general† be formed immediately after the act of ionization. We may regard the electron as being expelled with a certain velocity from an uncharged molecule, but owing to the positive charge acquired by the molecule the velocity of the electron will decrease as it recedes; in accordance with the above view we may imagine a sphere drawn round the parent molecule of such a radius that the electron will be effective in forming a negative ion only for impacts within this sphere. It is probable that the circumstances of an encounter as well as the relative velocity will determine the effectiveness of a collision so that only a fraction of these impacts will result in the formation of ions; outside the sphere, however, the electron must continue in the free state. It is easy to see that on this view the relative number of electrons will increase with decreasing pressure.

The potential required for the formation of a negative ion must of course be less than that required to ionize a molecule inasmuch as in the latter case a fresh pair of ions originates. We would expect that for those gases which have a high ionization potential the proportion of negative ions to electrons would in general be small. This is borne out by the results for the inert gases and hydrogen, although the value assigned by Franck and Hertz‡ for the ionization potential in nitrogen (viz. 7·5 volts) would not indicate on this view a very large percentage of free electrons.

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* Wellisch, Phil. Mag., vol. xxxi, p. 186, 1916.

† When the applied field is sufficiently great to generate the critical velocity in the electron, negative ions will again commence to be formed.

‡ Franck and Hertz, Verh. Deutsch. Phys. Ges., xv, p. 34, 1913.

It does not seem advantageous to discuss in great detail the question as to the nature of the gas ion; all that is proposed is to indicate here the leading features of this outstanding problem. It should be remembered that the notion of the ion as consisting at moderately high pressures of a cluster of molecules grouped round a charged nucleus was first introduced in order to account for the observed mobility and diffusion values, which were found to be considerably smaller than the values which were to be expected from theoretical considerations if we regard the ion as consisting of a single molecule. It was shown, however, by the author* that the observed values were consistent with the view that the ion was a single molecule provided we took into account the extra resistance to the motion of the ion resulting from the attraction between the charge on the ion and the charges induced on neighboring molecules.† A definite decision in favor of the cluster theory appeared to be given by the results of the series of experiments which indicated a departure from the law $pk=$ const. even when the gas was at a pressure of several cm.; the abnormally high mobility values were naturally interpreted as corresponding to the disintegration of the ionic cluster. The fallacy of this series of results has already been discussed in the present paper; it is sufficient here to repeat that no indication has been obtained of any change in the nature of either the positive or the negative ion as the pressure of the gas changes over a wide range.

We would certainly expect at least a partial disintegration of an ionic cluster when the electric field and the gas pressure were such that the ion acquired energy comparable with that required to ionize a neutral molecule. According to Townsend ionization by collision in air commences to be appreciable when $X/p=60$ (X being measured in volts / cm. and p in mm. Hg.). X/p is proportional to the energy acquired by an ion after traversing a distance equal to its mean free path. In the present experiments the positive ions are shown to have a normal mobility for values of X/p as great as 11, even if we take for X only the small values of the critical field from which the mobility was estimated. The normal character of the complete curves which were obtained in the process of determining the critical potentials indicates that neither the positive nor the negative ion is appreciably altered in nature for much greater

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* Phil. Trans., loc. cit., p. 272.

† It was the author's idea that this extra resistance was due entirely to increased frequency of collision between the ion and the molecules. Sutherland later maintained that the increased frequency was responsible only for part of the extra resistance and that it was necessary to introduce another type of electric viscosity. These points were discussed further in two communications. (v. Phil. Mag., xix, pp. 201, 817, 1910)

values of X/p. It should be remembered, however, that at the lowest pressures employed we are nearing the conditions for which the mobility law would be no longer valid even for an unchanging ion. A simple calculation gives that in air for $p = \cdot05^{\mathrm{mm}}$ and with 1 volt fall of potential, the positive ion makes about 330 collisions in traversing the distance of 2^{cm} between the electrodes. It is surprising that the mobility law should be so nearly valid at this stage; the explanation is probably that the velocity ($3\cdot3 \times 10^4$ cm./sec.) acquired by the ion after describing freely a distance equal to the mean free path is still smaller than the mean velocity of thermal agitation of the molecules ($4\cdot6 \times 10^4$). If we suppose that the mobility law is valid as long as the mean velocity of agitation predominates, we find by calculation that in air the law should hold for values of X/p up to 20. Loeb* has recently made a series of determinations of the mobilities of the ions in air under high electric fields and has shown that the mobilities remain normal at atmospheric pressure for field strengths up to 12,450 volts per cm.; the law $pk =$ const. was verified for values of X/p up to about 20.

The preceding considerations indicate that the notion of an ion as a cluster is unnecessary; the cluster theory must depend for its continued existence on arguments essentially different from those which have hitherto been advanced. Moreover, it should be stated that evidence of a more direct nature in favor of the single molecule theory has of late years been forthcoming. Chattock and Tyndall† in their experiments on the point discharge showed that the absorption of positive ions of hydrogen by a metal corresponded to a withdrawal of two atoms of hydrogen from the gas. Erikson‡ in experimenting with regard to the variation of ionic mobility with changes in temperature concluded that his results were not explicable by the notion of clusters. In the present experiments it has been shown that an electron passes unencumbered through ordinary gases at considerable pressures notwithstanding the strong electric field which is associated with it; it is hard to reconcile this fact with the basic idea of the cluster theory, viz., that the cluster of molecules is held together by the electric field associated with the ion.

Leaving the question as to the nature of the gas ion, we may now with advantage consider another outstanding problem of

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* Loeb, Proc. Nat. Ac. Sc., vol ii, No. 7, p. 345, 1916; also Phys. Rev., viii, p. 633, 1916. Loeb has misunderstood me when he states that I verified the law $pk =$ const. for the ions in air up to values of X/p as high as 34·5; as a matter of fact I maintained merely that the negative ions were still *in evidence* for this value, whereas Townsend's theory would necessitate their complete disappearance for a value of X/p equal to 0·2. (E. M. W.)

† Chattock and Tyndall, Phil. Mag., xvi, p. 24, 1908; also loc. cit., p. 601.

‡ Erikson, Phys. Rev., vol. vi, p. 345, 1915.

ionic theory, viz., the explanation of the difference in the experimental values obtained for the mobilities of the positive and negative ions in a gas. The greater mobility of the negative ion in most gases has usually been regarded as indicating that this ion is constituted by a smaller cluster of molecules. On another view* we could explain the greater mobility of the negative ion by supposing that the electron is able occasionally to leave the ion so that the increased velocity would arise during the free motion of the electron. The present experiments show, however, that this view is untenable as an explanation; it was shown that the electrons pass through the gas independently of the negative ions and still the latter have a mobility greater than that of the positive ions.

If we regard the ion as consisting of a single charged molecule it seems evident that the difference in the mobilities of the two kinds of ions must be ascribed to a difference in the attractive forces between each kind of ion and the uncharged molecules. In the Bakerian Lecture of 1890† Schuster remarked that 'if the law of impact is different between the molecules of the gas and the positive and negative ions respectively it follows that the rate of diffusion of the two sets of ions will in general be different.'

Franck and Hertz‡ were the first to bring out clearly the possibility of great differences existing in the nature of the collisions between an *electron* and the molecules of different gases; on their view the electrons are regarded as possessing different degrees of elasticity when in collision with the molecules of different gases, the collisions being extremely elastic in the case of the inert gases, but only partially elastic or even almost inelastic for most other gases. It seems to the writer to be perfectly natural and logical to extend this conception so as to apply to the collisions between the *ions* and the neutral molecules. The difference in the mobilities of the two kinds of ions is thus regarded as being due to the different degrees of elasticity between the neutral molecules and the positive and negative ions respectively.

If we regard the collisions between neutral gas molecules as being moderately elastic we would expect that collisions between an ion and a gas molecule would have a smaller degree of elasticity on account of the attractive forces resulting from the charge on the ion. These forces would result in a small fraction of the translational energy at collision being transformed into energy inside the ion or molecule. A very high degree of elasticity would imply (*v.* sec. 4B) either an acceler-

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* Cf. J. J. Thomson, Conduction of Electricity through Gases, 2nd edit., p. 28, 29.

† Schuster, Proc. Roy. Soc., vol. xlvii, p. 553, 1890.

‡ Franck and Hertz, loc. cit.

ated drift for the ion or a slow acquisition of terminal velocity; experiment shows that in general the ion quickly acquires a terminal velocity so that its collisions with gas molecules must be imperfectly elastic.

The experimental fact that the negative ion has the greater mobility would imply that at collisions between the neutral molecules and the positive and negative ions respectively the latter have the higher degree of elasticity. It is of interest to enquire whether we know any properties of the negative ion which would suggest that it should be associated at collision with a higher degree of elasticity; moreover, we have to explain the experimental fact that the difference in mobilities is especially marked in the case of the light gases (e. g. impure hydrogen and impure helium) and practically vanishes for the heavier gases and vapors.

The general effects can be accounted for by two considerations: firstly, the discrete nature of the electronic charge, and secondly, the assumption that the positive and negative charges are differently distributed in the respective ions. If we consider a negative ion which is about to collide with a neutral molecule, the discrete nature of the electronic charges both in the ion and the molecule will be manifested by an intense force of repulsion when the distance is very small. This field will be superposed upon the attraction due to induction and will resist any mutual penetration at collision. The ion and the molecule are at close approach resolved as it were into constituent charges and the simpler the structure the more effective the resolution. The effect of the forces due to polarization will be to decrease the elasticity of the collision while the repulsive forces will act in opposite manner. We would thus expect the collision in the case of the negative ion to be fairly elastic, this elasticity being especially marked with light gases, such as hydrogen or helium, which have a simple structure and a small coefficient of polarization.

In the case of the positive ion the charge is either more centrally situated than is the electron in the negative ion, or what is effectively the same, the positive charge is not discrete but distributed; the ionic charge will thus act so as to produce a collision of small elasticity; the ion will probably penetrate an appreciable distance into the molecule and the mobility will in consequence be diminished.

For the heavier gases and vapors we would expect the negative charge in the ion to be situated more centrally than for the light gases; in any case the discrete nature of the electronic charge would not be so readily manifested with these complex molecules which would approximate more closely to metallic conductors. The forces due to the approach of a positive or negative ion would be more nearly equal and, in consequence, there would be no great difference in the values of the two mobilities.

In pure hydrogen at atmospheric pressure the negative carriers consist practically entirely of electrons; a trace of an impurity such as oxygen is sufficient to convert the carriers into ions. An interesting question arises as to the nature of the negative ion in slightly impure hydrogen; is it constituted by the hydrogen or by the molecules of the impurity? Haines* has recently made an investigation with regard to the negative carriers in hydrogen, commencing with the gas in a very pure state and allowing impurities to accumulate. In this manner he has brought into evidence three distinct types of negative ions, the normal ion being the slowest of the three. His conclusion is that these ions are composed of clusters of hydrogen molecules, each type of ion comprising a definite number of molecules. The possibility that these ions are composed of the molecules of the impurity present is not discussed in the paper, nor indeed does the part played by the impurity receive consideration. No evidence was obtained in the present experiments of the intermediate types of ions described by Haines; this was possibly due to an excess of impurity in the hydrogen employed by the writer, although it should be observed that it was sufficiently pure to yield a copious supply of electrons at atmospheric pressure, whereas in some of the curves given by Haines the intermediate ions are in evidence when free electrons are practically absent. With regard to the question as to the nature of the negative ion in impure hydrogen the suggestion is here made that the molecule of the impurity may act as a catalyst enabling the electron to enter the hydrogen molecule; in the pure gas the electron will however remain in the free state.

In the present paper the motion of the free electrons through a gas at relatively high pressures has been considered. It appears that in general an electron is able to effect a permanent union with an uncharged molecule so as to form a negative ion only if the encounter take place quickly after the act of ionization when the electron still retains a considerable part of its velocity of projection; if it fails to combine initially it would seem that it can remain in the free state even in the presence of electro-negative molecules such as oxygen. However, there may arise occasionally certain systems (electron sinks) which possess the property of being able to absorb electrons which drift through the gas; the union appears in these cases to be of a loose nature and is liable to be broken by molecular encounters.

In a recent communication† Sir J. J. Thomson has expressed

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* Haines, loc. cit.

† J. J. Thomson, Phil. Mag., xxx, p. 321, 1915.

the view that the electron is able to unite with a molecule during its drift motion so as to form a negative ion; before such an attachment occurs the electron in general traverses distances through the gas which are large compared with its free path. The distinct separation between the ions and the free electrons which is shown in a whole series of EI curves lends, however, strong support to the view that the electron traverses the whole distance between the electrodes without effecting any permanent union with a gas molecule; a well-defined bend in the experimental curve could not have been obtained if any considerable fraction of the electrons had become attached to molecules during their passage through the gas.

6. SUMMARY.

1. The separation previously effected between the electrons and the negative ions in dry air at the lower pressures has in the present investigation been extended to other gases, notably CO_2 and H_2; for these two gases the electrons are relatively more numerous than in air at the corresponding pressure.

2. A trace of impurity is especially effective in reducing the number of free electrons when the gas is at a relatively high pressure; at low pressures the effect of the impurity is often inconsiderable.

In most cases a velocity greater than that arising from thermal agitation at ordinary temperatures appears to be necessary to enable the electron to effect a permanent union with an uncharged molecule of the gas or impurity.

3. For the vapor of petroleum ether, whose molecules contain only atoms of carbon and hydrogen, the negative carriers appear to consist practically entirely of free electrons; a trace of impurity, however, is sufficient to effect the production of a considerable number of negative ions.

4. A brief investigation has been made of the motion of free electrons through CO_2; the results do not indicate that the velocity of the electron is proportional to the applied field but suggest that the electron may traverse a considerable distance with accelerated motion before its terminal velocity is acquired.

5. In no instance was any evidence obtained of a change in the nature of either the positive or the negative *ion* as the pressure of the gas was reduced.

6. The present method was employed to determine the values of the ionic mobilities for a few vapors; the results have been compared with previous determinations.

7. A discussion is given with regard to the bearing of the results on certain outstanding problems of ionic theory.

The University of Sydney, December, 1916.

Art. II.—*Correlation of the Devonian Shales of Ohio and Pennsylvania;* by W. A. Verwiebe, Ohio State University.

Correlation of the Devonian Shales of Ohio and Pennsylvania.

The outcrop of the Devonian shales of Ohio occupies a narrow belt extending roughly north from the Ohio river through the center of the state to Lake Erie. It also follows the lake shore to the east and extends into Pennsylvania and New York, widening as the lake becomes narrower. The dip of the rocks in central Ohio is toward the southeast, but very gentle, averaging about 30 feet to the mile. In northern Ohio the dip becomes more and more directed toward the south and finally becomes southwest in Warren and McKean counties of northwestern Pennsylvania.

As is well known, the subdivisions of the Devonian were first studied and named in New York state. They were independently studied in Ohio and also in Pennsylvania. When the time came for more refined correlation of the rocks in these states great difficulty was encountered. The earlier formations including those below the Onondaga limestone were found to be missing in Ohio. The Onondaga because of its lithologic character was traced without much difficulty from its outcrop in New York, through Pennsylvania by means of well sections, to its outcrop in Ohio. However, a real problem developed when the attempt was made to trace the shales and shaly sandstones reaching a thickness of thousands of feet in New York in the same way. These are so similar among themselves in lithologic character and yet each appears so different, due to lateral gradation, that no satisfactory correlation has been offered up to the present.

Statement of Problems Involved.

A clear statement of the problems involved will assist materially in understanding the present status of the question and will also serve as a summary of work done in the past.

First: Where shall the limit of the Devonian be placed? The lower limit as a rule presents no difficulty but the upper limit has been much discussed and shifted, at least in Ohio. It has been variously placed at the top of the Chagrin shale, Cleveland shale and Bedford shale.

Second: Shall the 2000 feet of shale in eastern Ohio be considered synchronous with the 800 feet of shale on the western outcrop or shall the thinning be ascribed to overlap?

Third: Does the Huron shale extend from the river of that name in central Ohio east into Pennsylvania, or does it represent in part the Chagrin shale and Cleveland shale; or is it merely the western equivalent of the Cleveland shale?

Fourth: Does the Cleveland shale thin toward the east because of overlap in that direction or does it constitute a variation in facies of the Chagrin formation?

Fifth: Does the Bedford have a continuation toward the east in the Chemung rocks to which its fossils allies it, or in the Catskill which is more nearly on the same stratigraphic horizon, or does it thin out by overlap in Ashtabula County?

Sixth: Is it probable that a disconformity exists at the base of the Bedford and that this explains the discrepancy in the thickness of the shales as they are traced toward the west, and perhaps also the gap in paleontologic evidence which some authorities have mentioned?

Seventh: Are the formations of New York, particularly the Hamilton, Portage and Chemung, equally represented in the totally different shales of Ohio; is one or the other missing entirely; do they thin down so greatly because of overlap or do they simply 'wedge out' to a feather edge?

Finally: How much weight shall be given to the paleontological evidence? H. S. Williams* has shown that fossil evidence varies with the lithologic character of the rock and that faunas are frequently recurrent in such typical form as to lead to erroneous conclusions. J. M. Clarke† states that the Portage carries a Chemung fauna in the eastern part of New York State.

It is clear then that paleontologic evidence must be used with extreme caution and at this stage of our knowledge should probably be subordinated to stratigraphic evidence in case of disagreement.

No one realizes more strongly than the writer that a complete answer to these questions is impossible at the present time; however, the new light thrown on the problem by a field study of the formations involved, extending over a period of eight years, certainly justifies a review.

Devonian Shales of Ohio.

Bedford: This formation consists of bluish, reddish, and mottled argillaceous shale, with thin sandstones locally developed. It is somewhat fossiliferous especially toward the base, and on the strength of its fossils has been pronounced by several eminent geologists as Devonian in age. Its stratigraphic position also seems to warrant this conclusion. The Mississippian above is delimited by a marked disconformity.

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* U. S. G. S., Bull. No. 210.

† Report N. Y. S. Pal., 1902, p. 996 ff.

The base may also be the locus of a disconformity which is suggested by a rather abrupt faunal change and also by the discrepancy in thickness of the shales below as they are traced toward the east. In figure 1 the varying nature and thickness is shown from the Huron River to Ashtabula County in Ohio which marks the easternmost limit of the formation. Since it thins thus noticeably toward the east, it has been suggested that

Fig. 1.

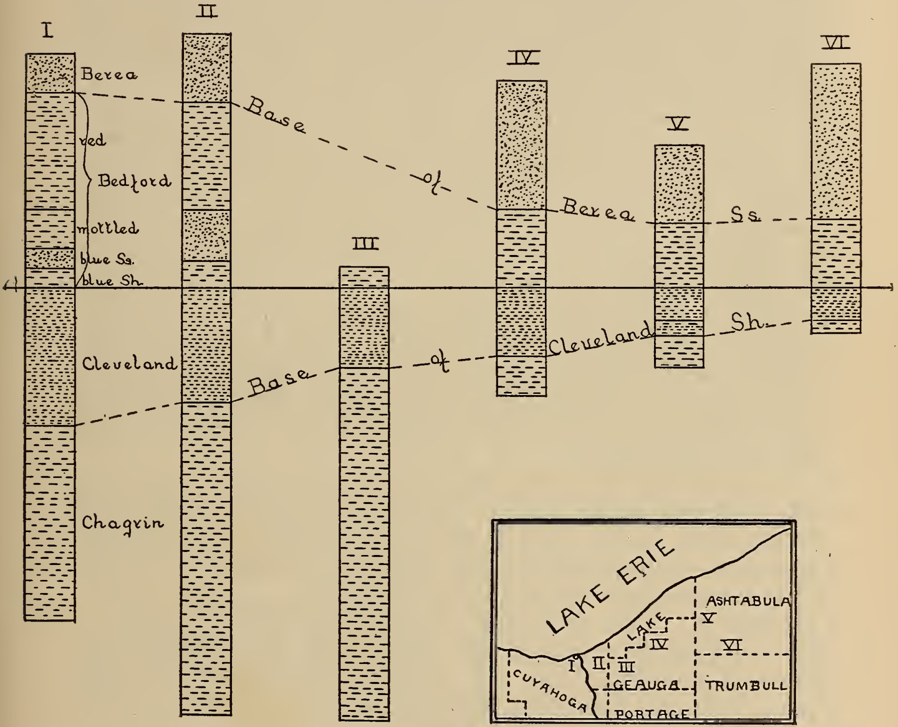

Fig. 1. Sections showing the Bedford and Cleveland formations across northern Ohio from west to east.

a land mass probably existed near the borderline of Ohio and Pennsylvania toward the close of the Devonian and that the Bedford overlaps upon this (Dr. Ulrich and others). However, other evidence that should be present to substantiate this is lacking. The lithologic character of the formation does not indicate near shore conditions in this direction, nor is there any indication of this in the dip of the rocks further east. There is unfortunately a gap in exposures for some distance on both sides of the state line, which makes it difficult to trace the formations stratigraphically. Still when the lower formations are traced from both directions it appears that the Bedford should be correlated with the Venango oil sand group of White. These in turn are clearly equivalent to a portion of the Catskill formation of New York state.

Cleveland: In the Report of Progress of the Ohio Geological Survey for 1869 Newberry first suggested this name. It applies to black shale which has a considerable thickness on its westernmost outcrop but rapidly thins to but 16 feet in its easternmost exposure.* This thinning suggested the same conclusion that was mentioned in regard to the Bedford, i. e., overlap toward the east. In this case the fallacy of such a conclusion can be seen even more clearly, for in many places evidence is presented showing that the Cleveland is simply a horizontal variation of the bluish grey shales known as Chagrin shales. Section No. V in figure 1 has 18 feet of black shale, beneath this is 7 feet of alternating black and bluish shale and beneath this again is the typical bluish shale of the Chagrin formation. Other sections which might be cited show this transition from black to blue equally plainly. In fact it appears that the name suggested by Cushing† applies to just such transition rocks in the region west of Cleveland. He describes the Olmstead shales as blackish and soft (instead of slaty as the typical Cleveland shale) and interbedded with thin bands of blue shale.

It seems therefore that conditions favorable for the formation of black shales existed in the central part of Ohio much earlier than in the eastern part, but that these conditions did become so widespread that they affected deposition in eastern Ohio toward the close of Chemung time.

Chagrin: This term was suggested by Prosser because of the excellent exposures of the formation of the Chagrin River above Willoughby, Ohio. It is intended to supplant the older term Erie of Newberry because this was preoccupied by Vanuxem. It consists of argillaceous and arenaceous shales, blue, grey and green in color. Dr. Newberry and in fact all who worked on the problem down to the present thought that it thinned down to a wedge from the east and that it was therefore bounded by the Cleveland shale above and the Huron shale beneath. This misconception has given rise to many erroneous conclusions and correlations. The fact is that the preponderance of black shale over blue and grey shale is so great west of the Vermillion River that it is quite impossible to pick out the particular zone which forms the continuation of the typical Chagrin.

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* Consult figure 1 in this connection.

† Age of Cleveland Shale, this Jour., xxxiii, p. 581, 1912.

On the other hand, since the Chagrin formation has received its name purely on lithologic grounds it is self-evident that it should be unrecognizable between the Vermillion River and the Huron River since the lithologic character of the shales changes so markedly here. The true state of affairs then seems to be that the 200 feet of black shale exposed along the Huron River and named Huron are the stratigraphic equivalent of the Cleveland as well as the upper part of the Chagrin shales.

As regards the lower portion of the Chagrin some difficulty is encountered at the outset since its lower limit was never clearly defined. This is largely due to the fact that it does not outcrop and can be known therefore only from well records. A scrutiny of these in the reports of the Ohio Geological Survey reveals the fact that the lithologic character of the Chagrin extends down to the limestone (Delaware). Some typical and reliable sections which illustrate this point very beautifully may be found in vol. vi of the Geol. Survey Ohio Publications. On page 429 a Cleveland well is cited in detail which shows but 95 feet of black shale in the lowest 500 feet. Another deep well drilled at Akron (idem, p. 358) shows but 20 feet of black shale in the lowermost 620 feet and but 200 feet of black shale in a total of 1862 feet, the remainder being principally blue, and light and dark grey. Hence to be consistent the top of the Delaware should also mark the base of the Chagrin. If we accept this premise then a new element is introduced into the discussion. Toward the western outcrop of the Devonian shales (between the Vermillon and Huron Rivers) a shale formation called the Olentangy, carrying a well-defined limestone near the top (Prout limestone), has been described. This rests directly upon the Delaware and is overlain wherever the contact is visible, by a black shale. The question now arises whether this formation shall be considered the western equivalent of the lower part of the Chagrin or not. On lithologic grounds it might well be, on paleontologic ground it should not be. These two, however, are not totally irreconcilable. As was indicated above, the Chagrin is known on the outcrop only toward its upper part and the fossils collected in this portion are generally thought to indicate affinity with the Chemung of New York.* This portion is represented by a part of the black shale in the west (where the lower part of the Chagrin outcrops). The lower portion (Olentangy) carries a fauna which is quite generally accepted to be Hamilton in age.† We must assume then that the term Chagrin applies to a series of rocks in Ohio which are the time equivalent of the upper

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* Prosser, Chas. S., Geol. Surv. Ohio, Bull. 15, p. 510.

† Stauffer, Clinton R., Geol. Surv. Ohio, Bull. 10, 1909, p. 156, + 177.

Hamilton, the whole of the Portage, and probably the whole of the Chemung (provided we assume the Cleveland to be but a local facies of the Chagrin).

Huron shale: This name was unfortunate from the beginning. It was suggested in a loose way and has been used loosely and in an indefinite manner ever since. Prosser* has suggested that the name should be replaced, but does not wish to take the responsibility until more field work is done on the problem. It seems to the writer that the term *Ohio shale* given by Andrews in 1870 and intended to be applied to the black shales extending through central Ohio from the Ohio River to Lake Erie might well supplant the term Huron, thus avoiding needless duplication and the possible addition of another term. As nearly as can be determined from the literature, the term Huron is used to designate a section of black shales intermingled with a trifling amount of blue shales occurring typically along the Huron River and reaching a thickness of perhaps 200 feet.† It has been assumed that this shale represented the basal portion of the Ohio shale and that since the latter was thought to be equivalent to three formations in northeastern Ohio it must underlie the Chagrin. No conclusive evidence exists that this is the case and it would be more logical to consider it as being the much thickened Cleveland shale. In this connection the reader is referred to the well records cited in the paragraph on the Chagrin formation. Dr. Kindle, in attempting to find some method of distinguishing the Cleveland and Huron, has suggested that the former never contains any spherical concretions, but does contain many layers of 'cone in cone' while the opposite holds true of the Huron. This is perhaps a satisfactory method of differentiation locally, but it is too insecure and unscientific to be used in correlating separated areas.

The true relationship of the Huron to the Ohio Devonian shales may be simply stated as follows: Two wedges of shales present themselves, one thinning toward the east, the other thinning toward the west. The former is characterized by a black color and slaty texture, the latter by blue and grey colors and a softer texture. Both are entirely isochronous, the thinner portions of the one corresponding to the thicker portions of the other. In other words, the blue and grey shales of the Chagrin or Erie formation are gradually replaced on going west from the boundary of Ohio by black shale. This is called Cleveland shale as far as the Vermillion River and mostly Huron shale beyond that. One exception must be made here and that is the very bottommost part retains its typical charac-

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* Geol. Surv. Ohio, Bull. 7, 1905, p. 23.

† Prosser, Chas. S., Jour. Geology, vol. xxi, No. 4, p. 362, 1913.

ter and is called Olentangy shale. It is of course a well-known fact that the whole body of Devonian shales thins toward the west, but that does not alter the conditions stated above. The source of clastic material was to the east, probably Appalachia, and it stands to reason that the amount deposited should decrease in proportion to distance from its source.

The cause of the black color of the shales is admittedly due to a high percentage of carbonaceous matter. Various theories have been presented to account for its presence. Twenhofel,* in a paper recently published, throws a good deal of light on the probable conditions existing at times of black shale formation. His article also includes an excellent summary of other theories. J. M. Clarke infers deep water conditions of a more or less isolated basin and refers to the report of Andrussow on the bionomic conditions obtaining at present in the Black Sea. Professor Schuchert thinks that conditions favorable to the formation of black shale imply the existence of 'cul de sacs' where incidentally the presence of many sulphur bacteria explains the abundance of pyrite and marcasite usually found in such shales. Ruedemann, on the other hand, does not think enclosed basins are necessarily demanded to explain the presence of carbonaceous matter but merely quiet conditions of deposition and hence distance from the shore line.

We can safely assume then that during upper Devonian times the island of Cincinnatia presented low-lying shore lines. Furthermore the erosion of the Ordovician and Silurian limestones from it would not be likely to furnish much detrital matter. The extensive swamps reaching far inland and overgrown with pteridophyte vegetation supplied an immense amount of slowly decaying plant material to the streams sluggishly entering the sea. For a long period this was not carried any great distance out, except at intervals, but transferred and distributed mainly along the shore by littoral currents. During Chemung times, however, strong currents tending toward the east became more pronounced and more consistent. The material was swept further away from the land and finally toward the close of the Chemung even reached the eastern border of the state.

Devonian Shales of Pennsylvania.

Venango: In his exhaustive study of the oil districts of western Pennsylvania, J. F. Carll delimited a series of rocks consisting of shales and three prominent oil-bearing sandstones under the term Venango oil sand group.† These rocks out-

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* Twenhofel, W. H., Note on Black Shale in Making, this Journal, xl, p. 272, 1915.

† See Reports of Progress of 2d Pa. Geol. Survey, I, 1875 and I^3, 1880.

crop in Crawford and Erie counties and consist mostly of bluish shales and bluish grey sandstones averaging about 325 feet in thickness. The writer has collected fossils from various parts of this group and these show great affinity with Chemung types. Such characteristic species as *Spirifer disjunctus*, *Productella Boydii*, *Rhynchonella contracta* are particularly abundant. On tracing this group to the east it becomes apparent that it is the marine equivalent of a part of the Catskill terrane or more definitely should be classed as upper Chemung. For further details it will be advantageous to consider this formation in conjunction with the following one.

Riceville: This name was given by I. C. White to the interval of shales between the first sand of the Venango oil group and the overlying Corry (Berea) sandstone. It comprises bluish and red shales and shaly sandstones and should be considered an integral part of the underlying oil sand group, being identical in lithology and fossil content. Its thickness is variable, ranging from perhaps 50 feet to over 200 feet. The red beds have not been seen on the outcrop in Crawford or Erie counties; however they are well evidenced in well records further south and east. A typical well record showing the lithologic character of the formation may be found in a paper by the writer on the Berea sandstone of Ohio and Pennsylvania.* In these red shales we have a connecting link with the Bedford shale of Ohio and the correspondence between these is further substantiated by the paleontologic evidence.

Much effort and time were spent in an attempt to find a disconformity between the Riceville and Berea; however, owing to the few exposures, without success. We can only conjecture its existence from a consideration of the variable thickness of the Riceville. The evidence in hand then points to the probability that the Bedford formation finds its continuation in the Riceville and Venango oil group of western Pennsylvania.

Girard shale: Another formation named and described from outcrops in northwestern Pennsylvania is the Girard shale. The name was suggested by I. C. White from its typical exposures along Elk Creek near Girard in Erie County.† Here it consists of very thinly laminated, grey and blue shales. The thickness is approximately 225 feet. On the outcrop the formation is easily recognized, because it readily disintegrates, forming talus slopes which at a distance resemble ash heaps very much. As regards fossils the formation seems to be barren with the doubtful exception of fucoid markings. Mr. White in correlating it was not willing to decide the matter on the basis of the evidence then available, but said that it might

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* This Journal, vol. xlii, p. 58, 1916.

† White, I. C., Pa. 2d Geol. Survey, Rept. Q^4, p. 118.

be considered "either as a Chemung group, or as a Portage group, or as a transition group, or as an independent intermediate group." It appears to the writer after careful study of its stratigraphy and lithology that its true relation lies with the Chemung of New York.

This takes us only a short distance into the state though, and further east Warren county geology obliges us to wrestle with a totally different nomenclature. Carll did some excellent work as shown in I⁴ of the publications of the Second Geological Survey. However, it is evident from the first that he was not aware of the pronounced unconformity at the base of the Olean and hence is severely troubled by the non-agreement of horizons which he traces by his rule of "parallelism of strata." He wrongly correlates the sub-Olean with the Shenango sandstone and tries to fit in the numerous conglomerates below this according to the interval between them. The credit for clearing up a good deal of this confusion belongs to Chas. Butts who has done much excellent work in western Pennsylvania recently.

Conewango formation: This name was proposed by Chas. Butts* for the interval between the Chemung rocks and the Knapp formation of Glenn. He describes the Conewango as consisting of "greenish sandy shale, with thin layers of very fine-grained greenish micaceous and argillaceous sandstone." In the middle is a persistent conglomerate, 20 feet thick, called the *Salamanca* and considered the equivalent of the third Venango oil sand. The total thickness is given as about 550 feet. In correlating these rocks Butts inclines to the belief that they are "the equivalent of some part of the Catskill formation." This is quite probably correct. In tracing the formations from the Ohio line toward the Alleghany River the writer reached the conclusion that the Conewango (including the Knapp) is essentially equivalent to the Venango oil group, which would imply the same correlation.

On this basis also, the Salamanca is considered the probable equivalent of the *second* Venango oil sand instead of the *third.* All who have worked on the problem will admit that the identification and tracing of the oil sands on the outcrop is a difficult matter; however, a careful study of the Tidioute region where the Salamanca first appears above ground and a comparison of the well records to the south, point strongly to that conclusion. Accepting this correlation it would seem but logical to conclude that the "Wolf Creek" conglomerate† is the repre-

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* U. S. G. S. Folio 172, p. 25.

† Glenn, L. C., Devonic and Carbonic Formations of southwestern New York: 56th Ann. Rept. N. Y. State Mus. for 1902, vol. 2, 1904, pp. 971 and 972.

sentative of the *third* Venango oil sand. This member has a strong development in Cattaraugus and Allegany counties of New York, but is rather difficult to trace over the intermediate area. Still Mr. Butts in this connection reports finding "a ledge of conglomerate, 3 feet thick and apparently in place," and concludes that: "If in place this lies near the horizon of the Wolf Creek conglomerate."* He also states that the Panama conglomerate appears to lie at about the same horizon. I. C. White† considered the Panama conglomerate as the equivalent of the third Venango sand. This correlation then bears out very well the conclusions stated above.

Knapp formation: The name Knapp was proposed by Glenn.‡ It has been traced south from Allegany County, N. Y. to Warren County in Pennsylvania by Chas. Butts and he describes it here as consisting of "three members, a conglomerate 20 to 30 feet thick at the bottom, a bed of shale and thin fine-grained sandstone 10 to 40 feet thick in the middle, and a conglomerate 20 to 60 feet thick at the top." The maximum thickness of the formation is given as 120 feet. An older and perhaps better known name of this formation is 'sub-Olean conglomerate.' Mr. Butts also states that it has been commonly regarded as the equivalent of the Shenango sandstone but that the latter in reality overlies the former by 350 to 400 feet and has been removed from this region by erosion. In another paper the writer has indicated his reasons for correlating the Knapp formation with the first Venango sandstone.§

Thus it will be seen that the Knapp and Conewango may be very logically treated as a unit as they correspond to the Venango oil sand group farther west and south. Girty with his intuitive farsightedness saw this relationship at an early date and proposed for them the series name of Bradfordian.

Bradfordian: In a paper on the Paleozoic of Ohio and Pennsylvania‖ G. H. Girty proposed the term Bradfordian and delimited it as follows: "The series of rocks and faunas in southwestern New York which overlie the true Chemung inclusive of the sub-Olean conglomerate, recently assigned by Prof. J. M. Clarke to the Carboniferous, really lie below the base of the Carboniferous system as at present recognized in this country, just as they lie above the Chemung beds, the recognized top of the Devonian. This series, having an approximate thickness of 500 feet, represents an interval not provided for in the geological time scale, and for it the term Bradfordian is proposed. This term which will rank with

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* U. S. G. S. Folio No. 172, p. 27.

† 2d Pa. Geol. Surv. Rept., Q^4, 1881, p. 112.

‡ Rept. N. Y. State Paleont. 1902, p. 980.

§ This Journal, vol. xlii, p. 55, July 1916.

‖ Science, vol. xix, p. 24, 1904.

Senecan, Chautauquan, etc. includes the Cattaraugus, Oswayo and Knapp beds of New York section."

"The Bradfordian faunas are equally distinct from those of the Chemung group, on the one hand, and those of the Waverly, on the other. They contain to some extent an intermingling of Carboniferous and Devonian species, and are in fact transitional between those of the two eras corresponding to the position of the rocks in which they are found."

In Professional Paper No. 71* Girty states that this series includes the Bedford, Cleveland, and Chagrin (Erie) formations in Ohio. In another place† he correlates it with the Pocono and part of the Catskill and also in western Pennsylvania with the "Riceville and considerable thicknesses of underlying beds."

It appears from the above conflicting correlations that the stratigraphy of northwestern Pennsylvania was but vaguely understood at the time the term Bradfordian was proposed. For if we should accept them as they stand it would mean including all the upper Devonian (from the Onondaga Limestone to the top of the Chemung) and the lower Mississippian (Pocono) in this new interval which is surely not warranted by the facts. If we limit the term strictly to its original meaning, i. e. beds including the Knapp, Oswayo and Cattaraugus of New York, then its correlation is not difficult. Butts considers his Conewango as the equivalent of the Cattaraugus and Oswayo formations of New York.‡ If then the Venango oil group is correctly identified with the Conewango and Knapp, and these with the Cattaraugus, Oswayo and Knapp, the Bradfordian turns out to be upper Chemung or the western marine equivalent of the Catskill of the east. One suggestion might be made here. The Riceville, which occupies the interval between the Knapp and Berea (Pocono), is also Catskill in age. If, then, the Bradfordian be expanded to take in the Riceville also it becomes a very useful term and represents, as explained above, the typical marine facies of the continental and palustrine Catskill found further east.

It is assumed that the term Catskill will not be misunderstood. Stevenson and Darton have shown years ago that the Catskill is the eastern facies of the Portage and Chemung. Also it is well known that the characteristic lithology of the Catskill extends farther and farther to the west as we rise in the geological scale. So that finally and at a time corresponding to the *upper Chemung* of western New York typical

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*Index Stratigraphy North America p. 421.

†The Relations of some Carboniferous Faunas, Pro. Wash. Acad. Sci., vol. vii, p. 7, 1915.

‡Op. cit. p. 32.

Catskill sediments are clearly recognizable as far west as McKean and eastern Warren county in Pennsylvania. It is this time unit which witnessed the deposition of the Bradfordian rocks in western Pennsylvania and southwestern New York.

It is also quite probable that this time interval is not entirely included in the ordinarily accepted meaning or range of the term Chemung in New York state. At least present evidence indicates that it is missing except in a few outliers, as the Olean region of New York.

The question of the age of the Bradfordian rocks is admittedly a difficult one. Mr. Butts thinks the evidence favors considering them as Carboniferous in age; however, he does not wish to take a definite stand and therefore treats them under the term Devono-Carboniferous. It may be of value to bring forward some additional evidence on this point. In a paper on the "Geologic Age of the Bedford Shale of Ohio," Mr. Girty* states in reference to the fauna described from the Bradfordian of New York: "The Carboniferous types cited by Mr. Butts make up a total of but seven out of a list of fifty-nine species. All the rest are Devonian forms most of which and possibly all have never been found in rocks of Carboniferous age, so that were we to consider the question whether the faunas show a predominating Devonian or Carboniferous facies, there could be but one answer." In the same article he also states that the Bedford fauna, though peculiar, should be considered Devonian. And, since the Bedford has been shown to be the time equivalent of the Bradfordian it implies Devonian age for this series as well.

J. M. Clarke in an article on the "Construction of the Olean Rock Section" states: "With proper regard for such modifications as additional evidence may require I am disposed to the conviction that in placing the dividing line between Devonic and Carbonic at the base of the Cattaraugus beds, as is done on the geologic map, we have the support of the most direct evidence.†

Mr. Glenn, who first carefully described the Bradfordian rocks in New York, concludes: "Because of the thickness of these red beds (in the Cattaraugus) and their reasonably certain stratigraphic equivalence with the red beds of the Catskill to the east, and because of the unconformity believed to exist between the Cattaraugus and Oswayo, the writer prefers to draw a provisional boundary between the Devonic and Carbonic at this point."‡

* Ann. N. Y. Acad. Sci., vol. xxii, p. 307.

† Rept. N. Y. State Pal. for 1902, p. 999.

‡ Op. cit. p. 985.

In summing up the evidence on this question then we must admit that there is at present no great uniformity of opinion. The most competent authorities are divided. The writer is disposed to believe that the evidence rather favors the Devonian age of these rocks and they are therefore so represented on the table of correlations.

Fig. 2.

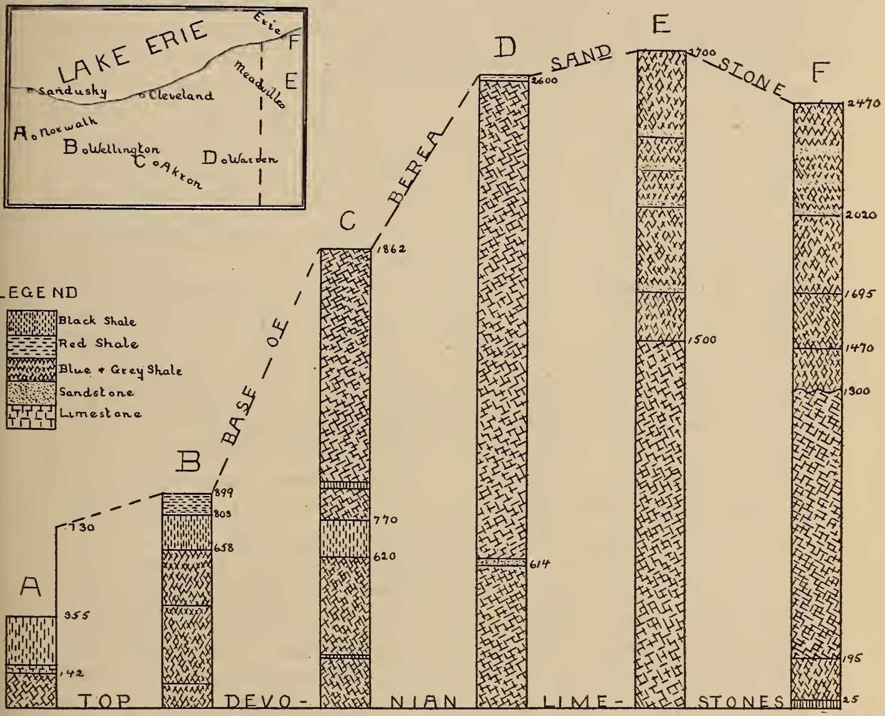

FIG. 2. Well records showing the thickness and character of the Devonian shales from central Ohio into western Pennsylvania.

Explanation of Figure 2.

In figure 2 are represented six carefully selected well records. It is not an easy matter to secure well records which penetrate the entire thickness of the shales and also give their character in detail; and those chosen are not as complete as desired. Still they will indicate in a general way the nature and thickness of the Devonian shales from the longitude of Sandusky, Ohio east to that of Erie, Pennsylvania. Section A is from Norwalk, Ohio and thus near the western outcrop of the shales in Ohio. It shows 203 feet of black (Huron) shale underlain by 10 feet of limestone (Prout) and 120 feet of shale (Olentangy). The base of the Berea is calculated from other wells in the vicinity. Section B from Wellington shows 96 feet of red shale (Bedford) beneath which are 145 feet of black shale (Cleveland). The remainder, 658 feet, is given as alternating blue and black shale. In section C from Akron there are three zones of black shale, the thickest being 150 feet. The rest consists of alternating dark and light blue and grey shales. This section was discussed above (p. 37). The next section (D) constitutes the record of a well drilled in the early part of 1916 three miles southwest of Niles in Trumbull County. It shows ten feet of red shale (top of Bedford) and below that 2589 feet of "blue, white, and cinnamon" shale. An interesting detail is the 35 feet of sandy shale and sandstone occurring 612 feet above the base. This showed a trace of oil and may represent one of the lower sands found in western Pennsylvania. Section E takes us into Crawford County, Pennsylvania. Unfortunately the record was not well kept and the sands indicated must therefore be considered as generalized. The Chemung is about 1200 feet thick, the Portage, Hamilton and Marcellus about 1500 feet, making a total of 2700 feet for the Devonian shales in Crawford County. The last section (Erie, Pa.) was introduced partly to show that the thickness of the shales increases toward the south and partly because this record has been kept with such perfect detail that the formations may be delimited with considerable confidence. At the base are shown 25 feet of black shale (Marcellus), above this 170 feet of Hamilton and finally 1105 feet of Portage and Genesee. The top of the section has been extended by the writer, from calculations based on a study of outcrops in the vicinity, to include the top of the Devonian. An addition of 170 feet of Portage is indicated. Above that 550 feet of Chemung (lower 225 feet–Girard) and 450 feet Bradfordian (Riceville and Venango group). In all the sections the top of the Devonian limestone is used as the lower datum plane and the base of the Berea sandstone as the upper.

Summary.

The correlation of the Devonian shales of Ohio and Pennsylvania with those of New York is a difficult problem because the ordinary criteria, lithology, and paleontology are unsatisfactory guides. A careful consideration of all the available data at hand seem to justify the following conclusions:

1. The 750 feet of shales in central Ohio expand into and are stratigraphically equivalent to the 2700 feet of shale in western Pennsylvania.

2. The shales in Ohio should be subdivided into two parts rather than three, an upper predominantly black colored division and a lower predominantly light colored division.

3. The detailed correlation of the various subdivisions in Ohio and Pennsylvania with those of New York is as follows:

Ohio		Pennsylvania		New York	
northcentral	northeast	northwest	westcentral	western	
Bedford	Bedford	Riceville Venango	(Riceville) Knapp Conewango	(Riceville) Knapp Oswayo Cattaragus	Bradfordian.
Huron (upper)	Cleveland	Chemung (upper)*			
Huron (lower) Prout Olentangy	Chagrin	Chemung (lower) Portage Hamilton (upper)			
	Delaware	Hamilton (lower) Marcellus			

Index to Sections Used in Figures.

The following were taken from Bull. 15 of the Geol. Survey of Ohio (C. S. Prosser):–No. 1—p. 30; 2—p. 54; 3—p. 185; 4—p. 242; 5—p. 300; 6—p. 316; section F.—p. 413. The following from vol. vi, Geol. Surv. Ohio, 1888 (Edw. Orton) A—p. 441; B—p. 348; C—p. 367. Section D by courtesy of J. A. Bownocker. Section E by courtesy of Frank Mossinger.

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* It is probable that the Chemung of western New York includes some of the Bradfordian also.

Art. III.—*Evidence of Uplift on the Coast of New South Wales, Australia*; by L. F. Harper.

During a geological survey of the Southern Coal Field of New South Wales, evidences of an uplift of a portion of the coastal belt of that State were studied.

The coastal plateau of the Illawarra district is formed of Permo-Carboniferous and Triassic strata capped by the resistant Hawkesbury sandstone. Contemporaneous lava flows are included in the series, and sediments aud lavas alike are intruded by dikes of basaltic rock, chiefly monchiquite and camptonite. The dip of the strata is northerly, parallel with the coast line, and vigorous wave erosion on the plateau edge has formed long lines of sheer cliffs in Triassic sandstone and cliffed headlands interspersed with shingly beaches in Permian beds and lavas.*

In the Illawarra district each rock headland is faced by a flat rock shelf, the surface of which is developed generally on a stratification plane. These shelves vary in width from 70 to 250 feet and stand 2 to 4 feet above high-water. They are most pronounced on headlands where a dense lava flow overlies sedimentary strata. Vertical dikes crossing the shelf are less resistant to weathering than their bordering walls and are usually represented by open channels at sea-level or by fissures in the cliff face. (Fig. 1.)

At three localities in the neighborhood of Kiama, so-called blowholes are found. These are openings into the cliff face at sea-level and consist either of a horizontal tunnel with an outlet vertical to the land surface, or of a tunnel only. In the case of the former, the water propelled by waves passes through the tunnel and escapes by the funnel-like, vertical opening as a shower of spray. Two blowholes with vertical outlets were noted. Although both occur in the same contemporaneous lava flow, each has a separate origin.

The principal Kiama blowhole was produced by the action of the sea on a decomposed dike in the lava. A tunnel about 60 feet long resulted. Owing to a depression of the land surface, the sea formed a vertical opening at the landward end of the tunnel, up which the spray is driven to a considerable height. (Figs. 2 and 3.)

In places, the lava flow is columnar and rests on a bed of volcanic tuff—factors leading to the formation of a second type

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* For a description of the geology of this region see:—Harper, L. F., Geology and mineral resources of the Southern Coal Field, Memoirs Geol. Survey New South Wales, Geology No. 7, Sydney, New South Wales, 1915.

of blowhole. Wherever the underlying bed of tuff has been subjected to maximum wave action, the lava sheet has been undermined. In one instance, at the landward end of a cave so formed, a basaltic column dropped out and left an opening about 15 feet deep and 1½ feet in diameter. The column was probably loosened both by the chemical action of the sea water forced up the joint faces and by the mechanical action of the waves on the unsupported prism of basalt.

Fig. 1.

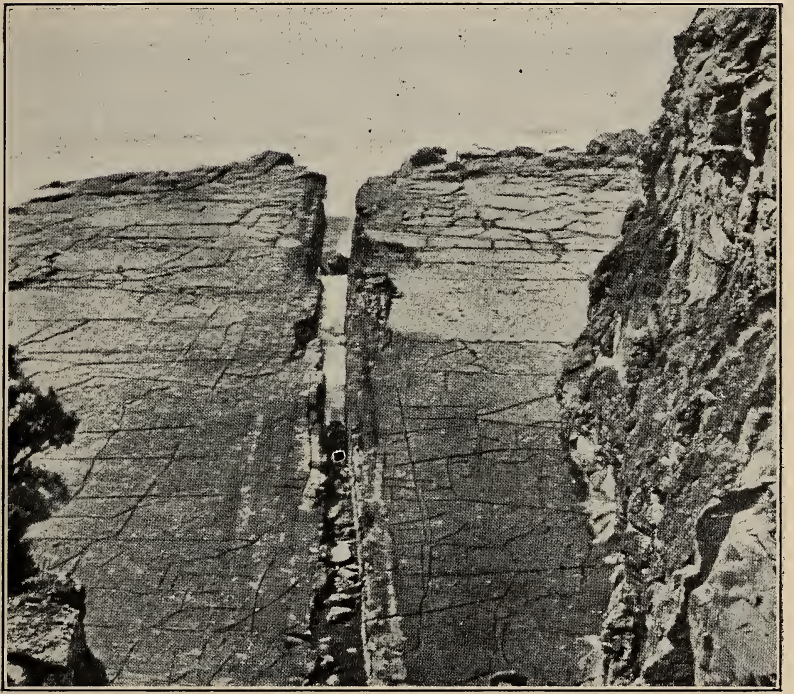

Fig. 1. Rock shelf crossed by a weathered dike. Illawarra district, New South Wales.

In the case of the horizontal blowhole, which has no vertical opening, an incoming wave compresses the air in the rock chamber, and as the wave subsides the water is forced out in a horizontal shower of spray. In the event of a heavy sea and favorable tidal conditions, the effect produced by blowholes is awe-inspiring as well as spectacular. At such times, a subterranean roar is accompanied by a tremor in the roof of the cavern and is followed by a jet of spray shot from 50 to 100 feet into the air. (Fig. 3.)

Caves and channels now 16 feet above high-water mark and similar in appearance to the blowholes described indicate a similar origin. As blowholes are necessarily formed at sea-level, the conclusion to be drawn is that the coast has been raised. Caves developed along dike channels extend under cliffs for distances ranging from a few feet to 200 feet. The dike material at the end and in the roof of these caves is from 2 to 4 feet wide, but caving of the walls has enlarged the openings and produced caverns from 6 to 30 feet wide. The largest of these caves—Hole-in-Wall—(formed in sediments of the Narrabeen stage, Triassic) is about 10 miles north of Sydney. The floor of this cave is strewn with sand and sandstone blocks accumulated long after it was elevated above the sea; and the present floor level does not, therefore, indicate the amount of uplift. Caves in Permo-Carboniferous strata about

Fig. 2.

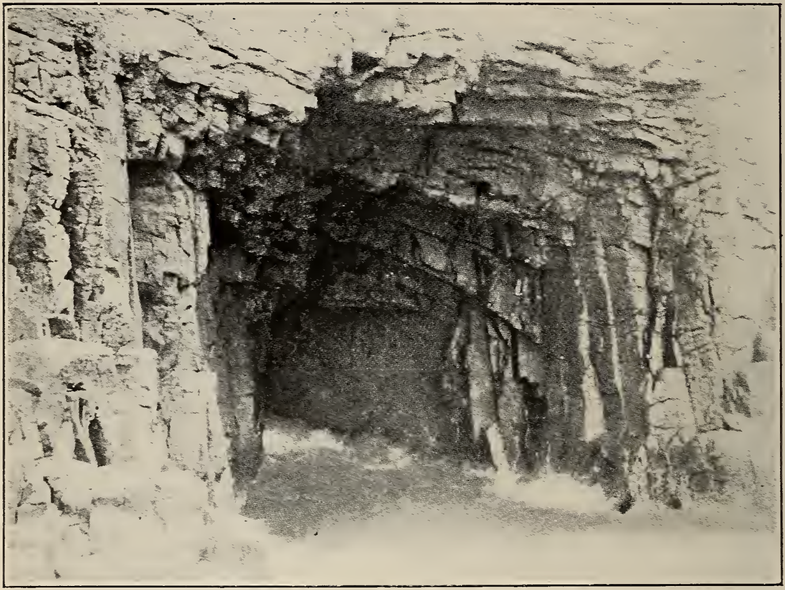

Fig. 2. Entrance to tunnel leading to blowhole. Kaima, New South Wales.

60 miles south of Sydney, at Kiama, record an uplift of about 16 feet.

Accumulations of coarse shingle at the heads of many small coves in the Illawarra district also indicate an uplift of the land. This shingle is from 10 to 15 feet above a similar accumulation which extends from below low-water mark to just above high-water mark, and is composed mainly of bowlders of basalt and rocks from the headlands. No modern storm could have deposited shingle at this elevation. The higher beach is separated from the present beach by a well-marked declivity and in many places maintains a stunted growth of vegetation.

Fig. 3.

Fig. 3. Spray issuing from Kaima blowhole. New South Wales.

A third proof of uplift is the presence of flat shelves of rock extending out from the cliff faces about 3 feet above high-water mark. Under present conditions, these shelves are reached by spray only during storms. When they were planed off, however, their surface must have been subjected to the maximum erosive action of the waves, which, judging by the depth of water, is probably about 10 feet below high-water mark.

A fourth proof of uplift is based on the presence of shallow lagoons or lakes which occur at intervals along the coast and are open to the sea only during exceptionally stormy weather, or when they are artificially opened to allow flood-waters to escape. Along other parts of the coast are extensive tracts of level, swampy land, containing fresh water—areas useful for grazing purposes only during very dry seasons. They are thought to represent ancient lagoons which have been raised above sea-level. In favor of this assumption, it may be added that fragments of recent marine shells are found along the margin of these fresh-water swamps.

That this uplift is comparatively recent is borne out by the geological evidence available, for there is little doubt that the intrusive dikes are of post-Tertiary age, and yet sufficient time elapsed prior to the uplift to permit of marine excavation along their courses to a maximum extent of 200 feet.

A review of the evidence leads the writer to estimate the amount of uplift as follows:

1. Coastal shelves, formed 10 feet below high-water mark, now 4 feet above	14 feet
2. Ancient blowholes formed at sea-level, now 16 feet above. After taking off for the shelf elevation	12 feet
The total uplift is, therefore, about	26 feet

Geological Survey, New South Wales, Australia.

ART. IV.—*The Use of the Platinized Anode of Glass in the Electrolytic Determination of Manganese;* by F. A. GOOCH and MATSUSUKE KOBAYASHI.

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

IN a recent paper* we have shown that the use of very small rotating electrodes of platinum in solutions of usual volume (100^{cm^3}) is perfectly feasible, although the time required for the complete formation of the electrolytic deposit increases with the volume of the solution from which deposition is made. The process was illustrated by the deposition of copper and nickel upon the cathode, and of lead dioxide upon the anode.

We have attempted, also, to effect the deposition of hydrated manganese dioxide upon the very small rotating anode from a solution of manganous sulphate, but in this case the special difficulty is presented that the superoxidation of the manganese to the condition of permanganic acid takes place under the action of the higher current density implied in the use of the usual strength of current and the same anode surface. Chrome alum, alcohol, and formic acid, used as deoxidizing agents, were introduced to effect the reduction of the permanganic acid, but the results which are summarized in the following statement show that the deposition of the manganese dioxide upon the small anode, under the ordinary current strength, is incomplete and unsatisfactory.

Preliminary Tests.

(Volume of solution, 100^{cm^3}: anode surface, $1{\cdot}5^{cm^3}$ (approx.): time, 90 min.)

Manganese taken as sulphate grm.	Manganese weighed as dioxide, dried at 200° grm.	Initial current amp.	volt	Reagents added to Electrolytic Solution
0·1085	0·0337	2·5	16	Acetic acid, 20^{cm^3} Chrome alum, 1 grm. Ammonium acetate, 5 grm.
0·1085	0·0389	2·	17	Alcohol, 15^{cm^3} Ammonium sulphate, 1 grm. Sulphuric acid, 15 drops
0·1085	0·0275	1·	30	Alcohol, 10^{cm^3} Formic acid, 5^{cm^3}
0·1085	0·0438	2·5	12	Acetic acid, 3^{cm^3} Chrome alum, 2 grm. Ammonium acetate, 10 grm. Alcohol, 10^{cm^3}

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* This Journal, xliii, 391, 1917.

These results point to the conclusion that the high current density which is a necessary consequence of the use of the very small anode with currents large enough to effect an electrolytic determination of manganese within a reasonable time is impracticable. In the succeeding experiments, therefore, the use was made of the rotating electrode of platinized glass, described by Gooch and Burdick,* since this device affords a large surface for the deposition with small expenditure of platinum. The anode used in these experiments was made by heating, to a temperature sufficient to volatilize glycerine, a tube of lead glass, shaped like a test tube, painting upon it a viscous emulsion of dry chloroplatinic acid in glycerine, and burning the film of deposited platinum into the glass at the softening point of the latter.

Connection of this platinum film with the rotating shaft was made by platinum wire bound about the tube, reaching over the edge of the latter, and pressed by a rubber stopper into contact with a strip of platinum foil in electrical contact with the metal shaft. An important modification of the original form of this type of electrode† is the attachment of the binding platinum wire at a point so low that the wire will be kept cool by immersion in the electrolyte and thus avoid the possibility of cracking the glass electrode by the over-heating of the wire when carrying a high current. This electrode is shown in the accompanying figure.

Fig. 1.

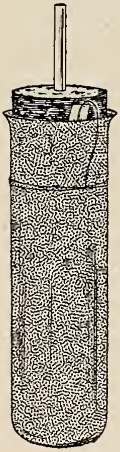

Fig. 2.

With the anode of platinized glass two sets of experiments were carried out. In one set the cathode was a piece of platinum foil measuring 0·5 cm. x 5 cm. In the other set of experiments three cathode foils of twice this size were employed, thus permitting the passage of the same strength of current under a lower potential.

At the end of the electrolysis the solution was drawn off by means of the filtering tube (fig. 2) made by fusing the flared end of a lead glass tube to a disc of platinum gauze and coating the disc with a filtering mat of asbestos by dipping it in an emulsion of asbestos and applying suction. The hydrated manganese dioxide deposited upon the anode

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* This Journal, xxxiv, 107, 1912.

† Loc. cit.

and collected upon the asbestos was dissolved in a cold mixture of sulphurous and sulphuric acids, and the solution, filtered on paper from the asbestos, was evaporated. The residue was dried over the radiator, at about 450°, and weighed as the anhydrous sulphate.

The material taken for analysis was a solution of manganese sulphate standardized by evaporating portions of the solution to dryness, drying over the radiator, at about 450°, and weighing as the anhydrous sulphate, $MnSO_4$.

Details of these experiments are given in the following table.

Electrolysis of Manganous Sulphate.

(Volume 100^{cm^3}: anode surface of platinized glass, 25^{cm^2} (approx.): anode revolutions, 150.)

Manganese taken as sulphate grm.	Manganese deposited as hydrated dioxide and weighed as sulphate grm.	Error grm.	Initial current amp.	Initial current volt	Time min.	Reagents added
Large cathode : 3 (1 cm. x 5 cm.)						
0·1080	0·1057	−0·0023	1·7	12·5	120	Chrome alum, 0·5 grm. Acetic acid, 5^{cm^3}
0·1080	0·0922	−0·0058	1·6	13·	120	"
0·1080	0·1080	0·0000	1·6	12·5	150	"
0·1080	0·1073	−0·0007	1·7	14·8	150	"
0·1080	0·1086	+0·0006	1·6	10·3	150	"
0·1098	0·1094	−0·0004	1·5	16·	150	"
0·1098	0·1095	−0·0003	1·6	15·	150	"
0·1098	0·1074	−0·0024	1·6	16·	180	Alcohol, 10^{cm^3} Acetic acid, 5^{cm^3}
0·1098	0·1040	−0·0058	1·5	18·3	180	"
0·1098	0·1097	−0·0001	1·6	18·	240	Alcohol, 5^{cm^3} Acetic acid, 5^{cm^3}
0·1098	0·1095	−0·0003	1·5	18·	240	"
0·1098	0·1098	0·0000	1·5	18·3	240	"
0·1098	0·1093	−0·0005	1·5	18·3	240	"
Small cathode : 0·5 cm. x 5 cm.						
0·1082	0·0875	−0·0207	1·2	27	150	Alcohol, 5^{cm^3} Acetic acid, 5^{cm^3} Ammonium sulphate, 2 grm.
0·1082	0·1081	−0·0001	1·2	26	180	"
0·1082	0·1080	−0·0002	1·2	25	210	"
0·1082	0·1081	−0·0001	1·2	25	210	"
0·1082	0·1084	+0·0002	1·2	26	210	"
0·1082	0·1080	−0·0002	1·4	25	240	"
0·1082	0·1079	−0·0003	1·2	33	240	Alcohol, 5^{cm^3} Acetic acid, 5^{cm^3} Ammonium sulphate, 1 grm.
0·1082	0·1085	+0·0003	1·1	35	240	Alcohol, 5^{cm^3} Acetic acid, 5^{cm^3}

These results show plainly that the estimation of manganese by electro-deposition of the hydrated dioxide upon the rotating anode of platinized glass, and subsequent conversion of the manganese to the anhydrous sulphate, is entirely feasible. From the electrolyte containing in a volume of 100^{cm^3} approximately 0·1 grm. of manganese in the form of sulphate, acetic acid (5^{cm^3}), and chrome alum (0·5 grm.) the time required for the complete deposition of the hydrated manganese dioxide was two and a half hours; and when alcohol (5^{cm^3}), preferably with ammonium sulphate (2 grm.), was substituted for the chrome alum (0·5 grm.) the time required was extended to a safe minimum of three and a half to four hours.

Art. V.—*Preliminary Note on the Occurrence of Vertebrate Footprints in the Pennsylvanian of Oklahoma*; by Willard Rouse Jillson.

During the summer of 1916, while mapping the structural geology of a portion of the Osage Nation, Oklahoma, the writer had the good fortune to discover a series of casts of vertebrate footprints in one of the sandstone members of the Middle or Lower Pennsylvanian. The location of the bed containing these fossil trails is in Township 27 North, Range 10 East, Section 31 in Elm Creek about six miles northeast of Pawhuska. Stratigraphically the clay-sandstone member in which the casts of the animal tracks are preserved is calculated to be about 200 feet below the top of the Elgin sandstone which Adams, Girty, and White* regard as the Oklahoma equivalent of the Kanwaka shales of Kansas. As the Elgin sandstone is somewhat thicker in Oklahoma than in Kansas this would correlate the track-bearing horizon of the formation with the uppermost part of the Le Roy shales of Kansas.† This correlation fixes these beds as middle or lower Pennsylvanian, which is probably as close a determination as can be made until the Oklahoma Carboniferous and Permian in their relation to the Kansas equivalents are better understood.

Fossil footprints, or casts, from this undoubted marine horizon of the Oklahoma–Pennsylvanian series have never before been described, and because of their rarity such occurrences are to be regarded with interest. The slab on which the casts

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* Upper Carboniferous Rocks of the Kansas Section, U. S. Geol. Surv. Bull. No. 211, p. 45, 1903.

† Idem, pp. 65–66.

occur is about one foot thick. It is overturned from its original position above a soft gray clay which has recently been removed at this point by the waters of Elm Creek. Both the impressed clay and the casting sandstone are small and unimportant members of a long series of interbedded layers of sandstone and shales. Although a diligent search was made, no exposure of the original upper surface of the clay could be found. Due to the nature of the clay deposit, it is not thought that it will ever be possible to collect anything of greater significance from this locality than these casts.

Fig. 1.

Fig. 1. Detailed study showing two series of tracks. Note the lack of heel impressions (horizontal surface ?).

The specimen shows a double trail of casts across the slab. In the upper trail the movement was from left to right, and just below one may note the probable return or "back tracking" of the same individual (fig. 1). Whether this creature was amphibian or reptilian there is no absolute proof, though many small factors point toward the former. Being adapted to a strandline habitat it undoubtedly possessed aquatic tendencies, which statement finds considerable support in the size and physical character of the foot impression. A five-toed animal, its feet were apparently almost as broad as long, and this taken into consideration with the close proximity of the footprints suggests: (1) a poor adaptation to land locomotion or crawling; (2) probably a more efficient adjustment to swimming or paddling; and (3) a compromising of these two in a bottom crawling. Detailed anatomical studies of these tracks are planned, and the results with a series of measurements and outline diagrams will be presented in a later paper.

One of the striking features of this slab of sandstone casts is the absence of the impressions of the feet of one side of the animal in both series of tracks. This peculiarity is generally to be accounted for in one of two ways. First, the animal may "back track" over one of the lines of fresh impressions with the result that the superimposed body weight flattens out and destroys the new undried tracks. In this case, however, the double track of the last movement should be left undisturbed. The specimen, however, does not show this double track. Second, an explanation for the single series of impressions is frequently found in the steeply dipping surface of muds on which the animal crawled along. Such a condition would of course give a series of good impressions on the lower side of the body, but on the upper side of the animal there would be very poor impressions or none at all. Tracks made under such conditions might be expected to show pronounced evidence of the fact in their increasing outward impression. A strong heel impression ought also to occur. Neither of these characteristics can be said to occur in these tracks, and as a result present speculations as to the reason for the absence of the complementary series of tracks have led to no definite conclusions. Only the very slightest and most occasional tail groovings could be detected, indicating very possibly the comparative physical insignificance of the caudal appendage.

The block herein described has been presented by the writer, at the suggestion of Drs. M. G. Mehl and R. L. Moodie, to the Department of Geology of the University of Oklahoma.

Yale University, New Haven, Conn.

Art. VI.—*New Evidence of a Recent Volcanic Eruption on Mt. St. Helens, Washington;* by Willard Rouse Jillson.

Every intelligent person returning from the wooded foothills or snow-capped summit of Mt. St. Helens, Washington (9671 feet—U.S.G.S.) brings back stories of recent volcanic action. The tourist, though he keep to the well-beaten, government trails, sees the evidence on every side, and if he will but listen, may still hear from the lips of a few old pioneering guides very interesting, though perfectly unreliable reports of "the last eruption of the mountain."

During the summer of 1915 the writer spent several weeks examining the geology and physiography of the Mt. St. Helens region, making the climb to the top on August 5th. Many recent flows were noted at elevations of 6000 and 7000 feet, but by far the greater masses of extrusive material lie below 4500 feet. In September while investigating the surficial character of the great recent flow on the southwest side of Mt. St. Helens, between Big and Cougar Creeks, the block of lava shown in the accompanying illustration (fig. 1) was collected. The specimen, which is now in the Yale University Geological Collections of Peabody Museum, in New Haven, was taken from the surface of the flow at the end of a spur of old metamorphic rock which rises out of the floor of the flood, like an island in the sea. The spur is, in effect, the lower end of the sharp divide between two old lava-filled valleys. At this point two long lava ribbons stretching down the side of Mt. St. Helens unite before cascading into the bottom of the Lewis River Canyon two hundred feet below.

In spreading out laterally at the lower end of this spur to join each other, the flows evidently became slower, and formed, if the comparison may be allowed, a "lava back-water." From the standpoint of the physical principle involved, the condition found here must have been essentially the same as that which is seen to be operative at the foot of any stream island. The slackening of the lava flow is obvious, for the surface consists of a series of roughly outlined terraces leading down from both main flows into a considerable depression which finds its greatest depth close to the spur-end. As far as the preservation of the tree moulds or casts is concerned, this slowing up and thinning out of the lava has been a fortunate thing. In places where the lava is much thicker and the flows were more rapid and more powerful, very few traces of tree casts are to be found. At the place where the specimen shown in the illustration was procured, are to be found the lava casts of a score or more of standing and fallen logs. The abundance of casts is a measure of the protection from the destructive force of the two main flows.

The occurrence of this small locality has not been mentioned before in the literature of the subject, although a number of other more conspicuous places adjacent to the main trails have been described. The vertical casts appear like man-holes in the lava floor, "the wells in lava" of Elliott.* At depths of from nine to twelve feet these regularly outlined cylindrical carbonized casts of the trees extend outwards and downwards into giant root casts. The horizontal casts appear as long, regularly cylindrical lava-moulds extending back considerable but undetermined distances into the rock. The horizontal casts are in general of a uniform size and from two to three feet in diameter. The vertical trunk or stump casts seem to be larger (which we should logically expect), some of them attaining five feet in diameter.

The museum specimen (fig. 1) was taken from one of the horizontal casts of this area. It shows in fine relief the longitudinal breaking or splitting of the wood, and the transverse or circumferential check rings, both of which are due to the special kind of carbonization and rapid contraction of the wood cells which the tree trunk underwent in its nearly-closed lava kiln. The fine longitudinal striæ-casts show the character of the annual growth layers of the wood. The size and rough character of the largest ridges on the cast indicate that the log had been greatly charred before the lava struck it. Studies of the carbonization of the cast have led to the placing of the cast-producing tree in the conifer group. This statement finds strong support in the great diameter of the casts themselves. The size of these trees is indicated by the flatness of the arch of the section of the lava cast shown in fig. 1.

The important bearing of these tree casts upon the determination of the dates of various flows is pointed out by Diller,† who also gives a résumé of the better known literature of the subject. He publishes a letter from Mr. F. V. Coville of the Department of Agriculture, who while studying the flora of Mt. St. Helens found some interesting charred trees under recent gravels of the Kalama River. The following statements occur in the second paragraph of Mr. Coville's letter: "The character of the charcoal, which need not be described in detail here, is such as at first to suggest that it was made in a very carefully prepared kiln. There are, however, no charcoal pits in the region. . . . It is evident from the peculiarities

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* Elliott, C. P., Nat. Geog. Mag., vol. viii, p. 227, 1897.

† Diller, J. S., Latest Volcanic Eruptions of the Pacific Coast, Science, N. S., vol. ix, pp. 639–40, 1899.

of the flora of Mt. St. Helens, and from its limited erosion, that it is a mountain of very recent volcanic origin." And a little further on, speaking of the tree casts, he says, "Though I was unable to visit the places where these tree moulds occur, I talked with . . . men who had seen these casts, but none of them had seen charred bark or wood in the holes." His conclusions are, however, that these casts are the source of the peculiarly charred logs of the Kalama. Diller agrees with Coville, and says these charcoal trees are probably at least 100 years old, and, "If this be true it is probable that some of the charred logs are not the result of the last eruption of Mt. St. Helens, but an earlier one." This statement virtually amounts to a recognition by Diller of volcanic activity on Mt. St. Helens within the last century.

FIG. 1.

FIG. 1. Base view of lava block. Shows the strongly carbon-casted surface of the lava where it found contact with the previously charred log. The lava is distinctly vesicular.

Of first significance then, and in line with the arguments of Diller and suggestions of Coville, was the discovery in the same locality from which the Yale cast was taken, of the decayed and disintegrating remains of a small tree trunk. The material lay in the bottom of one of the horizontal casts and extended back into it for several feet at least. A portion of this residue, which consisted mainly of broken, powdered charcoal and a small amount of the decayed wood, was collected but, unfortunately, was lost in packing out of the mountains.

In consideration of the fact that the temperatures of most fluid lavas are greatly in excess of the ignition point of wood, it is realized that any carbonized log producing a lava-cast would have a very slight chance of being preserved, even to the end of the period of volcanic activity, unless completely imbedded within the lava. In such an event the log would be reduced to absolute charcoal, but the chances of its discovery in recent, uneroded lavas would be slight. It is thought that the only possible means by which original spontaneous combustion could have been stopped, thus preserving the charred logs in the moulds, would be by the introduction of a completely encasing water jacket immediately following the contact of the lava with the wood. It may be noted again that the casts herein described occur in a considerable depression which might well have been a small collecting basin for the hot and rapidly vaporizing surficial waters which commonly accompany volcanic disturbances of this kind. The rough terracing of the lava seems to indicate the existence of a rising and widening water barrier and the spur described above is favorably situated for directing surface water into a depression at its base.

The woody material taken from the lava casts has received only superficial examination. The writer, therefore, considers it inadvisable at this time to enter into further abstract considerations. If new collections and detailed studies show that this decaying woody residue was a part of the original cast-producing log, and not, as has been suggested, foreign material introduced in some way into the case, the views of Coville and Diller regarding the recency of volcanic activity in the Cascades receive direct support. These facts, exclusive of much existing corroborative documentary evidence, would be sufficient to establish the occurrence of mild extrusive volcanics at Mt. St. Helens well within the last century.

Yale University, New Haven, Conn.

Art. VII.—*Some Notes on Japanese Minerals;* by Shimmatsu Ichikawa.*

V. *Natural Etching of Garnet Crystals.*

Although crystals of garnet are found abundantly at many localities, the natural etchings of the crystals have not yet been discussed by mineralogists. In 1908, I collected garnet crystals from Wadatoge, Sīnano Province, and at this time observed crystals with natural etchings. The results of the study of these specimens are shown in the accompanying figures (I).

Garnet crystals from Wadatoge occur in cavities of a vitreous andesite. Their color is black, luster vitreous, and crystal faces show the combination of the dodecahedron (*d*) and icositetrahedron (*n*); the habit varies according to which of these forms predominates (see figs. 1 and 2). Crystals are mostly imperfect and model crystals very rare: the etched crystals were collected from earth produced by the decomposition of a white, tufaceous rock accompanying obsidian; they measured 3 to 9^{mm} in diameter; etched figures were more frequent in imperfect than perfect crystals. Some of the crystals were so much etched as to be round like balls; in general etched crystals are distinguished by their stronger luster. The rounded edges of the etched crystals can be barely observed by the naked eye, and the pits, elevations, etc., can only be investigated minutely under a magnification of 75 to 140 diameters.

Fig. 1 shows the natural etching of an icositetrahedral crystal; details are given in figs. 3 and 4. Fig. 2 shows a crystal of dodecahedral type. Fig. 3 is a horizontal projection on the principal axis of fig. 1; the solid angles at the extremities of the axes are rounded by etching and elevations having the form of an octagonal pyramid are found on their surfaces. The cruciform edges on the extremities of the same axes are rounded or hollowed and similar elevations formed on the ridges or grooves. The edges formed by the combination of *d* and *n* are transformed by faces of the hexoctahedron, *mOn*, by solution.

Fig. 4 is a horizontal projection on the trigonal inter-axis of fig. 1; the triplane solid-angles on the extremities of the axes are leveled as faces of the octahedron by etching and pits of the form of a hexagonal pyramid formed on their surface; the pits appear as negative-crystals on the hexaplane solid angles on the trigonal inter-axes of the hexoctahedron. The trifurcate edges on the extremities of the same axes are cut vertically, as $-\frac{1}{2}R$, by etching, and the new faces show neither pits nor elevations, but sometimes striations are noted.

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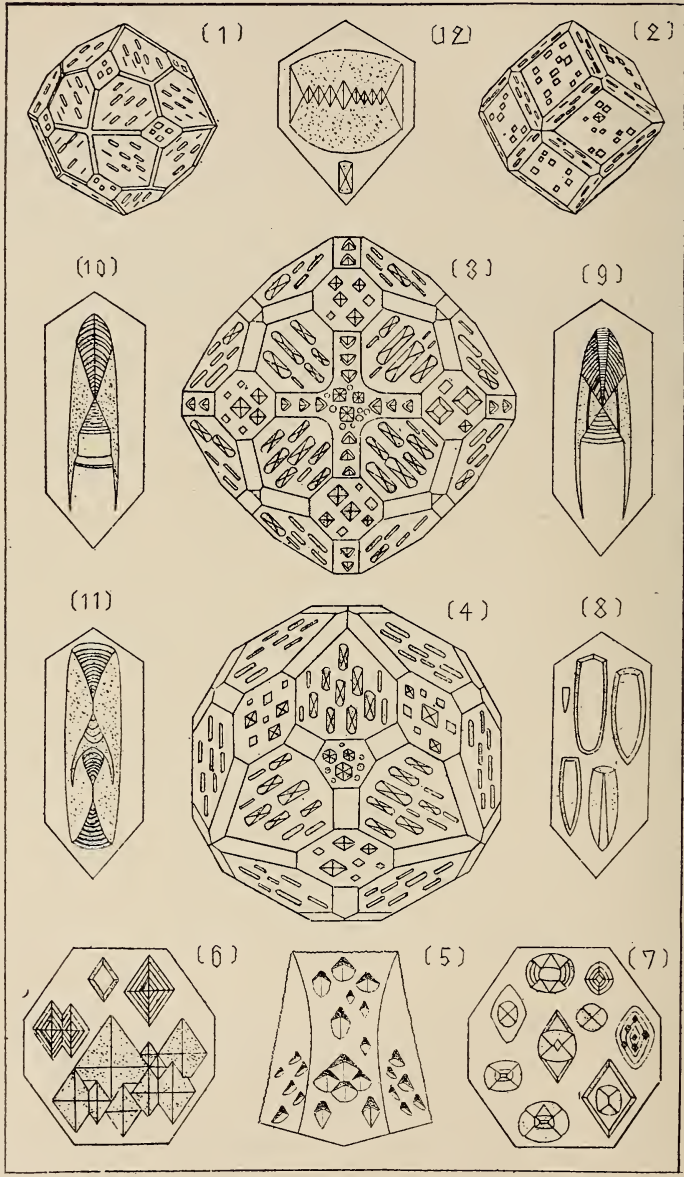
* For an earlier paper, see vol. xlii, pp. 111–119, August, 1916.

I.



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

Fig. 5 shows examples of octagonal pyramidal elevations and these groups formed on the rounded edges of *n*. The figure is a front view and the black parts show the shading of the elevations. Figs. 6 and 7 show the relation between the outlines of the different pits and the edges of the dodecahedron (d); the parallel lines in the figure give the zonal structure of the crystals. The former are observed abundantly but the latter very rarely. Figs. 8 to 11 show the relation between the outlines of the various forms of natural pits of very rare occurrence and the edges of the icositetrahedron (n); the parallel lines in the figures show the zonal structure of the crystal. Fig. 12 shows a single rectangular pyramidal pit; also a group of these as commonly observed on the cubic faces.

By the above study, it is proved that in the direction of the three principal axes of the crystal, elevations of an octagonal pyramid are formed; in those of the four trigonal inter-axes, pits of a hexagonal pyramid are formed; also that the edges through the three principal planes of symmetry are rounded or grooved. The resulting form of the etching is supposed to be a hexoctahedron.

VI. *Elongated Gypsum Crystals.*

In 1909 I visited Udo, Usagi-mura, Hikawa-gun, Izumo Province, and observed gypsum crystals of unusual length; notes on this gypsum and its use have already been published in Japanese.* The following is an abridged translation with only slight changes. The gypsum of Udo occurs associated with pyrite in a clay in massive (radial-fibrous) and lamellar (parallel-fibrous) forms. The massive gypsum appears as spots in a hard clay and the lamellar forms in a very soft clay easily pierced by the fingers; the elongated crystals were collected from the latter. Crystal faces observed are the ∞P, $\infty P \breve{\infty}$, and $\infty P \bar{\infty}$, etc. The prism is elongated in the direction of the axis c; individuals measure 5 to 25^{mm} on the axis b, and 60 to 200^{mm} on the axis c. The crystals are colorless and transparent. Inclusions are observed of powdery gypsum, pyrite, diatoms (*Cyclotella*, etc.), etc.; the diatoms were studied with a magnification of 350 to 650 diameters.

Fig. 1 (see II) shows a familiar swallow-tail twin; A is a front view and B a horizontal projection on the vertical axis of A. Fig. 2 shows a specimen in which at one end the same twin separates into three individual.

Fig. 3 is a regularly developed twin. A is a front view; B a horizontal projection on the vertical axis; C a cleavage fragment.

Fig. 4 is a hoop of a flat and long swallow-tail twin, artificially bent along the face $\infty P \breve{\infty}$; A is a front view. If the hoop in A is bent in the direction opposite along the face $\infty P \bar{\infty}$ a hoop like B is the result; in this case thin polished

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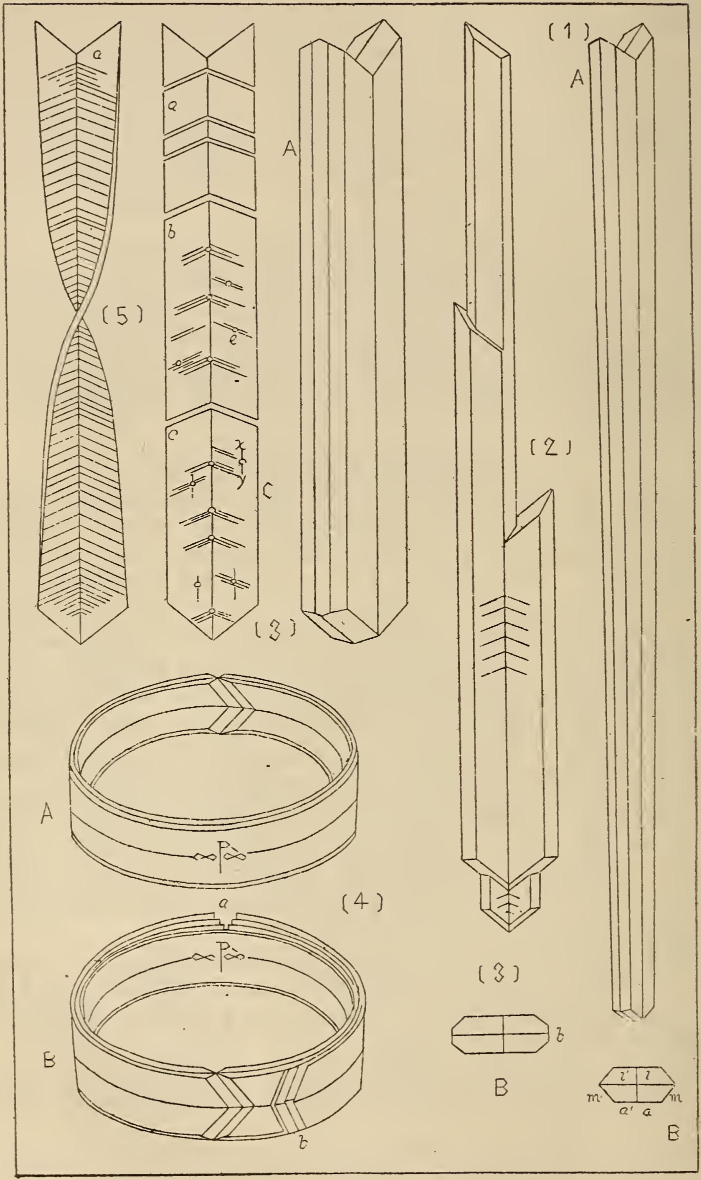
* See my notes in Jour. Geol. Tōkyō, vol. xv, p. 509, 1908; vol. xvi, p. 92, 1909.

II.



Elongated gypsum crystals. S. Ichikawa, del.

folia (ex. *ab*, etc.) are sometimes separated. Fig. 5 shows the same twin artificially twisted; the parallel lines in the figure are cleavage fissures parallel to the face *P*.

In the above study it is proved that the cleavages of gypsum crystals are in the direction of the faces $\infty P \grave{\infty}$, P, $\infty P \bar{\infty}$, etc., and the latter are less perfect than the first-named. The flexibility of the crystals is more conspicuous along the face $\infty p \bar{\infty}$ than in other directions.

VII. *Dendrites of Manganese Oxide.*

In 1912 I visited mineral localities in Echizen Province and collected some interesting specimens of manganese oxide in dendritic and circular forms; some of these are illustrated in the accompanying plate (III).

Fig. 1 (nat. size) shows dendrites formed in the fissure of a Tertiary siliceous sandstone from Yamanokoshi, Kamiyamamura, Nanjo-gun. The outlines of the dendrites, as is often the case, much resemble natural views with mountains, trees, etc.

Fig. 2 shows manganese oxide in concentric zonal rings, formed in the fissures of the platy joints of an andesite from Kurashita, Tani, Kitatani-mura, Ono-gun. When fresh the rings are black and yellow, but these colors are gradually bleached on exposure to the air. B and C show a group of concentric zonal rings; the rings marked *a* in each figure are yellow and the others black; *b* shows plagioclase crystals which form phenocrysts in the rock. A is reduced to one-third; B and C are natural size. A plate of the dendrites was presented to the Twelfth International Geological Congress in Toronto, Canada, in August, 1913.

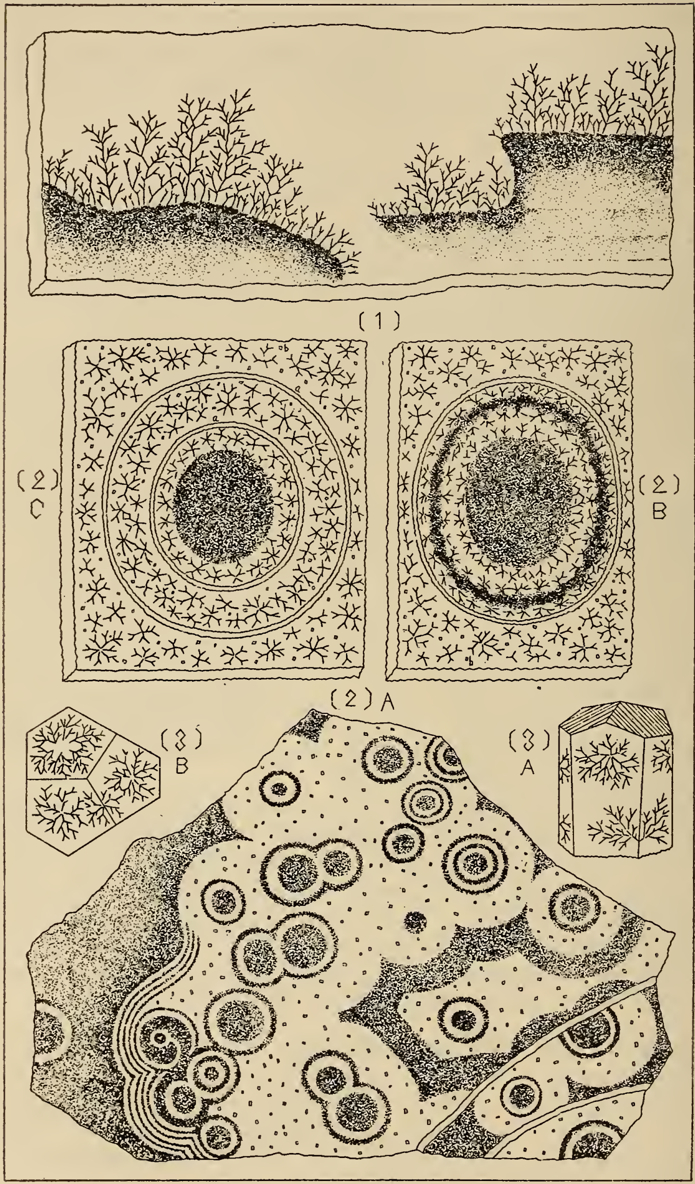
Fig. 3 shows dendrites formed on calcite crystal from Shimoshinjo, Shinyokoe-mura, Imatate-gun (magnified 10 times). A, front view; B, a horizontal projection on the vertical axis. The calcite crystal is colorless and transparent, but its surface is somewhat weathered. In the specimens a group of dendritic forms is sometimes changed to yellow. It is shown here that dendrites of manganese oxide, besides the usual forms, form concentric zonal rings, yellow and black, alternately.

Errata.—The following errata are to be noted in my papers in this Journal:

Vol. xxxix, April, 1915, p. 459, footnote: for vol. xvi, p. 197, *read* vol. xvi, p. 1.—P. 463, second footnote: for Jour. Geogr. Tōkyō, *read* Jour. Geol. Tōkyō.—P. 468, second footnote: for vol. iii, No. 13, *read* vol. iii, No. 12.

Vol. xlii, August, 1916, p. 115, line 14 from top and also in the second and fourth footnotes: for Jour. Geogr. Tōkyō, *read*

III.



Dendrites of manganese oxide. S. Ichikawa. del.

Jour. Geol. Tōkyō.—P. 115. fourth footnote, for 1904 *read* 1914. Pp. 119, last line, for Imitate-gun, *read* Imitate-gun.

Kitashinjo-mura, Imitate-gun, Fukui-ken,
Japan, December, 1916.

Art. VIII.—*The Retardation of Alpha Particles by Metals;*
by H. J. Vennes.

The retardation of alpha particles by metals has been investigated by several experimenters, and among the most recent is a series of experiments carried out by Marsden and Richardson.[*] They found that the amount by which a metal foil reduces the range of alpha particles depends on the part of the range in which the foil is placed. The air equivalent in the foil was shown to be considerably greater when placed directly over the source than when placed near the end of the range.

In an earlier experiment, Taylor[†] showed that when a layer of hydrogen was used in place of a metal foil, the ionization near the end of the range of alpha particles was greater when the layer of hydrogen was placed directly over the source than when placed near the end of the range. When a metal foil was used, ionization was greatest when the foil was placed near the end of the range. In the experiments carried out by Marsden and Richardson, the scintillation method was used for determining the end of the range. Taylor, in his experiments, did not actually determine the range of the alpha particles after passing through the foils and layers of hydrogen, but made experiments on the relative amounts of ionization when they were placed in different parts of the range.

The purpose of the experiments carried out by the writer was primarily to test the point discharge method in determining the range of alpha particles after passing through matter. This was done by carrying out experiments, firstly, using the scintillation method, the procedure being almost identical to that followed by Marsden and Richardson, and secondly, using the point discharge method of counting the alpha particles in place of the scintillation method.

The apparatus used in connection with this experiment is shown in the accompanying diagram, and consists of an ordinary microscope from which the stage has been removed. The zinc sulphide screen is held in place by means of a brass frame, the upper part of which is clamped to the objective of the microscope. The metal foils and source of alpha particles are held in position by two small arms which can be clamped in any position on the vertical rod fastened to the base of the instrument. The point discharge chamber is constructed as shown in the diagram at "B," and is provided with an arm

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[*] Phil. Mag., xxv, p. 184, 1913.

[†] Ibid., xviii, p. 604, 1909.

and clamp so that when in use it can be supported by the verticle rod of the instrument directly above the center of the supports for the foils and the alpha ray source. The microscope has a pivot joint near the base, so that it may be swung out of the way when the discharge chamber is used. The discharge point is connected to a string electrometer and a potential of about 1500 volts is used on the chamber. Polonium which had been deposited on a small copper plate was used as a source of alpha particles. This source was made very strong so there would be a large number of particles even at the end of the range entering the counting chamber. Measurements were made with aluminum, Dutch metal, silver, and gold foils. The results obtained with these foils by the scintillation method appear to be almost identical with those obtained by Marsden and Richardson, and especially in the case of gold and silver,

Fig. 1.

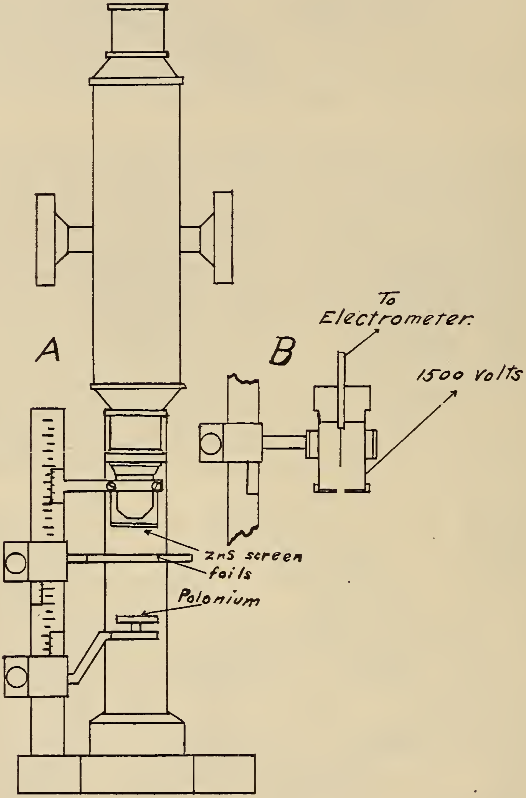
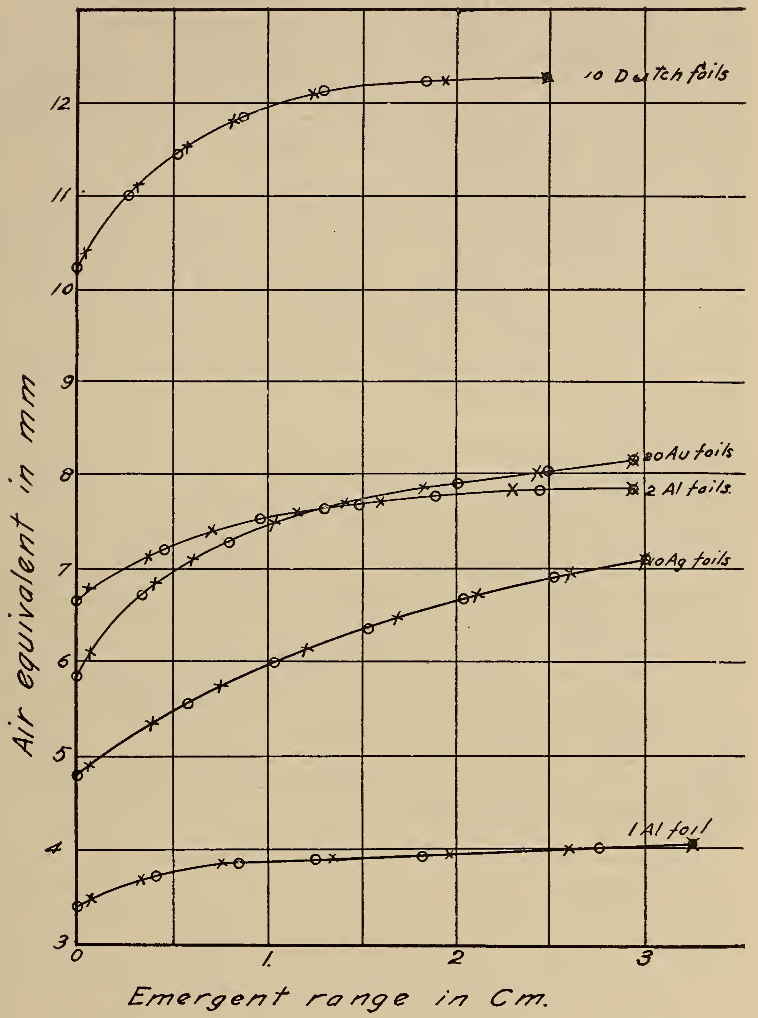


FIG. 2.


10 Dutch foils
20 Au foils
2 Al foils.
10 Ag foils
1 Al foil
Air equivalent in mm
3
4
5
6
7
8
9
10
11
12
0
1.
2
3
Emergent range in Cm.

the air equivalent drops off quite rapidly near the end of the range. The same results were also obtained when the point discharge method was used.

In order that the range may be accurately determined by the discharge point method, it is essential that the point be sensitive enough to respond to the small ionization produced in the chamber when the range of the alpha particle ends immediately after entering the chamber. In determining the end of the range by this method, the distance was measured from the lower end of the chamber.

The results obtained are shown by the curves plotted in figure 2, the emergent range being plotted as the abscissa, and the air equivalent of the foil as the ordinate. The points obtained by the scintillation method are given by circles, while those obtained by the point discharge method are given by crosses. As shown by the curves, the change in air equivalent near the end of the range is more pronounced in the case of the thicker foils and especially in the case of those of higher atomic weight.

It is quite evident that in any investigation where the range of alpha particles must be determined, the point discharge method is as equally well adapted as the scintillation method. In observing scintillations, there is always a certain amount of strain on the eye, and besides a considerable length of time is required for getting the eye adapted to darkness. This disadvantage is altogether eliminated in the point discharge method, for the deflection of an electrometer fiber indicating a discharge is very definite and can be seen without the aid of a dark room.

In conclusion the writer wishes to state that this work has been carried out under the direction of Professor Alois F. Kovarik, and much credit is due him for the success which was attained. The work was done at the Physical Laboratory of the University of Minnesota.

ARNOLD HAGUE.

Arnold Hague, the able geologist and a man of rare personal gifts, was born in Boston December 3, 1840, and died at his home in Washington May 14, 1917. The immediate cause of his death was cerebral hemorrhage and was undoubtedly hastened by his recent fall in Albany while attending a meeting of the Geological Society of America. For nearly fifty years he was prominent in the geological affairs of the country. His parents, the Rev. Dr. William Hague, a noted clergyman and writer, and Mary Bowditch (Moriarty) Hague, lived in Boston during his youth. There his education began but later he attended the Albany Academy.

James D. Hague, his elder brother, studied mining engineering at the Lawrence Scientific School of Harvard, and Arnold may have acquired from him his taste for geology. At the Sheffield Scientific School of Yale where Arnold Hague graduated (Ph.B.) in 1863 he met as classmate Clarence King, who had much to do with his career. Three years in succession Hague studied in Europe at the Universities of Göttingen and Heidelberg, and the Freiberg School of Mines. While in Bunsen's laboratory he devoted himself chiefly to chemistry and mineralogy. The spring of 1865 found him in Freiberg, where he met S. F. Emmons. They were especially congenial, and with the same bent they soon became and continued through life devoted friends and colleagues. Hague in his excellent memoir of Emmons tells much of himself. Indeed, much of that loving tribute to his friend reads like an autobiography. He writes "I was always ready to lay aside metallurgical studies for field geology. Together we took all the week-end excursions with dear old Bernhard von Cotta, visiting many parts of Saxony and studying petrology as laid down in that now antiquated text-book, Cotta's 'Die Gesteinlehre' (Zweite Auflage, 1862). Many an evening Emmons and I spent together over the map of Saxony, acquiring our initiative experience in geological cartography which later stood us in good service. Both came to realize the influence of Cotta upon our future careers, as he gave us much of his time. In this way, during these few months of German student life, was formed a friendship that always endured."

Hague returned to his home in Boston in December, 1866, and soon received from his friend, Clarence King, an offer to join in the Geological Exploration of the 40th Parallel which King was just succeeding in carrying through Congress without the customary delay. Hague lost no time in bringing Emmons to the attention of King, who secured him, at first as a volunteer, for the 40th Parallel Survey. Work began on the Pacific Coast in 1867, and the party went thither by way of Panama. The only other available route was by Wells, Fargo and Company's overland stage, a tedious not to say dangerous, journey.

Hague and Emmons had separate parties in the field, and King with his own camping outfit and greater freedom of motion conducted special investigations over the whole region, all parties meeting frequently for conference. The topographic and geologic surveys of a belt 100 miles in width along the proposed route of the Central and Union Pacific Railroad proceeded together from the Humboldt country of western Nevada to the Great Plains east of the Rockies. Field work was finally completed late in the autumn of 1872, but it should be borne in mind that finished topographic maps on which the areal geology was to be shown, as Hague remarks, were seldom in the hands of the geologists till a year after completing the field work.

After the completion of the field work the final preparation of the report with its accompanying atlas was accomplished in New York, where Mr. King and his two colleagues worked together and lived in ties of closest friendship.

Hague's first scientific publications, "Chemistry of the Washoe Process" and the "Geology of the White Pine District," occurred in 1870 when he was 30 years of age. They grew out of his 40th Parallel work and appeared in Volume III of that organization. The great work, Descriptive Geology, of which Hague and Emmons were joint authors, appeared as Volume II, in 1877. King published Systematic Geology, Vol. I, in 1878.

For a comparative study, the 40th Parallel geologists in 1870 visited the Cascade Range. King climbed Mt. Shasta, Hague climbed Mt. Hood and Emmons Mt. Rainier. They observed about these lofty volcanoes the first active glaciers noted in the United States, and, using the lavas collected, Hague and Iddings made a comparative study of the volcanic rocks of the Cascade Range and the Great Basin.

In 1877 Hague received the appointment as government geologist of Guatemala and traveled extensively over the republic visiting mines and active volcanic centers. The following year he was engaged by the Chinese government to examine gold, silver, and lead mines in Northern China.

Congress created the bureau of the U. S. Geological Survey in 1879, thus withdrawing Congressional authorization from existing surveys and exploration parties and accomplishing a complete reorganization. Clarence King was appointed the first director, and took the oath of office May 24. Arnold

Hague, who had returned to the United States, was appointed a geologist in the U. S. Geological Survey July 8, 1879, but did not take the oath of office until April 10 of the following year.

Under the new organization he was sent to Nevada to study the geology of the Eureka district. His report, published in 1893, is Monograph 22 of the U. S. Geological Survey. In 1883 he was made geologist of the Yellowstone National Park. With the aid of a number of able assistants and specialists the general study of the Yellowstone National Park was completed some years ago and the results published as Monograph 32, part 2, leaving part 1 to be prepared as a final report by Mr. Hague. It is to include a special study of the geysers which engaged his attention for a number of years. This work, his last and greatest, Hague leaves practically complete.

Mr. Hague in addition to his larger reports has contributed papers to a number of scientific periodicals, especially to this Journal. Among these may be mentioned the "Early Tertiary Volcanoes of the Absaroka Range," delivered as his presidential address before the Geological Society of Washington and "The origin of the thermal waters in the Yellowstone National Park," his presidential address before the Geological Society of America. His bibliography of scientific papers includes 39 titles, the last of which is the memoir to his lifelong and devoted friend, S. F. Emmons, published in 1913 by the National Academy of Sciences.

Hague was a fellow of the Geological Society of America of which he was president in 1910, of the Geological Society of London, and a member of numerous other scientific societies. In 1885 he was elected to the National Academy of Sciences, of which he was an active member and officer. As a member of the Commission appointed at the request of the U. S. Government by the National Academy of Sciences, he had much to do with the plan for our National Forest reserves.

Columbia University honored him with the degree Sc.D. in 1901, and in 1906 he received the degree of LL.D. of the University of Aberdeen. He was vice-president of the International Geological Congress at Paris 1900, Stockholm 1910, and Toronto 1913. Nov. 14, 1893, he married Mary Bruce Howe, of New York.

Mr. Hague was not a ready writer nor voluminous, but exact. He aimed more to write well and truly than much. He was a charming host, and there are but few scientific men in America who have had so wide a circle of devoted friends as Arnold Hague.

J. S. DILLER.

U. S. Geological Society,
Washington, D. C., May 26, 1917.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Analysis of Pyrolusite and other Oxidized Manganese Ores.*—O. L. Barneby and Geo. M. Bishop have devised a very simple and convenient iodometric method for the determination of active oxygen in these ores. A sample of about 0·2 g. of the very finely powdered ore is placed in an Erlenmeyer flask with 10^{cc} of a normal solution of potassium or sodium iodide, followed by 5^{cc} of concentrated hydrochloric acid. The flask, covered with a watch glass, is allowed to stand with frequent shaking until the reaction is complete. Under these circumstances iodine is liberated, not only by the higher oxides of manganese, but also by the ferric oxide that is always present in the ores. Then from 0·2 to 0·5 g. of powdered sodium tartrate is added and the solution is diluted to about 150^{cc}. This reagent prevents the subsequent precipitation of iron by sodium bicarbonate, which is now added in small portions until a considerable excess is present. In the resulting solution the iron is changed back by the free iodine to the ferric condition. The remaining free iodine, corresponding to the higher oxides of manganese, is now titrated with standard arsenite solution, using starch as an indicator.—*Jour. Amer. Chem. Soc.*, xxxix, 1235. H. L. W.

2. *The Life of Robert Hare, an American Chemist;* by Edgar Fahs Smith. 8vo, pp. 508. Philadelphia, 1917 (J. B. Lippincott Company).—The present-day student of physics and chemistry may probably know that Robert Hare of the University of Pennsylvania invented that very important piece of apparatus, the oxy-hydrogen blowpipe, and by its aid succeeded in melting considerable quantities of platinum, and showed that practically all of the hitherto refractory substances could be melted by the use of this powerful means of heating. The student may have learned also that Hare's "deflagrator" was a galvanic battery of much importance for currents of great heating power in the times preceding the modern development of electric generators. While these well-known facts indicate the remarkable experimental ability of this early American chemist, the present biography shows him to have been a man of varied and high attainments in science and of admirable personal character.

Provost Smith has produced a very attractive and interesting biography of his eminent subject. He admits that he has become an enthusiast in regard to him and consequently, while he has allowed Hare himself to tell much of his story, largely through previously unpublished letters and other documents which were buried in forgotten journals and pamphlets, he has evidently devoted a vast amount of research to his task, and his comments show much admiration for his hero.

One of the most interesting features of the book is the presentation of a large number of letters between Hare and Benjamin Silliman, the elder, the founder of this Journal. This correspondence records a close and sincere friendship between these two early American scientists, which began in the time of their youth when they studied and lived together in Philadelphia in 1802, and continued until the time of Hare's death in 1858. They consulted each other in the most intimate way in regard to their work, and the letters have an interest similar to those of Liebig and Wöhler. It should be mentioned also that the greater part of Hare's scientific publications appeared in this Journal under Silliman's editorship.

Hare was born in 1781, and was about two years younger than Silliman. The historical position of these men may be shown by the statement that Silliman, Davy and Berzelius were of almost exactly the same age. Only a few of Hare's achievements can be alluded to here. It is interesting to find that his best known invention, the oxy-hydrogen blowpipe, was made when he was only 20 years of age. It was on account of this invention that the Rumford medal, granted for the first time, was conferred on him in 1839. It appears that he was the first experimenter to convert charcoal into graphite by heat, that he was the first to isolate metallic calcium, and that he produced calcium carbide and obtained acetylene from it, although the latter was not recognized by him. He was a wonderful experimenter, particularly interested in electricity, and his experiments before his classes were performed usually on a large scale and in a most impressive manner.

The book contains much of Hare's theoretical discussions. Many of the theories advocated by him have not survived, but others are still important. He was fond of argument, wrote long letters to such celebrated men as Berzelius and Faraday criticizing their views, and was regarded highly enough by them to receive their elaborate replies, which add much interest to the book. Three portraits of Hare, here presented, show him to have been a man of imposing appearance. H. L. W.

3. *A Course in Food Analysis;* by ANDREW L. WINTON. 8vo, pp. 252. New York, 1917 (John Wiley & Sons, Inc.).—The purpose of this book is to provide a laboratory course comprising about 40 periods of work. The author suggests that the course may be used as a substitute for the usual training in inorganic analysis, since it presents more variety in methods and is perhaps of more general interest and of greater practical importance to many students. As the author has had a vast amount of experience and is one of the highest authorities in this line of work, it is found, as would be expected, that the best methods and their most important applications have been presented. It may be added that the operations are very clearly and fully described. The examination of a great variety of products is presented, with due attention to the detection of various preserva-

tives, substitutes and adulterations. An important feature is an excellently illustrated chapter on the microscopic examination of vegetable foods, a subject of which the author has made a special study. H. L. W.

4. *A Text-Book of Sanitary and Applied Chemistry;* by E. H. S. BAILEY. 12mo, pp. 394. New York, 1917 (The Macmillan Company).—This is the revised fourth edition of a book dealing very satisfactorily, in a general way, with the chemistry of water, air and food. While the book is intended primarily for the use of students, the scope is rather popular, so that it may be highly recommended for the use of general readers who desire information in regard to the chemistry of the necessities of life, especially of foods. The composition of all the important articles of food is given, and much good advice is imparted concerning the proper balancing of rations. The book makes no attempt to describe the methods of quantitative analysis, but many experiments are supplied for the use of students. Most of these experiments are qualitative and simple in their character, but they are well selected and instructive. H. L. W.

5. *The Nature of Solution;* by HARRY C. JONES. Pp. xxiii, 380. New York, 1917 (D. Van Nostrand Co.).—The present volume was written by Jones during the last summer of his life and put into the hands of the printer, but later he withdrew it from publication. After his death his friends and colleagues decided to issue it as a memorial volume. The text proper is preceded by a full and accurate bibliographical sketch written by E. Emmet Reid who also surpervised the bringing out of the volume. There are also brief tributes by Professors Arrhenius, Ostwald, and Woodward. The frontispiece is a reproduction of an excellent autograph photograph of the author.

In his preface Jones says: "The present work is not a textbook, but a general discussion of some of the more important properties of solutions, true and colloidal. It is therefore written in a nonmathematical, indeed, largely in a semi-popular style." The first chapters deal with the importance of solution and the historical development of the earlier views as to the nature of solution. These are followed by chapters on osmotic pressure, on the relations between solutions and gases as demonstrated by Van't Hoff, on Arrhenius' theory of electrolytic dissociation, on freezing-point depression, etc. The twelfth chapter comprises a lucid and extended account of the phenomena presented by colloidal solutions. The last two chapters deal with the newer hydrate theory and the solvate theory of solutions, for the final development of which Jones is almost entirely responsible. The author and subject indexes are immediately preceded by a complete bibliography of articles and books written by Jones and his coworkers.

In the opinion of the reviewer this is the best of Jones' literary efforts, since the entire text forms an extremely well-balanced whole, since the ideas and arguments succeed one another with perfect smoothness, and since the perspective is unusually broad. If it be not inappropriate in this place, the writer of this inadequate notice desires to add emphasis to the remarks made by Reid concerning the cordiality always shown by Jones to his students and friends, since he belonged to the latter group from early boyhood and since he later had the honor of being one of Jones' students and assistants on the Carnegie Foundation.

H. S. U.

6. *The Theory of Measurements;* by LUCIUS TUTTLE. Pp. xiv, 303, with 66 figures. Philadelphia, 1916 (The author).—In writing this text the author has kept in mind the needs of the student of mathematics as well as those of the student of physics. No knowledge of trigonometry, however, is presupposed, and none is imposed upon the reader of the book. In addition to the statements of facts and theory each of the chapters of the book includes directions for actual experimental work to be performed by the student, and the amount of this work has been so planned that each lesson will require about three hours for the pupil of average skill and ability.

Although the field covered is comparatively small the subject matter is taken up in elaborate detail. This may be seen at once from the following list of topics: weights and measures, angles and circular functions, significant figures, logarithms, small magnitudes, the slide rule, graphical representation, curves and equations, graphic analysis, interpolation and extrapolation, coördinates in three dimensions, accuracy, the principle of coincidence, measurements and errors, statistical methods, "deviation" and "dispersion," the weighting of observations, criteria of rejection, least squares, indirect measurements, and systematic and constant errors. The index follows an appendix of physical and mathematical tables which have been prepared with extreme care.

Notwithstanding the fact that the material is presented in great detail the text has not been "padded" or overexpanded. It has been carefully graded and many parts may be omitted if the student is already conversant with them. This book undoubtedly merits the attention of all earnest teachers of elementary physics and mathematics since it contains a wealth of valuable pedagogical material and since it is admirably designed to cause the student to think for himself in a clear, concise, logical manner.

H. S. U.

7. *Laws of Physical Science;* by EDWIN F. NORTHRUP. Pp. vii, 210. Philadelphia, 1917 (J. B. Lippincott Co.).—This volume is designed as a reference book on the general propositions or laws of physical science. The material is systematically arranged in six parts pertaining respectively to I Mechanics, II Hydrostatics, Hydrodynamics and Capillarity, III Sound, IV Heat and Physical Chemistry, V Electricity and Magnetism, and VI Light. Whenever doubt arose as to whether an important fact could be classified as a law "a policy of inclusion has been followed in preference to one of exclusion." The manner of pre-

senting a law may be readily seen from the following typical illustration:

"Coulomb's Law.

The electric intensity of a point p close to the surface of a conductor surrounded by air is at right angles to the surface. It is equal to $4\pi\sigma$ where σ is the surface density of the electrification. If the surface of the conductor is in contact with a diaelectric of specific inductive capacity K, then the electric intensity at the point p is,

$$R = \frac{4\pi}{K}\sigma.$$

(Thomson, *Elements of Electricity and Magnetism*, pp. 36, 122.)" The text proper is followed by a bibliographical list of authors, reference books, and journals, and by an index. The publishers have taken pains to make the volume as convenient as possible by using clear type, matt paper, and limp leather binding.

Although the book is useful and much can be said in its favor, nevertheless it seems desirable and fair to point out a few of its general and specific defects. In the first place, a reference book of this kind should be as full and complete as possible. It fails in this respect since no mention is made of the laws and fundamental phenomena of radio-activity (save only the "heat produced by radium"), spectroscopy, and X-rays.

Again, with regard to details, there is room for improvement. (*a*) The formula given (p. 187) for Newton's rings is a purely mathematical relation between the sagitta, the associated semichord, and the radius of a circle, when the square of the sagitta is negligible. The formulæ for the bright and dark rings are not even suggested. It would be just as fair to imply that "$t = \frac{r^2}{2R}$" is the formula for a thin lens, since it is often used as a lemma in deriving the lens equation by the wave-front method. (*b*) The statement of Fermat's principle of least time (p. 167) refers only to the minimum and thus gives no clue to the cases involving maxima of time. (*c*) There are two unfortunate typographical errors on page 51. The mass per unit length of a string or wire is specified as "grains per cm." instead of *grams* per cm. The formula for the frequency of a transversely vibrating cord has 2l omitted under the symbol 1. H. S. U.

II. Geology and Natural History.

1. *United States Bureau of Mines;* Van H. Manning, Director.—Recent publications from the Bureau of Mines (see earlier, vol. xliii, pp. 86, 87) include the bulletins whose titles are given below; also a series of Technical Papers and Miners' Circulars. It is announced that owing to the expense involved in the preparation and publication of the bulletins and the limited printing funds available, it has been necessary to place a definite

price on each bulletin (usually 25 or 30 cents). Orders should be addressed to the Superintendent of Documents, Government Printing Office, Washington, D. C.

BULLETINS: No. 107. Prospecting and mining of copper ore at Santa Rita, New Mexico, by D. F. MACDONALD and CHARLES ENZIAN. Pp. 122; 10 pls., 20 figs.

No. 109. Operating details of gas producers, by R. H. FERNALD. Pp. 74.

No. 111. Molybdenum; its ores and their concentration, with a discussion of markets, prices, and uses, by F. W. HORTON. Pp. 132; 18 pls., 2 figs.

No. 119. Analyses of coals purchased by the Government during the fiscal years 1908–1915; by G. S. POPE. Pp. 118.

No. 121. The history and development of gold dredging in Montana; by HENNEN JENNINGS; with a chapter on placer mining methods and operating costs, by CHARLES JANIN. Pp. 63; 29 pls., 1 fig.

No. 122. The principles and practice of sampling metallic metallurgical materials, with special reference to the sampling of copper bullion; by EDWARD KELLER. Pp. 102; 13 pls., 31 figs.

No. 124. Sandstone quarrying in the United States, by OLIVER BOWLES. Pp. ix, 143, 6 pls.

No. 125. The analytical distillation of petroleum, by W. F. RITTMAN and E. W. DEAN. Pp. 79; 1 pl., 16 figs.

No. 126. Abstracts of current decisions on mines and mining reported from January to April, 1916; by J. W. THOMPSON. Pp. xi, 900.

No. 128. Refining and utilization of Georgia kaolins, by IRA E. SPROAT. Pp. 59; 5 pls., 11 figs.

No. 143. Abstracts of current decisions on mines and mining, reported from May to August, 1916; by J. W. THOMPSON. Pp. 72.

An address delivered by Dr. Manning in Washington, May 25, 1917, before the editorial conference of the Business Publishers Association, gives an interesting and instructive account of the present petroleum and gasoline situation in this country, due chiefly to the very large increase in the number of motor vehicles.

2. *Canada, Department of Mines.*—Of the many publications issued by the Canadian Department of Mines in recent months, the following should be specially mentioned (see vol. xli, pp. 467–469, and vol. xlii, p. 84):

(1.) *Geological Survey Branch.* R. W. BROCK, Director. MEMOIRS.—No. 51. Geology of the Nanaimo Map-Area; by CHARLES H. CLAPP. Pp. vii, 135; 13 pls., 10 figs.

No. 73. The Pleistocene and Recent Deposits of the Island of Montreal; by J. STANSFIELD. Pp. iv, 80; 2 maps, 2 pls., 10 figs.

No. 83. Upper Ordovician Formations in Ontario and Quebec; by A. F. FOERSTE. Pp. viii, 277, vii; 1 colored map, 8 figs. Noticed on p. 438, vol. xlii.

No. 84. An Exploration of the Tazin and Taltson Rivers, Northwest Territories; by CHARLES CAMSELL. 124 pp., 18 pls., 1 map.

No. 85. Road Material Surveys in 1914; by L. REINECKE. Pp. viii, 244; 5 maps, 10 pls., 2 figs.

No. 86. Iroquois Foods and Food Preparation; by F. W. WAUGH.

No. 87. Geology of a Portion of the Flathead Coal Area, British Columbia; by J. D. MACKENZIE.

No. 88. Geology of Graham Island, British Columbia; by J. D. MACKENZIE. Pp. viii, 221; 2 maps, 16 pls., 23 figs.

No. 89. Wood Mountain-Willowbunch Coal Area, Saskatchewan; by BRUCE ROSE. Pp. 103; 1 map, 7 pls., 1 fig.

No. 90. Time Perspective in Aboriginal American Culture, a Study in Method; by E. SAPIR.

No. 91. The Labrador Eskimo; by E. W. HAWKES.

No. 92. Part of the District of Lake St. John, Quebec; by JOHN A. DRESSER. Pp. 88; 1 map, 5 pls., 2 figs.

No. 93. The Southern Plains of Alberta; by D. B. DOWLING. Pp. 200; 3 maps, 35 pls., 3 figs.

No. 94. Ymir Mining Camp, British Columbia; by CHARLES WALES DRYSDALE. Pp. vii, 185; 1 map, 15 pls., 16 figs.

No. 95. Onaping Map-area; by W. H. COLLINS. Includes Map 153A.

No. 97. Scroggie, Barker, Thistle and Kirkman Creeks, Yukon Territory; by D. D. CAIRNES. Pp. 46; 1 map, 6 pls., 2 figs.

In addition, a considerable number of maps have been issued, some of them in connection with the above memoirs.

MUSEUM BULLETINS.—No. 23. The Trent Valley Outlet of Lake Algonquin and the Deformation of the Algonquin Water-Plane in Lake Simcoe District, Ontario; by W. A. JOHNSTON. Pp. 22; 3 pls., 1 map.

No. 24. Late Pleistocene Oscillations of Sea-Level in the Ottawa Valley; by W. A. JOHNSTON. Pp. 14; 1 fig.

No. 25. Recent and Fossil Ripple-mark; by E. W. KINDLE. Noticed on p. 491, vol. xliii.

No. 26. The Flora of Canada; by J. M. MACOUN and M. O. MALTE.

(2.) *Mines Branch.* EUGENE HAANEL, Director. Summary Report for the Calendar Year ending December 31, 1915. Pp. viii, 213; 12 pls., 3 figs.

Also numerous separate reports on the production for 1915 of the metals (copper, gold, lead, etc.); iron and steel; cement, lime, clay, etc.; coal and coke.

Preliminary Report of the Mineral Production of Canada during the calendar year 1916. Prepared by JOHN MCLEISH, Chief of the Division of Mineral Resources and Statistics. Pp. 25.

Annual Report on the Mineral Production of Canada, during the calendar year 1915; JOHN MCLEISH. Pp. 364.

Report on the Building and Ornamental Stones of Canada, vol. iv; WM. A. PARKS. Pp. 333; 56 pls., 7 figs.

Bulletin No. 11. Investigation of the Peat Bogs and Peat Industry of Canada, 1913–14; by Aleph Anrep. Pp. xii, 185; 92 pls., 66 figs., 69 maps.

Feldspar in Canada; by Hugh S. de Schmid. Pp. viii, 125, xxiii, 22 pls., 12 figs., 2 maps. The output of feldspar has increased from 700 tons in 1890 to 19,166 tons in 1916.

3. *Pennsylvania Glaciation. First Phase:* by E. H. Williams, Jr. Pp. x, 101, 56 figs., Woodstock, Vt., 1917.—The glacial deposits over a strip 300 miles long in Central Pennsylvania are unlike normal glacial drift. They more nearly resemble overturned local soil and the disturbed shell of bed rock. Most of the exceedingly rare erratics were furnished by floating ice. Dr. Williams emphasizes the conclusion that such drift is the natural result of a first phase of glaciation, since the first glacier was of necessity burdenless and passed over an aged, soft, and deep surficial mantle, with no frontal moraine. The aged appearance of the drift is "inherent and not acquired" and may not be used to determine the date of glacial advance. An interesting feature of the region is the presence of unaltered anthracite immediately beneath glacial gravels. H. E. G.

4. *Nebraska Pumicite;* by E. H. Barbour. Nebraska Geol. Surv.; vol. iv, pp. 357–401, 1916.—This paper gives an illuminating idea of the vast extent of the Great Plains which have been covered by volcanic ash deposits. It has been found in most of the counties of the state and undoubtedly occurs in all of them. The beds run from 6–10 feet where exploited, but some are 25–30 and even 50–100 are known. The reviewer pauses to note that if a deposit of one foot in thickness covered the state it would equal nearly 15 cubic miles of rock which gives some notion of the enormous amount of material carried out over the plains from the western volcanoes during their period of activity. The beds range in age from the Oligocene into the Pleistocene. The characters of this material and the chemical analyses which have been made of it show it to be a very pure rhyolite tuff, to which the author gives the name of pumicite. Considerable use for it has been found commercially, as an abrasive, a non-conductor and for constructive purposes, some 27,000 tons of it having been mined annually for the past two or three years. L. V. P.

5. *Guide to the Insects of Connecticut; Part III, The Hymenoptera, or Wasp-like Insects;* by Henry Lorenz Viereck, with the collaboration of A. D. MacGillivray, C. T. Brues, W. M. Wheeler and S. A. Rohwer. Pp. 824, with 10 plates. Bulletin 22. State Geological and Natural History Survey, Hartford, 1916. — This extensive work consists of systematic descriptive keys to all the families, genera and species of hymenoptera at present known from the State of Connecticut and the adjacent regions. A total of 2411 species, of which 126 are new to science, have been included. More than eleven hundred of these have actually been collected within the state. They are represented by 634 genera and 86 families.

The coöperation of the group of widely known experts represented in the authorship of this work has produced an authoritative monograph of the greatest importance to the science of entomology. For, in spite of the fact that this order of insects includes some of our most destructive pests as well as many of the most beneficial forms, it has hitherto been impossible for even the trained entomologist to identify many of the species. This report now makes the identification of genus and species possible to the general student of insects. The publication of such a volume as this should be a source of much gratification not only to the authors and to other entomologists but to the citizens of the State under whose auspices it has appeared. W. R. C.

6. *The Biology of Twins (Mammals)*; by HORATIO HACKETT NEWMAN. Pp. xiv, 185. Chicago, 1917 (University of Chicago Press).—The writer bases his discussion of this interesting subject on his own researches on the process of twinning in armadillos. He presents evidence to support the generally accepted view that twins in sheep, cattle and man are sometimes produced by the fertilization of two distinct eggs, while in other cases they may result from the division of a single egg or embryo. The latter are the so-called identical twins. The conditions found in twins help to elucidate some of the important biological problems connected with heredity, sex, and general development.

W. R. C.

7. *The Theory of Evolution, with Special Reference to the Evidence upon which it is Founded*; by WILLIAM BERRYMAN SCOTT. Pp. xiv, 183. New York, 1917 (The Macmillan Company).—This volume consists of six lectures designed for presentation before a popular audience. The principal evolutionary doctrines are explained and as critically examined as the brief course of lectures will permit. The evidences of evolution as supported by comparative anatomy, embryology, blood tests, paleontology, geographical distribution and experimental work are logically presented and in sufficient detail to give the general reader a good idea of what the theory of evolution stands for at the present time. W. R. C.

8. *A Chemical Sign of Life*; by SHIRO TASHIRO. Pp. ix, 142. Chicago, 1917 (University of Chicago Press).—In this little volume the author discusses irritability as a sign of life, and explains the relation between irritability and metabolism resulting in the production of carbon dioxide. By means of an ingenious apparatus sufficiently small quantities of this gas can be detected to determine whether a single seed, a nerve fiber, or any plant or animal tissue, still possesses the irritability characteristic of life. Hence the test for life is the capability of carbon dioxide formation, and the quantity of life present can be measured by the relative amount of this gas produced in a given time. The "biometer," by means of which these tests are made, is fully described in an appendix. W. R. C.

9. *Fundamentals of Botany;* by C. Stuart Gager. Pp. xix, 640, with frontispiece and 434 text-figures. Philadelphia, 1916 (P. Blakiston's Son & Co.).—Dr. Gager's text book presents so many interesting features that it is difficult to call attention to them in a brief review. In his opinion the purpose of an introductory course in any subject is not so much to prepare the student for advanced courses as to introduce him into a new realm of thought. With this end in view he emphasizes certain phases of botany which are not usually taken up in introductory works. After describing the nature of the science, and the various fields of botanical activity, he gives a short account of plant organs and of plant cells. He then proceeds at once to a consideration of the functions of plants, taking up such subjects as the loss and absorption of water, nutrition, respiration and growth. He then discusses the structure and life histories of typical plant-forms, beginning with the fern and taking up in order mosses, liverworts, algae, and fungi. Then, in an ascending series, he continues with the horsetails, lycopods, cycads, conifers, and angiosperms. Into these discussions he introduces many collateral topics. Some of these illustrate theories or generalizations and others call attention to matters of economic importance. In connection with the ferns, for example, alternation of generations, reduction, inheritance, variation, and adjustment to environment are clearly presented; while, in connection with the fungi, the use of these plants as food, the diseases which they cause, the nature of fermentation, and the significance of bacteria to the human race are among the subjects considered. The concluding chapters of the book are devoted to such subjects as evolution, Darwinism, and heredity. Throughout the volume the author lays especial stress on the historical development of botany and introduces portraits of eminent workers, calling attention to the definite services which they have rendered. In many places he illustrates his text with original outlines or diagrams; these and the excellent text-figures, many of which are new, deserve high commendation. The book on the whole represents a distinct contribution to botanical pedagogy. A. W. E.

10. *A Laboratory Guide for General Botany;* by C. Stuart Gager; pp. viii, 191. Philadelphia, 1916 (P. Blakiston's Son & Co.).—The directions given in this helpful work are unusually explicit, their purpose being not only to help acquaint the student with botanical facts but also to teach him how to observe and how to record his observations. In many cases his knowledge is tested by suitable questions. The order of topics is the same as in the author's Fundamentals of Botany, although the book could easily be used in connection with other texts. A. W. E.

11. *Laboratory Manual of Agricultural Chemistry;* by Charles Cleveland Hedges and William Thoreau Bryant. Pp. x, 94, with frontispiece and 8 text-figures. New York, 1916 (Ginn & Company).—This little book is designed to meet the special needs of students in agricultural chemistry and presupposes a

knowledge of general chemistry. It describes a long series of experiments, the significance of which is brought out by appropriate questions. The introductory experiments deal with methods of quantitative analysis and these are followed by definite applications to the analysis of feedstuffs, of soil, of insecticides and fungicides, of milk and of water. In the hands of a capable teacher the book should yield excellent service. A. W. E.

12. *Manuring for Higher Crop Production;* by E. J. RUSSELL. Pp. iv, 69, with 16 text-figures. 1916 (Cambridge University Press).—Although written principally for the use of farmers in the British Isles the present work gives information of much value to farmers in general. At the same time emphasis is laid on the impossibility of giving advice which will hold good under all circumstances. After an introductory chapter on the improvement of the soil, natural and artificial manures are described, and the methods of manuring arable and grass lands are discussed at length. The book is based largely on actual experiments carried out at the Rothamsted Experimental Station at Harpenden, of which the author is director. A. W. E.

13. *A Manual of Organic Materia Medica and Pharmacognosy;* by LUCIUS E. SAYRE. Fourth edition, revised. Pp. xviii, 606; 4 pls., 302 figs. Philadelphia, 1917 (P. Blakiston's Son & Co.).—This work deals concisely and thoroughly with the sources, characteristics and constituents of drugs of vegetable and of animal origin. It has been extensively recast. Not only is it brought into conformity with the new U. S. Pharmacopeia IX, but the newer botanical classification (leading from Cryptogams to Compositæ) is followed. Besides the elaboration of the matter relating to inorganic drugs, chapters on therapeutic action and serotherapy have been added. These contain valuable matter but a good deal of antique therapeutic superstition is fostered (e. g. the employment of gold salts, sarsaparilla, etc.).

Plant histology has been largely omitted, the reader being referred to Stevens' "Plant Anatomy." Sayre's new edition will attract and be of high service to those who are interested in the study of drugs. H. G. BARBOUR.

OBITUARY.

PROFESSOR GEORGE HAPGOOD STONE, formerly a member of the Faculty of Colorado College, died on February 20 at the age of seventy-five years. He early studied the glacial geology of Maine and in 1881 came to Colorado Springs where he resided for most of the remainder of his life. He was active as a mining geologist and was especially interested in the geology of the Pike's Peak region.

PROFESSOR H. F. E. JUNGERSEN, the Danish zoologist who made important contributions to the knowledge of the fauna of Greenland, died recently at the age of sixty-three years. He was particularly interested in the Danish expeditions concerned with the investigation of the North Atlantic and the Polar seas.

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VOL. XLIV. AUGUST, 1917.

Established by **BENJAMIN SILLIMAN** in 1818.

THE
AMERICAN
JOURNAL OF SCIENCE.

FOURTH SERIES

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Kunzites
Garnets
Opals
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THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. IX.—*Physiographic Development of the Tarumai Dome in Japan*; by Hidezô Simotomai (Tanakadate), Tôhoku University, Japan.

The rise of a new dome on the top of Tarumai volcano in Japan attracted much attention among the naturalists of the world. Though it was not an unusual type of lava eruption, itsphysiographic development is observed better than others of the same kind. As the structure of the volcano and the history of its recent eruption in the year 1909 have been described by many authors, they will be touched upon only briefly here.

Tarumai is a flat volcanic cone formed principally of andesitic scorias and ejectas and its site is in the volcanic region of Hokkaidô in lat. 42° 41′ 30″ N. and long. 141° 21′ 40″ E. Towards the south it slopes gradually to the Pacific coast, while to the north a short ridge connects it with an extinct volcano called Hu-uppusi-nuppuri. Both cones rise from the deep water of Sikots Lake, of which the area is 78 sq. km., with surface 298^m above sea-level and bottom about 60^m below sea-level.

The volcano has a double crater on its summit and the *Somma*-wall is much dissected on the southwest and southeast. The eastern side culminates in Higasiyama at the height of 1016^m above sea-level and before the eruption this was the highest point of the volcano.

According to Prof. Ôinoue, the inner crater, which is now full of the recent lava, was formerly oval in shape, with major axis of 670^m running N.10°W. and minor axis of 550^m; its depth was about 80^m. The circular bottom of the crater had a diameter of 60^m, and from some pits in it sulphurous gas continuously issued.

Several eruptions are recorded in history, but they have few direct bearings on the present discussion. From 1896 until the beginning of 1909 the volcano was quiet. In the latter year, between January and March, small activities were noted eight times by the inhabitants of the territory in the form of ash-rain, fire phenomena, detonation, and earthquake. On the 30th of March a tremendous explosion took place, throwing out ashes, bombs, lapilli, etc., and therewith a smoke column about 7 km. high rose from the volcano. On April 4th Ôinoue visited the mountain and saw a new, deep, fuming pit on the floor of the crater bottom. On April 12th another explosion occurred in full violence, accompanied by ashes, bombs, lapilli of several sizes, and an enormous smoke column. The surrounding inhabitants did not notice any change on the mountain until April 19th; when, the cloud clearing up, a dark elevation on the summit came in sight. Indeed, a dome of augite-andesitic lava was rising in the inner crater. On April 23d

Fig. 1.

Fig. 1. The location of Tarumai Volcano.

Ôinoue again visited the mountain and the photographs taken on that date show a smooth, round-headed dome which filled the inner crater and rose more than 100^m above it. The pictures taken on May 1st show the dome to have become larger and flatter at the top.

The trigonometrical measurement of the Ôinoue party on May 1st gives the dimensions of the dome. The base of the dome was about circular, covering an area of 152,000 sq. m. It was about 200^m in height above the floor of the crater bottom and 134^m above the lowest part of the inner crater-wall; its whole volume was computed at 20,000,000 cubic meters.

The dome was 1046^m high above sea-level and 30^m above Higasiyama, so that the volcano had become a little higher than before. On May 15th an explosion occurred on the southern foot of the dome and thereby the inner crater-wall was cracked. The new fissure was 3^m to 8^m wide, about 18^m in visible depth, and 150^m long in the direction of N.60°W., ending directly on the side of the dome. From a point in the middle of the crack, sulphurous gas was issuing in great volume. In the winter of the same year snow covered the dome, though it was still fuming on the surface.

After that time seven years elapsed without any further information about the dome. The writer had occasion to visit it three times in the year 1916, and will give here some short observations about the development of the dome, adding some new data to that of my former publication.*

Since 1909 the dome has remained without any important change in form, conserving all the main elevations and angles, and most of the large lava blocks scattered in the vicinity had kept their original shape. Talus had developed on all sides, covering the lower three-fifths of the dome. Its maximum development is at the southern half, where the prevailing wind attacks it directly, while the minimum is at the opposite side, where the dome is protected from the wind through the inner crater-wall. The southeastern side of the mountain near the termination of the large fissure shows the least steepness caused by the falling of lava, and it is now not difficult to reach the summit, which was never visited by anybody before and it was doubted whether there existed any crater or not.

From out of the talus arises the dome proper, showing steep cliffs of lava in its sides which are very instructive.

The superficial lava layer does not form a continued crust but is broken by vertical fissures into many irregular parts, some of which are fallen down between others as wedges. Each lava-mass is divided into numerous layers, feldspathic, iron-rich, etc. These layers must originally have been parallel

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* Zeitschrift, Gesellschaft für Erdkunde, Berlin, 1912, page 433.

to the cooling surface. The thickness of the layers varies from a few centimeters to half a meter.

The sulphurous gas is still issuing from numerous parts around the lava cliff, though it is now in minimum activity.

The upper surface of the dome is practically flat, but it is so rough and uneven with sharp edges, spears, and spines of yellowish-gray lava that walking on its surface is almost impossible. Such slaggy, porous lava was seen everywhere around the dome at the beginning of the eruption, but now one can scarcely find any on the sides, for there this phase of the lava has fallen away and become buried in the talus.

Fig. 2.

Fig. 2. Tarumai before the eruption of 1909. Seen from south from the coast of the Sikots Lake with the old pier in front.

The maximum elevations are at the southwest and northeast sectors on the upper surface, and between these two heights a fissured zone runs from southeast to northwest. Many cracks of different sizes run nearly in radial directions from the center. In some cases the intervening mass between pairs of the fissures is dropped down as a wedge, forming a trench-depression (Graben). Many cracks are still open. These features of the upper surface are like those seen on the sides of the dome. One of the large trenches begins at the southeastern periphery of the top-area, a little northward from the termination of the fissure on the inner crater-wall, and runs to N.60°W., in the same direction.

Towards the center of the dome the trench gradually loses its character, but at the other end it is 50^m wide and is bounded on both sides by steep slickensided cliffs which are locally about 20^m high. Within this depressed zone, many minor fissures run in the same direction; some of them are open and about 10^m deep. Another large depression runs from the center of the top surface and goes to N.N.W., and its breadth is about 60^m. Its maximum depth lies a little distant from the center and forms a long, oval basin about 20^m wide, and its bottom is 30^m under the highest point of the dome.

Fig. 3.

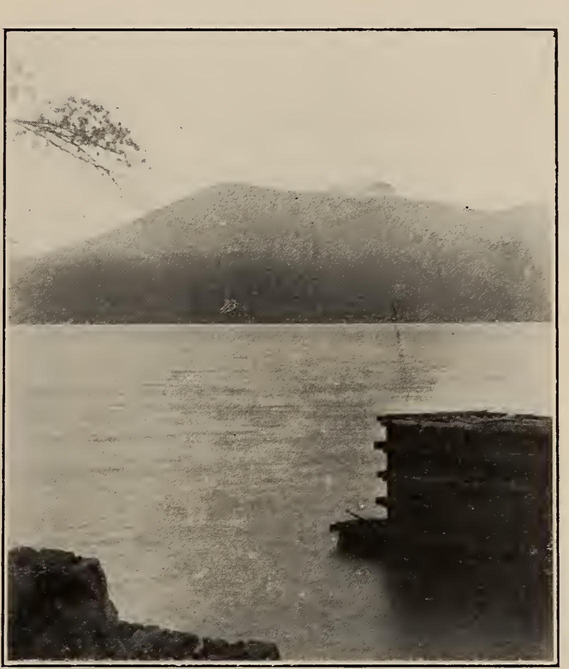
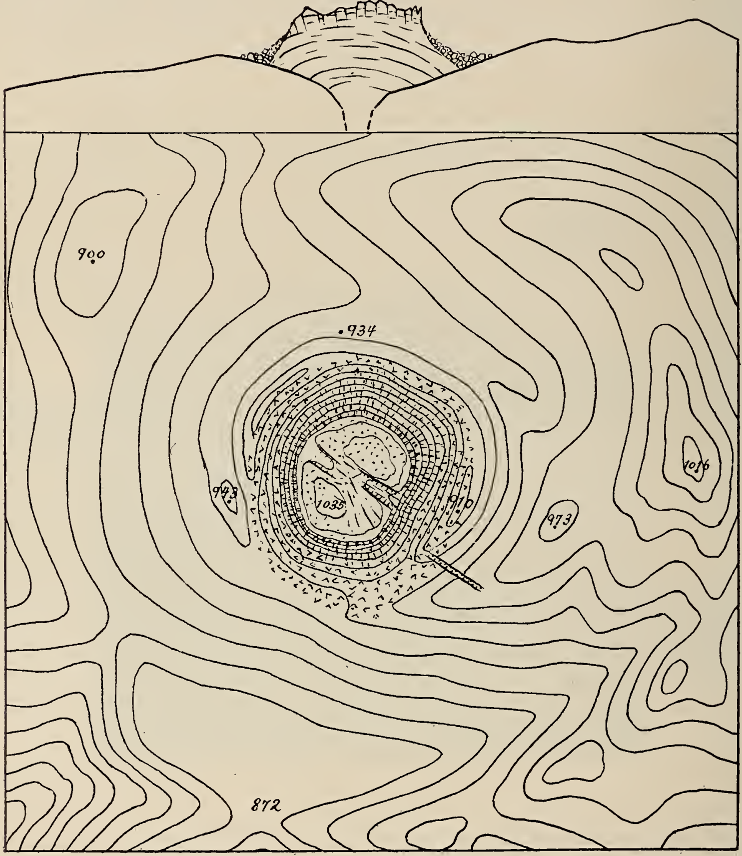


Fig. 3. Tarumai after the eruption of 1909. Seen from about the same place as fig. 2, with the new pier in front.

Moderate amounts of sulphurous gas are issuing through these numerous fissures. Prof. Kusakabe in Sendai, who visited Tarumai in August with us, reported to me that the photographic films which I took on the dome for his party gave positive instead of negative images when developed by the normal process. This curious phenomenon was afterwards experimentally proved by him to have been caused by a momentary attack of the sulphur dioxide on the films.

The exact date of the formation of these fissures is unknown,

FIG. 4.



Map and section of Tarumai, 1916.

FIG. 4. In the map the meridian is marked by a lateral edge. The schematic section passes from east to west, including the highest point in the *somma* wall (1016 m.). Scale, 1 : 150,000 approx.

but in photographs which were taken on the 23d of April such depressions are not visible, while in those taken on the 1st of May, 1909, we can recognize, on the eastern side of the dome, some traces of the termination of the trench just as we now see it.

Fig. 5.

Fig. 5. Slaggy lava surface of the dome with cracks in front. Photograph by the author, October 20th, 1916.

Fig. 6.

Fig. 6. Tarumai dome from the S.E., at a point in the *atrio* of the volcano. Photograph by the author, October 20th, 1916.

In October, 1916, we carried a small transit and a mountain barometer to determine the exact height of the dome. For the measurement of the heights, I took one point common with the former survey as a base, that is, the triangular point of Higasiyama, 1016^{m} high above sea-level. From this base, I took the readings of the several characteristic points on the dome, upon which the former surveyor and I had agreed. This method gave the same result as that furnished by the mountain barometer. The exact height of the dome is 1035^{m}. Comparing this measurement with that made by Ôinoue on the 1st of May, 1909, my result is 11^{m} less, so that we can be sure that the dome has sunk a little since the 1st of May, 1909. But this sinking of the dome surface ended probably before the summer of 1909, for since that time it has remained practically the same in size and the shape, so far as I remember it.

On the slaggy surface of the dome, much fragmental material, similar to that seen all around the base, is scattered. This material might be regarded as having been thrown up by the explosion on the 15th of May, 1909.

In August, 1916, I found many dead cicadas (*Cicadina bihamata* Motsch.) on the dome, which perhaps were traversing the mountain and were killed by the sulphurous gas.

It is of further interest that three species of plants are found on the dome surface; these are: 1, *Pentstemon frutenscens* Lam.; 2, one species of moss resembling Decranum sp.; 3, another species of moss resembling Pognatum sp. The two latter have not yet been classified by species. The first of them was determined by Prof. Miyabe in Sapporo. It is very common on the high mountains of northern Honsyû and Hokkaidô, and it was first found in Japan on Tarumai; so the name "Tarmai-Sô," or grass of Tarumai, is applied by him. It is not strange that this plant, whose dry seeds weigh only about 0·002 gram, has migrated to this dome from the outer slope of Tarumai, but it is remarkable that the development succeeded in only seven years on the still fuming lava dome.

The smoke is continuously issuing with much violence from the same point of the main fissure on the inner crater wall as before.

In January of this year, under the smoke column, the dome stood covered with snow except in the middle belt, where the cliffs show their maximum steepness, and also at several fuming spots on the top.

Summary.

1. The activities preliminary to the 1909 lava eruption continued about four months, from the middle of January to the

FIG. 7.

FIG. 7. View from a point in the large trench on the top surface of the dome. In the background, the *somma*-wall is seen. The large fissure, traversing the inner crater-wall, was formed on May 15th, 1909. In front is seen the steep cliff of the south wall of the trench. Photograph by the author, October 20th, 1916.

FIG. 8.

FIG. 8. Slickened surface on the north wall of the large trench on the top of the dome. Photograph by the author, October 20th, 1916.

middle of April, and it ended with the great explosion on the 12th of the same month.

2. The lava followed this, and on the 19th of April it accumulated in the crater so much as to be seen from a great distance, and on the 23d of April the growth of the dome was not yet completed and it was smooth and round-headed.

3. On the 1st of May, 1909, the maximum growth of the dome had already been reached, though we know neither the exact time of its completion nor the exact shape at that time. The surface of the dome became very uneven through lateral expansion, which was caused by the further accumulation of lava. On the other hand, the sinking of the dome began through the settling of the lava mass, and it probably ended soon after the above date. Such depression after the maximum growth of the dome must have produced the change from a small, round shape to the large, flat-headed one.

Fig. 9.

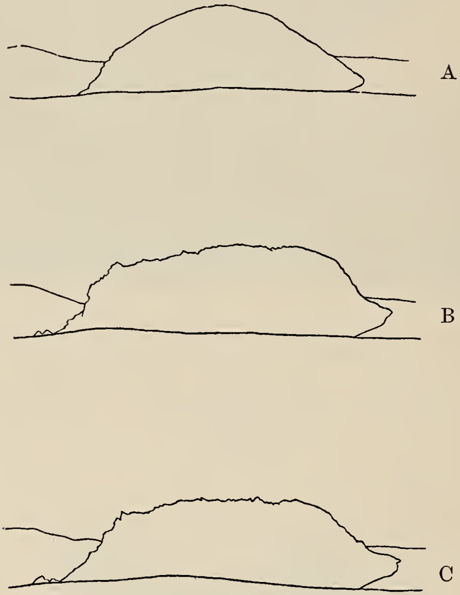


Fig. 9. Dome seen from the trigonometrical point on Higasiyama (1016 m.); tracings from photographs to the same scale. A, view taken on the 23d of April, 1909, by Prof. Ôinoue; B, view, on the 11th of May, 1909, by Prof. D. Sato; C, view, on 19th of October, 1916, by the author.

4. As the parallel layers in the lava masses show, the mode of growth of the dome was concentric, as suggested in fig. 4, and the upper crust is split into irregular sections by the sinking of the central part of the dome.

5. The vent through which the lava rose is probably at the most 60^{m} in diameter, because the lower part of the crater pit measured that width before the eruption. According to this supposition, the lava must have consolidated more rapidly in the narrow vent than the nucleus of the dome, so that the connection of the viscous lava between the dome and the subterranean deep chamber was cut off. This accounts for the fact that the settling of the lava-mass of the dome (20,000,000 cubic meters), due to consolidation, was comparatively less than in the case of Usu after its eruption in 1910, when connection with the subterranean chamber was probably not so quickly cut off.

It is impossible to calculate exactly the diminution of the lava mass by settling, but a rough estimate gives about 5–10 per cent of the whole volume.

6. The principal fissure formed on May 15th, 1909, on the inner crater-wall just at the foot of the dome, and it opened a way for the gas which issued from the consolidating lava in the central part, thus tending to remove the danger of the dome's destruction through gas explosion. The endogenetic development of the dome was completed in about one month.

7. The formation of the rock talus continues slowly and the principal epigenetic cause is wind action.

8. During seven years, some plants have migrated to the dome on the still-fuming surface of lava.

9. Tarumai is the representative type of this kind of dome.

Literature of the recent eruption of the Tarumai volcano.

Immanuel Friedländer: Ueber einige japanischen Vulkane, II Teil, Mitteilungen der Deutschen Gesellschaft für Natur- und Voelkerkunde Ostasiens. Bd. XII, Tokyo, 1910.

—— Ueber den Usu in Hokkaidô und ueber einige andere Vulkane mit Quellkuppenbuldungen, Petermann's Geographische Mitteilungen, Juni Heft, 1912.

Bunjiro Kotô: On the volcanoes of Japan II, Journal of the Geological Society of Tôkyô, vol. xxiii, No. 269, 1916.

Synkusuke Kôzu: Preliminary notes on some igneous rocks of Japan, Journal of Geology, xix, No. 7.

Yositika Ôinoue: Report on the Tarumai eruption (Japanese), Publications of Imp. Earthquake Investigation Comm., No. 64.

Sidney Powers: Volcanic Domes in the Pacific, this Journal, xlii, No. 249, Sept., 1916.

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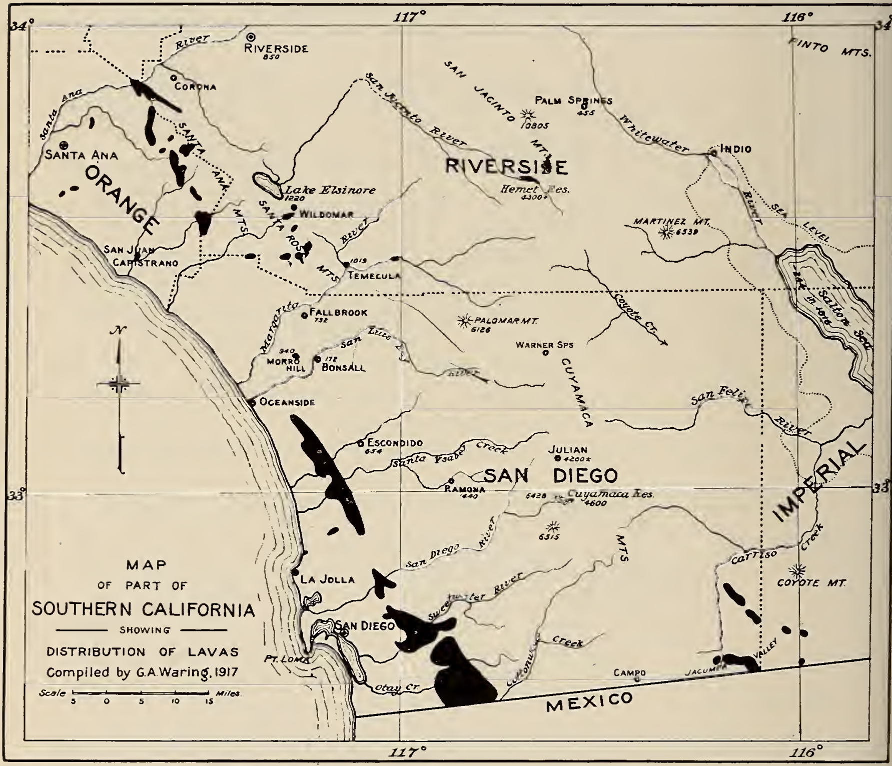
Hidezô Simotomai: Der Tarumai Ausbruch in Japan 1909, Zeitschrift der Gesellschaft für Erdkunde zu Berlin, Heft 6, 1912.

Art. X.—*Lavas of Morro Hill and Vicinity, Southern California*; by Gerald A. Waring and Clarence A. Waring.[*]

Morro Hill is in northern San Diego County, in the foothills region of southern California. It is about three miles west of the village of Bonsall, which is 14 miles by highway northeast of Oceanside (see fig. 1). A wagon road formerly passed at the base of the hill, but for a number of years this road has been abandoned and is now fenced across in several places.

Fig. 1.



The hill rises to an elevation of 940 feet above sea-level, or about 250 feet above the rolling slopes at its base, as is shown in fig. 2. Both its height above the near-by hills and its

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[*] Acknowledgment is due E. S. Larsen, Jr., and A. J. Ellis for data kindly furnished concerning other lavas in southern California.

rounded outlines as contrasted with the bowlder-strewn and irregular outlines of the granitic hills of the region make it locally conspicuous. The immediately surrounding area is composed of ancient crystalline rocks, chiefly granitic, but there are narrow zones of chloritic schist and other metamorphic rocks. A mile to the west, sedimentary materials of Tertiary age overlie the ancient crystalline rocks, and cover the bedrock thence westward to the ocean.

Fig. 2.

Map showing distribution of lavas of Morro Hill and vicinity.

▤ *Gray andesite* ▦ *Mottled andesite* ▨ *Pink andesite.*

Scale 0 ¼ ½ ¾ 1 *Mile*

Contour interval 100 feet

Morro Hill and the slopes immediately to the southeast are of lava and tuff that seem to be of special geologic interest because of their difference from other lavas of the region. The materials appear to form a capping directly imposed upon the

Fig. 3.

Fig. 3. Morro Hill from the north.

Fig. 4.

Fig. 4. Morro Hill from the south.

granitic basement rock, for granite and diorite are exposed completely around both hills, as is indicated in fig. 2, in which the unruled areas are of the ancient crystalline rocks.

The eastern slope of the hill, although steep, may be ascended without great effort. On the west face there is a cliff 50 feet or more in height, as is seen in figs. 3 and 4. At one place in the top of this cliff the rock is disintegrated and has been markedly honeycombed by the wind.

In the main hill and the subsidiary one adjacent to the southeast there are at least three classes of material, whose approximate areal extents are indicated in fig. 2. The rock of the main hill, locality 1 (fig. 2), is a fine-grained, gray andesite. A slide of the rock shows a groundmass composed principally of felsite with some glass and orthoclase. The feldspars in places show flow structure. Some magnetite and carbonaceous material are also present.

On the north side of the hill, nearly half-way up its slope, at locality 2, a small cliff of coarse-grained dioritic rock is exposed. A slide shows it to be composed principally of plagioclase and orthoclase with some quartz, magnetite and hematite. The rock appears to have been considerably altered, as the ferro-magnesian minerals have been entirely oxidized, leaving only the shapes of the former hornblende crystals.

On the south side of the hill at locality 3, between the lava and the underlying diorite, is a rock composed of grains of dioritic material. A slide shows it to be composed principally of plagioclase and orthoclase with quartz, magnetite and hematite. The rock is much finer grained than that of locality 2, on the north side of the hill, and the minerals are considerably broken up into grains, as if by water action. It seems probable that the andesitic intrusion took place after a period of weathering of the diorite and that this rock which immediately underlies the andesite consists of the baked, decomposed diorite. The absence of ferro-magnesian minerals would bear out this supposition.

The lower hill, locality 4, immediately southeast of Morro Hill, is composed of andesite which is a blend of that exposed at locality 1, with small fragments of the dioritic rock or its minerals, through which it has been intruded, and also small fragments of pink tuff. A slide of the rock exhibits a felsitic groundmass with considerable glass and carbonaceous material, and occasional corroded crystals of plagioclase and orthoclase. Green epidote forms patches throughout the groundmass. On the north and west the limit of the lava is marked by steep slopes and small landslide scars, where the material has disintegrated to a deep black adobe immediately overlying the granite. Along the eastern and southern borders of the hill the rock grades into homogeneous pink tuff, of the same character as the fragments it encloses. The greater part of the slopes southeast of this lower hill near Morro Hill is composed of the pink tuff, which is mainly of a uniform color and texture, but along its borders is agglomeratic in character, as is shown in fig. 5. A slide of material from locality 5 shows it to be andesite with felsitic and glassy groundmass and a considerable proportion of fine crystals of light-green epidote. Some magnetite is also present.

Fig. 5.

Fig. 5. Tuff agglomerate near the north margin of the andesite flow, southeast of Morro Hill.

The distinct difference in petrographic character of the lava composing Morro Hill and that of the lower hill to the southeast indicates that they represent two phases of intrusion. As there are no other evidences of volcanic activity in the immediate vicinity, it seems possible that each hill has been built up over a small vent, for the fragments of dioritic mineral in the rock at locality 4 indicate that the lava here has been forced up through the diorite, and the shape of the larger hill is believed to indicate that its lava also issued from a vent beneath the present capping. The restricted areas covered by the lavas indicate that the locality was the seat of only minor activity. So far as is known to the writers this is the only occurrence of lavas of the kind for a radius of at least 20 miles. At this distance to the northeast—at the mouth of Nigger Canyon, on Temecula River,—there is a small area of lava agglomerate which may prove on detailed examination to be similar in character to the tuff southeast of Morro Hill.

No positive criteria for judging of the period of intrusion were found but the rounded shape of Morro Hill is indicative of submerged erosion. The elevations of the bottom of the cliff of Morro Hill and of the top of the hill to the southeast are about the same. It therefore seems possible that the steep, cavernous western slope may indicate wave-action and that the top of Morro Hill stood above a Tertiary sea-level at a time when the lower hill was planed down to that sea-level. As the sedimentary deposits along the nearby coast are believed to be of Eocene age it seems probable that the intrusion was pre-Tertiary.

Along the crest of Santa Rosa Mountains, about 15 miles north of Morro Hill, there are four or more mesas formed by a sheet of basaltic lava. A few miles farther north, on the east slope of the mountain, there are two other small areas of similar rock. The occurrence has been described by Fairbanks* who says that the sheet which has been eroded into the several detached mesas is about 100 feet thick at its eastern side and is underlain by 200 or 300 feet of sandstone that rests on the granitic and metamorphic basement rocks. To the west the lava has been worn thin by erosion. A notable feature of this lava region is a narrow flow that extends for a vertical distance of 1800 feet down the southern slope of Avenaloca Mesa or Cienaga Peak. The lava of these mesas is in large part coarsely vesicular, but contains dense, massive portions. The two small areas on the mountain-side north of the mesas are of basaltic material that is fine-grained and in places conglomeratic. A slide made of rock from the northernmost basaltic occurrence, 1½ miles south of Wildomar, shows it to be an olivine basalt. It has a groundmass of fine crystals of labradorite interspersed with magnetite. Olivine crystals, somewhat altered, are irregularly distributed throughout the rock.

Between the two northern basaltic areas Fairbanks mentions a ridge of tuff intersected by dikes, and says that this ridge seems to be of an older period of effusion. Fairbanks (pp. 78–80) has also described areas of basaltic lava in and near Jacumba Valley in southeastern San Diego County, and areas of volcanic tuff farther east and northeast on the slopes leading down to the Salton Basin. He considers both these lavas and those in the Santa Rosa Mountains to be of late Tertiary age.

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* Fairbanks, Harold: Geology of San Diego County, also portions of Orange and San Bernardino Counties. Eleventh report Cal. State Mineralogist, pp. 101–104, 1893.

In the San Joaquin Hills, 7 or 8 miles south of Santa Ana, and also in the Modena Hills, 5 miles northeast of Santa Ana, small areas of lava have been examined by E. S. Larsen, Jr., in connection with geologic mapping of the Corona Quadrangle for the U. S. Geological Survey, and found to be of basalt, probably Miocene in age. Farther east, in the Santa Ana Mountains, there are areas of greenstones, which Larsen finds to be chiefly andesites and quartz latites, with minor areas of basalts and rhyolites. They are intruded by granite, and are probably of early Cretaceous or pre-Cretaceous age.

South of Morro Hill, in a zone extending approximately parallel with the coast, and widening to the south, there are areas of felsitic intrusives, described by Fairbanks (pp. 77, 86 and 92) and recently mapped in some detail by A. J. Ellis during studies of the region for the U. S. Geological Survey. These rocks are chiefly latites, and are tentatively classed by Ellis as of pre-Cretaceous age. The only lava of later age in southwestern San Diego County that was noted by Fairbanks or by Ellis is on the shore, 3 miles north of La Jolla. A basaltic dike, there exposed for a distance of 1800 feet, cuts Tertiary shales. It varies in width from 2 feet at its northeastern exposed portion to 30 feet in the southwest, where it disappears beneath the surf.

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ART. XI.—*On Tri-Iodide and Tri-Bromide Equilibria, especially in Cadmium Solutions;* by R. G. VAN NAME and W. G. BROWN.

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

THE generally accepted view that iodine dissolved in a water solution of a metallic iodide is present chiefly in the form of tri-iodide, is based to a large extent upon evidence of the kind first furnished by the work of Jakowkin, published in 1894 and 1896.* The principle involved consists in calculating the concentration of the iodine which remains uncombined in the aqueous iodine-iodide mixture from the observed concentration of iodine in a layer of carbon bisulphide in equilibrium with the water phase, by means of the previously determined distribution coefficient of iodine between water and carbon bisulphide. Jakowkin showed that if the addition compound which is formed is assumed to be tri-iodide (the simplest possibility) the data obtained as above give a good constant, within fairly wide limits of concentration, for the thermal dissociation of the tri-iodide according to the equation:

$$RI_3 \rightleftarrows RI + I_2, \text{ or } \frac{(RI)\ (I_2)}{(RI_3)} = \text{constant.}$$

This equilibrium constant, which we shall hereafter designate by K_1, proved to have approximately the same value in dilute solutions of each of the five iodides studied by Jakowkin, which means, of course, that equivalent amounts of these iodides combined with almost exactly the same amount of iodine under like conditions. The iodides tested were those of potassium, sodium, lithium, hydrogen and barium. At 25°, $K_1 = 0·0014$, approximately, the low value showing that the tri-iodides of these five elements are only to a very small extent dissociated into iodide and iodine.†

Although Jakowkin's work has been corroborated and extended by other investigators, these later researches have included very few iodides not studied by him. We have been able to find in the literature the data necessary for the calculation of K_1 for only three such, namely, calcium and strontium iodides studied by Herz and Bulla,‡ and cupric iodide covered

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* Zeitschr. phys. Chem., xiii, 539, 1894, and xx, 19, 1896.

† A slight difference was noted by Jakowkin in the case of hydrogen iodide, which in the more dilute solutions gave $K_1 = 0·00134$. This discrepancy, which merits further investigation, probably tends to disappear with increasing dilution. We have confined our study of the case to a single series of determinations in 0·0605 molar hydrogen iodide, which gave $K_1 = 0·00133$, in close agreement with Jakowkin's result at this concentration.

‡ Zeitschr. anorg. Chem., lxxi, 254, 1911.

by the work of Bray and MacKay,* and of Fedotieff.† By the work with cupric iodide it was proved that this iodide behaves "normally," that is, it gives at 25°, and in dilute solution, the same value of K_1 as the other five mentioned above. Herz's results with calcium and strontium iodides, however, would seem to show that the former is to some extent abnormal, and the latter decidedly so. This appeared so improbable that the writers have reinvestigated the case of strontium, using materials purified with especial care, and have found, as will be shown later, that strontium iodide is wholly normal in its behavior toward iodine. Since the same is known to be true of barium iodide, there is hardly a doubt that calcium iodide is in reality also normal, and that the discrepancies observed by Herz and Bulla were due to some accidental disturbance.

Excluding the results of Herz and Bulla, the data in the literature prove that six iodides give at 25° practically the same value of K_1, There is, of course, no reason to doubt that this agreement extends to other temperatures. To the question whether or not all simple metallic iodides behave alike in this respect, the data hitherto published furnish no definite answer. As a matter of fact, exceptions do occur, as the present investigation will show.

Behavior of Divalent Halides.

Before considering our experimental results we wish to call attention to a point upon which some confusion seems to exist in the literature. Jakowkin in studying barium iodide assumed that both iodine atoms (or ions) were equally active in the reaction with iodine, and accordingly based his calculations on the equation:

$$\tfrac{1}{2}BaI_6 \rightleftarrows \tfrac{1}{2}BaI_2 + I_2.$$

As already stated, the value of the equilibrium constant so obtained agreed with that of the univalent iodides.

Quite recently, Herz and Kurzer‡ have made similar measurements with barium iodide, but although they cite Jakowkin's article they ignore his results, and base their calculations on the assumption that only one of the two iodine atoms combines with iodine, giving the equation:

$$BaI_4 \rightleftarrows BaI_2 + I_2.$$

The authors seem to consider that this procedure is sufficiently justified by the fact that the equilibrium constant calculated according to this equation shows a fair degree of constancy,

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* Jour. Am. Chem. Soc., xxxii, 1207, 1910.
† Zeitschr. anorg. Chem., lxix, 22, 1910.
‡ Zeitschr. Elektrochem., xvi, 869, 1910.

notwithstanding that its value is only about half* that given by the univalent iodides. Herz, working in collaboration with Bulla on the iodides of barium, strontium and calcium, again employs this assumption with similar results.

Abel and Halla† point out the significant fact that Herz's results for these three iodides give nearly the same value of the equilibrium constant as that obtained by Jakowkin for the iodides of barium and the alkalis, if calculated in the same way. They add, however, the statement that no decision between the two possibilities can be made on the basis of measurements of distribution coefficients.

This last statement is evidently based on a misapprehension. Let us, following Herz's notation, represent by a the original concentration in mols per liter of the barium iodide, by b the molar concentration of titrable iodine in the water layer as directly measured, and by x the concentration of free iodine as found by dividing the observed concentration in the non-aqueous layer by the distribution coefficient.

Herz's assumption then obviously leads to the equilibrium expression:

$$\frac{(a-(b-x))\,x}{b-x} = \text{constant} \qquad \text{(I)}$$

while Jakowkin's point of view calls for:

$$\frac{(2a-(b-x))\,x}{b-x} - \text{constant} \qquad \text{(II)}$$

The ratio of these two expressions evidently varies with the values of a, b, and x, that is, if one is constant the other can not be. Hence, when applied to actual experimental results, the one based on the assumption which is the more nearly correct ought to show the better constancy.

TABLE I.

Barium Iodide.

(From Experimental Data of Herz and Kurzer.)

K_1 (assuming BaI_4)	K_1 (assuming $Ba(I_3)_2$)
0·00074	0·00148
0·00070	0·00143
0·00072	0·00149
0·00071	0·00148
0·00071	0·00150
0·00069	0·00148

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[*] Herz expressed concentrations in millimols per 10 cm³ instead of the customary mols per liter, and his constants must therefore be divided by ten to render then comparable with those of Jakowkin and others.

[†] "Handbuch der anorganischen Chemie" (Abegg and Auerbach), vol. iv, part 2, p. 443, 1913.

This inference is tested by Table I. In the first column are Herz and Kurzer's constants for barium iodide as calculated by them, but divided by 10 to reduce to mols per liter. The second column gives the constants calculated according to Jakowkin's method from the same data. The superior constancy of the second column is apparent in the smaller total variation (4·9% as compared with 7·0%), and in the less systematic character of the variations. Another and more striking example is furnished by Table II which contains a similar comparison based on some of our own results for strontium iodide (Table III, Exp. 2). These tables make it clear that a decision between the two possibilities can be reached in this way, and prove that the assumption made by Jakowkin is unquestionably more correct than that of Herz.

Table II.

Strontium Iodide.

K_1 (assuming SrI_4)	K_1 (assuming $Sr(I_3)_2$)
0·000382	0·00134
0·000516	0·00141
0·000587	0·00141
0·000622	0·00140
0·000642	0·00142
0·000651	0·00138
0·000696	0·00143

Moreover, it may be inferred by analogy, that in the case of tri- and polyvalent iodides each iodine atom of the original iodide should be active in uniting with iodine, and this we have actually proved to be true in the case of a trivalent iodide, LaI_3.

We have therefore, throughout this investigation, followed Jakowkin in our method of calculating the constants, the general expression which we have used for iodides and bromides both of uni- and polyvalent metals being:

$$K_1 = \frac{(na - b + x)\,x}{b - x} \qquad \text{(III)}$$

in which n is the valence of the metal, a the original molar concentration of the halide, b the molar concentration of the titrable halogen, and x that of the free halogen, all referring to the water layer.

If, for an iodide, (ΣI) and $(\Sigma I)_3$ represent the total concentrations of the iodide and tri-iodide radicals respectively, equation III takes the form:

$$K_1 = \frac{(\Sigma \mathrm{I})(\mathrm{I}_2)}{(\Sigma \mathrm{I}_3)}, \qquad \text{(IV)}$$

and similarly for a bromide.

Preparation of Materials.

Carbon bisulphide was purified by the methods of Cloëz* and of Obach,† which involved two distillations, one over quicklime, the other over mercuric chloride, after previous digestion with metallic mercury. The carbon tetrachloride employed was free from carbon bisulphide, as shown by the copper xanthogenate test.

Of the various salts used, potassium bromide and iodide, cadmium iodide, zinc iodide, and mercuric iodide, were all first quality reagents, and were used as purchased without further purification. The rest were prepared as described below.

Since the nature of the experiments called for only moderate accuracy in the standardization of the halide solutions, these were, when practicable, made up of the desired strength by direct weighing of the salt. This method was followed with cadmium iodide, potassium bromide and iodide, and mercuric iodide. Zinc iodide solutions, after dilution to the required strength and several days' standing, were filtered to remove the zinc hydroxide thrown out by hydrolysis, and the total iodide concentration then determined gravimetrically by weighing as silver iodide. The zinc content was then found by precipitation as the carbonate and weighing as ZnO, and the proportion of hydrogen iodide was calculated by difference.

Nickel iodide was prepared by the action of a mixture of iodine and water upon commercial "pure nickel." After diluting to the desired concentration the solution was allowed to stand for some days and the resulting precipitate, consisting of nickel hydroxide and ferric hydroxide (from iron present as impurity in the metal), was filtered off. A little hydriodic acid was then added to prevent further hydrolysis. Solutions so prepared showed very little iron by the sulphocyanate test, but contained free iodine as well as hydriodic acid. In standardizing these solutions free iodine was titrated with thiosulphate, total (iodide + iodine) estimated by the method of Gooch and Browning,‡ and nickel determined both by weighing as the salt of dimethyl glyoxime and by electrolysis. From the data so obtained the concentrations of nickel iodide and of hydrogen iodide could be calculated.

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* Jahresbericht der Chemie, 1869, 243.

† Jour. prak. Chem. (2), xxvi, 282, 1882.

‡ This Journal (3), xxxix, 188, 1890, and xlv, 334, 1893.

The strontium iodide, for reasons already mentioned, was prepared with especial care. Iodine resublimed from potassium iodide was converted by the hydrogen sulphide method into hydriodic acid, which was purified by two distillations, and finally treated with an excess of pure strontium carbonate. The filtered solution was diluted to the desired extent and then standardized by precipitation as strontium sulphate in the presence of alcohol, and weighed on asbestos in a platinum crucible.

To prepare the lanthanum iodide a portion of the hydriodic acid solution just mentioned was allowed to act upon an excess of ignited lanthanum oxide,* and after diluting and filtering, the iodide content was found by determining the free iodine (of which a small amount was present) with thiosulphate, and the total (iodide + iodine) by the method of Gooch and Browning. This solution showed only a faint acid reaction, indicating that the amount of hydrolysis was very small, and for this reason no attempt was made to determine the concentration of free hydriodic acid.

Cadmium bromide was prepared by dissolving the pure metal in a mixture of water and bromine; mercuric bromide in the same way, except that the product was further purified by several recrystallizations. In both cases the solutions prepared were standardized by precipitation and weighing as silver bromide.

The solutions of the double iodides and double bromides were made up by simple mixture of the constituents in weighed quantities or in measured volumes of standard solutions.

Experimental Method.

The experiments were conducted in glass stoppered bottles of about 200^{cm^3} capacity. In these were placed $40–60^{cm^3}$ of the solution under investigation, and $20–25^{cm^3}$ of a strong solution of iodine in carbon bisulphide or, in the case of bromides, of bromine in carbon tetrachloride. Carbon bisulphide was used with all iodides except mercuric potassium iodide. In this case, on account of the solubility of mercuric iodide in carbon bisulphide, carbon tetrachloride was substituted.

The bottles, with their necks covered by water-tight rubber caps, were rotated in a thermostat at 25° until equilibrium had been reached† and then removed from the stirring axle and

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* This oxide had only a faint brownish color indicating that it was comparatively free from the oxides of the didymium earths.

† This requires only a very short time. Our experience was in agreement with that of Jakowkin (Zeitschr. phys. Chem. xviii, 585) who found five minutes vigorous shaking sufficient.

allowed to stand in the thermostat until the two layers had separated and become entirely clear. Finally, samples of each layer were taken with carefully calibrated pipettes and the concentration of the halogen determined by titration with thiosulphate. In the case of the bromine solutions the pipettes were not filled by suction, but by applying air pressure to the bottle, and the samples were run into an excess of potassium iodide solution before titrating. In the following tables the concentrations so found are given in the columns headed b and g, the former referring to the aqueous and the latter to the non-aqueous layer. These values together with a, the initial concentration of the halide, and c, the distribution coefficient, furnish all that is needed for the calculation of K_1 from Equation III, since x in that equation is merely g/c. For c we have used throughout values determined by Jakowkin, or derived from Jakowkin's results by graphic interpolation.

TABLE III.

Strontium Iodide.

1. $a = 0·1312$ molar SrI_2. $(\Sigma I)+(\Sigma I_3) = 2a = 0·2624$ molar.

b	g	c	x	(ΣI_3)	(ΣI)	K_1
63·65	257·3	590	0·4360	63·2	199·2	0·00137
38·24	137·5	580	0·2371	38·00	224·4	0·00140
22·63	76·9	578	0·1331	22·50	239·9	0·00142
14·07	46·5	578	0·0805	13·99	248·4	0·00143
8·84	28·31	578	0·0490	8·79	253·6	0·00141
					mean	0·00140$_6$

2. $a = 0·0328$ molar SrI_2. $(\Sigma I)+(\Sigma I_3) = 2a = 0·0656$ molar.

b	g	c	x	(ΣI_3)	(ΣI)	K_1
20·35	353·6	610	0·580	19·77	45·8	0·00134
14·24	220·8	585	0·3773	13·86	51·7	0·00141
9·76	139·2	580	0·2399	9·52	56·1	0·00141
6·59	87·8	578	0·1520	6·44	59·2	0·00140
5·85	78·2	578	0·1353	5·71	59·9	0·00142
3·341	41·67	578	0·0721	3·269	62·3	0·00138
1·758	22·24	578	0·03849	1·720	63·9	0·00143
					mean	0·00139$_7$

After each determination, to continue the series, a volume of the original halide solution equal to that removed from the water layer, and a volume of the pure bisulphide or tetrachloride equal to that taken from the non-aqueous layer, were placed in the bottle and the whole process repeated as before.

A few of the determinations of K_1, as is indicated in the tables, were made in solutions saturated with iodine, using no carbon bisulphide. Here x is evidently equal to the solubility of iodine in pure water (0·00132 mols / liter at 25°, according to Bray*) so that the presence of a carbon bisulphide phase could give no further information. In these cases the bottles, which contained a little solid iodine, were rotated in the thermostat for 48 hours before analysis, and the liquid was forced into the pipettes by air pressure through an asbestos filter contained in a narrow glass tube.

The tables call for little further explanation. It must be borne in mind that electrolytic dissociation is disregarded in calculating the constant K_1. The columns headed (I_2), concentration of uncombined iodine in the water solution, (ΣI), concentration of uncombined iodide, and (ΣI_3), concentration of tri-iodide, are given in only a few cases, since these three quantities (or their equivalents for bromine) are only derived values, and can be easily calculated if needed by means of the equations

$$(\Sigma I) + (\Sigma I_3) = na$$
$$(\Sigma I_3) = b - x$$
$$(I_2) = x = g/c$$

All concentrations in the tables, where not otherwise stated, are in millimols or milli-formula weights per liter. The values of K_1, however, are those calculated in the usual way, in terms of mols per liter. A few obviously faulty values of K_1, indicated by enclosure in parentheses, have been omitted in calculating the averages.

TABLE IV.

Nickel Iodide.

1. $a = 0·3715$ molar $NiI_2 + 0·0148$ molar HI.

$(\Sigma I)+(\Sigma I_3) = 0·7577$ molar.

b	g	c	K_1
108·1	116·7	585	0·00120
67·7	66·1	582	0·00116
32·24	31·87	580	0·00124
19·48	30·19	580	(0·00198)
15·98	16·87	580	0·00135
8·99	9·13	580	0·00131
7·13	6·99	575	0·00128
4·47	4·38	575	0·00129
2·190	2·982	575	(0·00179)
		mean	$0·00126_1$

2. $a = 0·1366$ molar $NiI_2 + 0·00425$ molar HI.

$(\Sigma I)+(\Sigma I_3) = 0·2775$ molar.

b	g	c	K_1
68·9	259·9	595	0·00133
46·32	158·8	587	0·00136
27·77	90·4	585	0·00140
14·26	61·1	580	(0·00196)
7·36	23·39	580	0·00148
3·919	11·14	580	0·00135
2·460	7·94	575	0·00155
1·636	5·68	575	(0·00168)
1·165	3·357	575	0·00139
		mean	$0·00140_8$

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* Jour. Am. Chem. Soc., xxxii, 936, 1910.

Table V.

Zinc Iodide.

1. $a = 0·2135$ molar $ZnI_2 + 0·011$ molar HI.

$(\Sigma I) + (\Sigma I_3) = 0·438$ molar.

b	g	c	K_1
38·48	76·9	580	0·00138
32·41	65·2	580	0·00141
13·06	25·09	579	0·00141
5·69	11·01	578	0·00145
2·985	5·97	578	0·00151
1·632	3·171	578	0·00147
0·643	1·222	578	0·00144
0·3451	0·672	578	0·00148
0·2573	0·515	578	0·00152
		mean	$0·00145_2$

2. $a = 0·1283$ molar $ZnI_2 + 0·00104$ molar HI.

$(\Sigma I) + (\Sigma I_3) = 0·2577$ molar.

b	g	c	K_1
76·2	330·4	607	0·00131
51·0	195·0	590	0·00135
22·20	78·5	580	0·00145
8·07	39·55	579	(0·00213)
3·591	11·57	578	0·00142
1·539	4·88	578	0·00141
0·975	3·164	578	0·00145
0·4104	1·352	578	0·00147
0·2052	0·830	578	(0·00181)
		mean	$0·00140_9$

Table VI.

Lanthanum Iodide.

$a = 0·02179$ molar LaI_3.

$(\Sigma I) + (\Sigma I_3) = 3a = 0·0654$ molar.

b	g	c	K_1
28·7	660·0	650	0·00138
18·94	333·0	610	0·00139
10·29	151·5	580	0·00144
5·98	80·7	578	0·00142
3·648	47·9	578	0·00144
		mean	$0·00141_4$

Table VII.

Zinc Potassium Iodide. $ZnI_2.KI$.

$a = 0·1239$ molar $ZnI_2 +$ 0·1239 molar KI.

$(\Sigma I) + (\Sigma I_3) = 0·3717$ molar.

b	g	c	K_1
45·4	105·3	585	0·00130
24·10	58·6	580	0·00146
10·04	27·45	580	(0·00171)
7·42	16·42	578	0·00141
3·345	7·11	578	0·00137
1·515	3·272	578	0·00140
0·933	2·031	578	0·00141
0·605	1·331	578	0·00142
		mean	$0·00139_6$

Discussion of Results.

Considering first the results obtained with iodides, as given in Table III to VII, we find two different types of behavior. Strontium iodide, nickel iodide, zinc iodide, and lanthanum iodide behave "normally," that is, they give a value of the equilibrium constant K_1 which agrees with the value given by the iodides of the alkali metals. The nickel iodide, zinc iodide, and lanthanum iodide solutions contained a small amount of hydrogen iodide, but since the calculations in the case of both of these solutions were based upon the total iodide concentrations, and since hydrogen iodide itself falls in the normal class, it is reasonable to conclude that the presence of this hydrogen iodide can not have had any appreciable effect upon the results.

This inference is supported by the fact, shown in Table VII, that when zinc iodide and potassium iodide are present together

Table VIII.

Cadmium Iodide.

1. $a = 0·5$ molar CdI_2. $(\Sigma I) + (\Sigma I_3) = 2a = 1·0$ molar.

b	g	c	x	(ΣI_3)	(ΣI)	K_1
*55·3			1·32	54·0	946	0·0231
27·14	384·1	612	0·627	26·51	974	0·0230
14·42	196·8	590	0·3335	14·09	986	0·0233
7·14	95·9	582	0·1649	6·98	993	0·0234
5·04	70·3	580	0·1212	4·92	995	0·0245
3·001	40·2	580	0·0693	2·932	997	0·0236
1·622	21·86	578	0·03782	1·584	998	0·0238
0·884	11·54	578	0·01996	0·864	999	0·0230
					mean	$0·0234_6$

2. $a = 0·25$ molar CdI_2. $(\Sigma I) + (\Sigma I_3) = 2a = 0·5$ molar.

b	g	c	x	(ΣI_3)	(ΣI)	K_1
*44·84			1·32	43·52	456	0·0138
27·14	440·4	620	0·710	26·43	474	0·0127
13·62	231·5	590	0·3924	13·23	487	0·0144
7·43	122·8	585	0·2099	7·22	493	0·0143
4·047	65·2	580	0·1124	3·935	496	0·0141
2·227	34·40	580	0·0593	2·168	498	0·0136
1·213	18·76	578	0·03245	1·181	499	0·0138
0·662	9·74	578	0·01686	0·645	499	0·0130
					mean	$0·0137_1$

3. $a = 0·125$ molar CdI_2. $(\Sigma I) + (\Sigma I_3) = 2a = 0·25$ molar.

b	g	c	x	(ΣI_5)	(ΣI)	K_1
*35·67			1·32	34·35	215·7	0·0083
16·23	343·4	607	0·566	15·66	234·3	0·0085
10·75	216.0	590	0·3661	10·38	239·6	0·0085
5·50	108·7	585	0·1857	5·31	244·7	0·0086
4·99	93·3	583	0·1600	4·83	245·2	0·0081
3·372	61·9	582	0·1064	3·266	246·7	0·0080
1·626	29·55	580	0·0510	1·575	248·4	0·0080
1·557	28·04	580	0·0483	1·509	248·5	0·0080
0·624	11·31	578	0·01958	0·604	249·4	0·0081
0·2923	5·36	578	0·00928	0·2830	249·7	0·0082
					mean	$0·0082_3$

4. $a = 0·01$ molar CdI_2. $(\Sigma I) + \Sigma I_3) = 2a = 0·02$ molar.

b	g	c	x	(ΣI_3)	(ΣI)	K_1
*8·16			1·32	6·84	13·16	0·00254
2·540	175·1	590	0·2967	2·243	17·76	0·00235
1·397	91·0	580	0·1569	1·240	18·76	0·00237
0·646	41·35	580	0·0713	0·575	19·42	0·00241
0·3104	19·88	580	0·03428	0·2761	19·72	0·00245
0·1411	9·76	580	0·01682	0·1243	19·88	0·00269
					mean	$0·00246_8$

* These values were obtained from solubility determinations.

in the ratio $ZnI_2.KI$, the constant K_1 calculated from the total iodide concentration, that is, upon the assumption that the power of each iodide to combine with iodine is unaltered by the presence of the other, has the normal value. It is worth noting that this is a case where some slight tendency toward complex salt formation might possibly have been anticipated, but is in no way indicated by the results.

Cadmium iodide, on the other hand, furnishes an example of abnormal behavior. (See Table VIII.) This salt gives, as compared with normal cases, a much larger value of K_1 which, moreover, increases rapidly with the iodide concentration, but tends at high dilution to approach the normal value. This is evident in the following tabular comparison of the values of K_1 for potassium and cadmium. The iodide concentrations are expressed in gram-equivalents per liter.

Iodide concentrations	0·02	0·25	0·5	1·0
K_1 for KI	= 0·0014	0·0014	0·0013	0·0013
K_1 for CdI_2	= 0·0023	0·0082	0·0137	0·0234

For constant iodide and varying iodine concentration, however, the constancy of K_1 may be fairly good, even in an abnormal case.

TABLE IX.

Cadmium Potassium Iodide.
$CdI_2.2KI$.

a = 0·23 molar $CdI_2.2KI$.
$(\Sigma I) + (\Sigma I_3) = 4a = 0·92$ molar.

b	g	c	K_1
35·78	226·3	590	0·0096
17·53	103·4	583	0·0092
8·11	46·4	580	0·0091
6·16	34·79	580	0·0090
2·308	13·15	578	0·0091
0·839	5·21	578	0·0100
		mean	$0·0093_3$

TABLE X.

Mercuric Potassium Iodide.
$HgI_2.2KI$.

a = 0·125 molar $HgI_2.2KI$.
$(\Sigma I) + (\Sigma I_3) = 4a = 0·5$ molar.

b	g	c	K_1
14·34	45·1	85·7	0·0185
8·66	25·81	85·5	0·0178
5·83	16·58	85	0·0171
3·512	10·05	85	0·0173
2·284	6·03	85	0·0160
		mean	$0·0173_4$

In the case of the double iodides $CdI_2.2KI$, and $HgI_2.2KI$ (Tables IX and X) abnormality of the same general nature is apparent. Pure mercuric iodide could not be studied by this method on account of its insolubility in water.

The experiments conducted with bromine in equilibrium with bromides were confined to cases in which abnormal behavior was to be expected from analogy with the corresponding iodides. The results are given in Tables XI to XIV. For bromides the normal value of K_1 at 25°, as shown by Jakowkin's work with bromides of the alkali metals, is 0·0623. Evidently cadmium bromide, cadmium potassium bromide, $CdBr.2KB_2r$, and mercuric potassium bromide, $HgBr_2.2KBr_2$, like the corresponding iodides, must be classed as abnormal. The same thing is no doubt true of mercuric bromide, though the low solubility of this salt made the experiments difficult and the results inaccurate.*

TABLE XI.

Cadmium Bromide.

1. $a = 0·1556$ molar $CdBr_2$.
$(\Sigma Br)+(\Sigma Br_3) = 2a = 0·3112$ molar.

b	g	c	K_1
83·6	965	30·6	0·157
41·0	437	28·8	0·168
22·12	229·8	28·0	0·175
10·85	105·7	27·6	0·166
5·07	48·1	27·4	0·163
2·533	24·21	27·3	0·167
1·319	14·08	27·2	(0·139)
0·598	5·65	27·2	0·165
		mean	0·165$_8$

2. $a = 0·0610$ molar $CdBr_2$.
$(\Sigma Br)+(\Sigma Br_3) = 2a = 0·122$ molar.

b	g	c	K_1
51·7	883	30·4	0·128
27·94	432·0	28·8	0·12
14·80	218·0	28·0	0·12
7·77	108·7	27·6	0·122
3·673	46·6	27·4	(0·104)
1·823	25·05	27·3	0·123
0·934	12·91	27·2	0·126
0·469	6·56	27·2	0·129
0·2239	3·198	27·2	0·135
		mean	0·127$_1$

TABLE XI. (continued)

3. $a = 0·03827$ molar $CdBr_2$.
$(\Sigma Br)+(Br_3) = 2a = 0·0765$ molar.

b	g	c	K_1
61·3	1268	31·7	0·104
13·45	230·6	28·0	0·113
13·03	223·4	28·0	0·113
6·15	102·0	27·6	0·111
3·408	56·0	27·4	0·112
1·655	27·04	27·3	0·113
		mean	0·111$_0$

TABLE XII.

Mercuric Bromide.

$a = 0·01447$ molar $HgBr_2$.
$(\Sigma Br)+(\Sigma Br_3) = 2a = 0·02894$ molar.

b	g	c	K_1
26·97	797	30·0	1·8
10·71	300·4	28·5	1·8
6·53	178·7	28·0	1·2
4·16	113·5	27·6	2·4
2·664	72·5	27·6	2·1
		mean	1·8$_6$

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*Herz and Paul (Zeitschr. anorg. Chem., lxxxv, 214, 1914) have also studied the equilibrium between bromine and mercuric bromide at 25°. Their results, recalculated on the same basis as our own, are as follows:

$(\Sigma Br)+(\Sigma Br_3)$	(ΣBr_3)	(Br_2)	(ΣBr)	K_1
39·98	0·9	8·1	39·08	0·352
42·4	0·8	7·6	41·6	0·395
39·46	0·7	7·0	38·76	0·388
39·46	0 6	6·5	38·86	0·421
42·4	10·6	212·5	31·8	0·638

The last determination was not included in the original table of Herz and Paul, but has been calculated from data, given elsewhere in their article, for the solubility of bromine and of mercuric bromide in water saturated with both. Though their values of K_1 are smaller throughout than ours, they also show great abnormality in the behavior of mercuric bromide.

TABLE XIII.

Cadmium Potassium Bromide. $CdBr_2.2KBr$.

1. $a = 0{\cdot}1371$ molar $CdBr_2.2KBr$.
$(\Sigma Br) + (\Sigma Br_3) = 4a = 0{\cdot}548$ molar.

b	g	c	K_1
73·1	413·0	28·8	0·119
42·2	226·6	28·1	0·121
23·52	122·7	27·5	0·124
13·67	70·9	27·0	0·128
8·03	41·4	27·0	0·128
		mean	$0{\cdot}124_0$

2. $a = 0{\cdot}0686$ molar $CdBr_2.2KBr$.
$(\Sigma Br) + (\Sigma Br_3) = 4a = 0{\cdot}2745$ molar.

b	g	c	K_1
82·4	763	29·7	0·099
35·42	282·1	28·5	0·097
17·62	135·4	27·8	0·100
9·23	68·2	27·0	0·101
5·10	37·34	27·0	0·101
		mean	$0{\cdot}099_6$

TABLE XIV.

Mercuric Potassium Bromide. $HgBr_2.2KBr$.

1. $a = 0{\cdot}125$ molar $HgBr_2.2KBr$.
$(\Sigma Br) + (\Sigma Br_3) = 4a = 0{\cdot}5$ molar.

b	g	c	K_1
46·8	686	29·5	0·470
26·94	378·3	28·6	0·469
20·07	273·3	28·4	0·451
12·23	161·1	27·8	0·444
7·42	97·1	27·0	0·467
		mean	$0{\cdot}460_2$

2. $a = 0{\cdot}05$ molar $HgBr_2.2KBr$.
$(\Sigma Br) + (\Sigma Br_3) = 4a = 0{\cdot}2$ molar.

b	g	c	K_1
32·53	613	29·6	0·330
14·89	263·5	28·3	0·324
9·90	190·8	28·0	0·434
6·09	104·4	27·4	0·330
3·941	67·9	27·0	0·350
		mean	$0{\cdot}353_4$

It is very noticeable that the only halides which give abnormal results are those of cadmium and of mercury, salts which are conspicuous for abnormal behavior in many other ways. *All other iodides and bromides, so far as yet tested, give in dilute solution normal values of* K_1.

Before taking up the discussion of the abnormal cases we must examine a little more closely the nature and meaning of the results in the normal ones. It is evident that the equilibrium in normal cases is practically independent of the nature and the valence of the positive ion. This indicates that the equilibrium is primarily an ionic one, which, for an iodide, can be written

$$K = \frac{(I')\,(I_2)}{(I_3')} \qquad (V)$$

Comparison with the expression for our equilibrium constant

$$K_1 = \frac{(\ I)(I_2)}{(\Sigma I_3)} \qquad (IV)$$

shows that $K = K_1 \frac{\gamma}{\gamma'}$ where γ and γ' are the degrees of ionization of the iodide and tri-iodide, respectively, in the equilibrium mixture. Assuming the constancy of K, i. e. the validity of Equation V, the observed constancy of K_1 requires that the ratio γ/γ' shall be constant even when the ratio $(\Sigma I)/(\Sigma I_3)$ varies widely. This is at first sight an unexpected result, but the correct explanation has probably been given by Bray and MacKay* who show that it is in agreement with the principle governing ionization in a mixture of two largely ionized salts having an ion in common. The same reasoning and corresponding mathematical relations must also hold in the case of bromides.

A number of direct determinations of the value of K for iodides have been made by Bray and MacKay,† who obtained them by measurements of the conductivities of potassium iodide solutions saturated with iodine, and independently from the conductivities of iodine solutions saturated with cuprous iodide. These experiments were all made in rather dilute solutions, $(\Sigma I) + (\Sigma I_3) = 0{\cdot}1$ molar and below. Values for K for potassium iodide solutions from 0·1 to 1·0 molar, saturated with iodine, have also been calculated by Bray and MacKay from experimental data given by Laurie.‡ Comparison of the observed values of K and K_1 for iodides shows that these two constants are in close agreement in dilute solution, and probably agree fairly well in solutions up to normal strength. For concentrations in the neighborhood of 0·1 normal iodide both constants are nearly independent of the iodine concentration, but in the stronger solutions the values of the constants decrease very materially, as saturation with iodine is approached.

The identity of K and K_1 means that the ratio γ/γ' in the dilute solutions is not only constant but approximately unity, or in other words, that the iodide and tri-iodide in the equilibrium mixture are ionized to practically the same extent, irrespective of the value of the ratio $(\Sigma I)/(\Sigma I_3)$. An important consequence of this, from a practical standpoint, is that a determination of K_1 is in effect an approximate determination of K. This, however, is only true in "normal" cases.

Finally, reasoning by analogy, we are naturally led to the conclusion that for bromides also, the values of K and K_1 in dilute solutions are probably identical, but until independent determinations of K for bromides are available, this inference can not be directly tested.

Nature and Probable Cause of Abnormal Results.

What we designate as "abnormality" with respect to the tri-halide equilibrium actually consists, as a reference to the above tables will show, in a lower capacity to unite with the halogen, and one which varies greatly with the concentration

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* Jour. Am. Chem. Soc., xxxii, 916, 1910.

† Jour. Am. Chem. Soc., xxxii, 914, also xxxii, 1207, 1910.

‡ Zeitschr. phys. Chem., lxvii, 627, 1909.

of the halide. It occurs, so far as yet proved, only with cadmium and mercury.

Cadmium iodide and mercuric chloride are conspicuous among inorganic salts for their low ionization, and for a number of other peculiarities of behavior which have long been ascribed to the presence in their solutions of complex molecules and ions. These peculiarities are known to be shared to a greater or less extent by the other halide salts of the same metals. Putting these facts together, the most obvious explanation for the abnormality which these salts display toward the trihalide equilibrium is to assume that the power to unite with the halogen is possessed only by the normal molecules and ions and not by the complex molecules and ions.* This hypothesis seems to afford a satisfactory explanation of the observed facts, and will be assumed hereafter to be approximately true.

An important result of this point of view is that it permits the calculation of the extent to which the simple molecules have united to form complexes. We shall hereafter designate the fraction of the total halide concentration which is in the form of simple molecules, whether ionized or not, as the "active fraction." Let us consider, for example, the case of cadmium iodide. The apparent value of K_1 as calculated from the equation $K_1 = (\Sigma I)(I_2)/(\Sigma I_3)$ is abnormally high, but plainly the observed values of (I_2) and (ΣI_3) are independent of the presence of complexes, and only subject to the normal experimental error. Assuming the correctness of (I_2) and (ΣI_3) we can calculate the actual value of (ΣI) in the equilibrium mixture from the equation

$$(\Sigma I) = \frac{(\Sigma I_3) K_1}{(I_2)} \qquad \text{(VI)}$$

in which (ΣI_3) and (I_2) have their observed values in the given cadmium iodide solution, and $K_1 = 0{\cdot}0014$, the value of that constant for a normal iodide in moderately dilute solution.

The "active fraction" is then obtained by dividing $(\Sigma I) + (\Sigma I_3)$ by the equivalent concentration of cadmium iodide, the value of (ΣI) used here being, of course, the one calculated from equation VI. The same method applies in the case of any other iodide or mixture of iodides, and also for bromides, though the value of K_1 at 25° in the latter case must be taken as 0·0623 instead of 0·0014.

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[*] It might, at first sight, seem possible to explain the variation in K_1 by assuming that the degree of ionization of the tri-halide in the abnormal cases was very much greater than that of the halide; or in other words, by ascribing this variation to the failure of the relationship. $\gamma/\gamma' =$ const., on which the constancy of K_1 depends. This, however, is contradicted by the comparative constancy of K_1 in such cases when the iodine concentration is varied, and fails to explain the rapid rise in K_1 when the halide concentration is increased.

TABLE XV.

(CdI_2)	(ΣI_3)	(I_2)	(ΣI) (calculated)	(ΣI)+(ΣI_3)	Active Fraction %.
500	54·0	1·32	57·2	111·2	11·1
	26·51	0·628	59·1	85·6	8·6
	14·09	0·3335	59·1	73·2	7·3
	6·97	0·1649	59·3	66·2	6·6
	4·92	0·1212	56·9	61·8	6·2
	2·932	0·0693	59·2	61·1	6·1
	1·584	0·03782	58·6	60·2	6·0
	0·864	0·01996	60·6	61·4	6·1
	0·0	0·0	60·0	60·0*	6·0
250	43·52	1·32	46·2	89·7	17·9
	26·43	0·710	50·1	76·5	15·3
	13·23	0·3924	47·2	60·4	12·1
	7·22	0·2099	48·2	55·4	11·1
	3·934	0·1124	49·0	52·9	10·6
	2·168	0·0593	51·2	53·4	10·6
	1·181	0·03245	51·0	52·1	10·4
	0·645	0·01686	53·6	54·3	10·8
	0·0	0·0	53·0	53·0*	10·6
125	34·35	1·32	36·4	70·8	28·3
	15·66	0·566	38·72	54·4	21·6
	10·39	0·3661	39·72	50·1	20·0
	5·41	0·1857	40·82	46·2	18·4
	4·82	0·1600	42·20	47·0	18·8
	3·266	0·1064	43·0	46·3	18·4
	1·575	0·0510	43·25	44·82	17·9
	1·508	0·0483	43·75	45·3	18·1
	0·605	0·01958	43·25	43·85	17·5
	0·283	0·00928	41·15	41·43	16·6
	0·0	0·0	42·0	42·0*	16·8
10	6·84	1·32	7·25	14·09	70·5
	2·243	0·2967	10·58	12·82	64·0
	1·240	0·1569	11·07	12·31	61·5
	0·574	0·0713	10·28	10·85	54·2
	0·2761	0·03428	11·19	11·46	57·3
	0·1243	0·01682	10·35	10·47	52·4
	0·0	0·0	11·0	11·0*	55·0

Table XV gives the results of applying this method of calculation to the experimental data for cadmium iodide previously recorded in Table VIII. It is evident that the magnitude of the active fraction decreases with the iodine concentration, which is entirely natural since the transformation of a part of the simple molecules into a new substance (tri-iodide) would

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* Found by extrapolation.

necessarily shift the equilibrium between simple molecules and complex molecules in favor of the former.

What is of the greatest interest and importance, however, is not the value of the active fraction in solutions containing free iodine, but its magnitude in a pure solution of cadmium iodide. This value can easily be found by plotting the values of the active fraction against the iodine concentrations, and extrapolating graphically back to zero iodine concentration. When several concordant determinations are available, especially in the region of low iodine concentration, this extrapolation can be carried out with a good deal of certainty, and furnishes what, so far as known to the writers, is an entirely new point of attack, for solving the problem of the composition of iodide and bromide solutions which contain complex molecules. It should be noted that this process, unlike the E.M.F. method and the catalysis method of Walton,* does not give the concentration of the iodide ions, but the total concentration of simple iodide molecules, ionized and un-ionized.

By this method we find, as shown in Table XV, that the active fraction in a pure solution of cadmium iodide increases with the dilution as would naturally be expected, its values in 0·5, 0·25, 0·125, and 0·01 molar CdI_2 being 6·0 per cent, 10·6 per cent, 16·8 per cent, and 55·0 per cent, respectively.

TABLE XVI.

$(CdBr_2)$	(ΣBr_3)	(Br_2)	(ΣBr) (calculated)	$(\Sigma Br)+(\Sigma Br_3)$	Active Fraction %.
155·6	52·1	31·5	102·9	155·0	49·8
	0·39	0·208	117·2	117·6	37·8
	0·0	0·0	119·5	119·5†	38·4
61·0	22·68	29·05	48·6	71·3	58·4
	0·2275	0·241	58·8	59·0	48·4
	0 0	0·0	59·0	59·0†	48·4
38·3	21·27	40·01	33·14	54·4	71·1
	0·665	0·991	41·75	42·4	55·4
	0·0	0·0	42·0	42·0†	54·9

Similar calculations, using the data in Table XI, give the values recorded in Table XVI, which indicate that in cadmium bromide solutions the active fraction is much larger. The active fraction in 0·125 molar $CdBr_2$, as found by interpolation from the data in Table XVI, is about 40 per cent, as compared with 16·8 per cent for CdI_2 of the same concentration.

For the other abnormal iodides and bromides our experimental data are less complete and less accurate, making the

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* Zeitschr. phys. Chem., xlvii, 185, 1904.

† Found by extrapolation.

extrapolation rather uncertain. The resulting values for the active fraction, as summarized in Table XVII, are therefore to be regarded only as rough approximations.

TABLE XVII.

Salt.	Total Halide Concentration. (grm. equiv. per liter.)	Active Fraction %.
$CdI_2.2KI$	0·92	15
$CdBr_2.2KBr$	0·55	47
" "	0·27	61·5
$HgI_2.2KI$	0·5	8·5
$HgBr_2.2KBr$	0·5	13·2
" "	0·2	17
$HgBr_2$	0·029	4

In considering these results for solutions of double or mixed halides it should be remembered that in the case of a mixture of zinc and potassium iodides, in the proportions $ZnI_2.KI$, the value of K_1 was found to be normal, and the active fraction, therefore, 100 per cent. In other words, both iodides, which are normal when alone, act entirely independently in the mixture, a result which is probably true in general.

This, however, is not the case when one of the halides is abnormal. Let us take, for example, the case of $CdI_2.2KI$, where the active fraction was found to be 15 per cent. Since the potassium iodide made up 50 per cent of the total iodide, it follows that even assuming that the cadmium iodide united with no iodine, only 30 per cent of the potassium iodide was active. It is evident that a large part of the latter must have been taken up in the formation of complexes. The same effect is visible with $CdBr_2.2KBr$ to a slight extent, while with $HgI_2.2KI$ and $HgBr_2.2KBr$ it is even larger than in the first example.

As already stated, it is very difficult to obtain any trustworthy results with pure mercuric bromide. Considering the low concentration of the mercury salt, the result in the table indicates that the tendency to complex formation in mercuric bromide solutions is very great.

An entirely different hypothesis to account for the properties of the iodine-iodide mixture has been proposed by Parsons, who ascribes the phenomena to simple solubility of the iodine in the dissolved iodide—"solution in a dissolved solid." The acceptance of this view, however, would leave the constancy of K_1 entirely without explanation, and, indeed, would involve the complete rejection of evidence of the kind we have been considering.

Parsons* likens the case to that of iodine (or camphor) dis-

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*Jour. phys. Chem., xi, 664, 1907; also Parsons and Corliss, Jour. Am. Chem. Soc., xxxii, 1374, 1910.

solving in a mixture of acetic acid and water, but this would only be a parallel if it could be shown, for example, that a number of different esters of acetic acid, in equivalent concentration, increased the solubility of iodine (or camphor) in water by exactly the same amount, or if the same thing were proved for a series of substituted acetic acids.

The experimentally established fact which calls for explanation is that in dilute water solution equivalent concentrations of all metallic iodides, excepting only, so far as yet known, those of cadmium and mercury, take up, at the same temperature, the same concentration of titrable iodine, when brought into equilibrium with solid iodine or with a carbon bisulphide layer containing iodine in a fixed and constant concentration. That this relation should become inaccurate with increasing concentration and finally fail altogether, is only what would be expected from the deviations from the law of mass action which are normally observed in concentrated solutions. Its failure for cadmium and mercury is wholly in keeping with the other abnormalities of the halides of these two metals.

The existence of such clear-cut stoichiometric relations between the concentrations of iodide and of iodine is the strongest possible proof that the phenomenon is not due to solubility in the ordinary sense, but rather, to the formation of a definite compound. Application of the law of mass action leaves no doubt that this compound is the tri-iodide.

Summary.

1. The iodine-iodide equilibrium has been studied at 25° in a number of cases not previously investigated, and the value of $K_1 = (\Sigma I)(I_2)/(\Sigma I_3)$ determined.

2. For the iodides of strontium, zinc, nickel, and lanthanum, the value of K_1 in dilute solution is normal. For cadmium iodide, and double iodides containing cadmium or mercury, the value of K_1 is much higher, and rises rapidly with increasing iodide concentration.

3. Similar abnormality in the corresponding constant for the bromine-bromide equilibrium was found in the case of cadmium bromide, mercuric bromide, and double salts containing either of these.

4. The measurement of K_1 in abnormal cases furnishes a useful method for determining the percentage of complex molecules and ions, not only in the equilibrium mixture, but also in solutions containing no free halogen. This method is based on the very probable assumption that the complex molecules and ions do not combine with the halogen.

ART. XII.—*The Environment of the Amphibian Fauna at Linton, Ohio*;* by E. C. CASE.

THE group of vertebrates including amphibians, fishes, and the probable reptile *Eosauravus copei*, from the Lower Freeport Coal at the old station of Linton in eastern Ohio has been known since 1856, when the first description of *Pelion lyelli* was published by Wyman in this Journal. Since that time papers have been published by Newberry, Cope, Williston, and Moodie, all dealing with the morphology of the animals. A complete bibliography of the subject appears in Moodie's Monograph, The Coal Measures Amphibia of North America,† and need not be repeated here.

As our knowledge of the taxonomy and morphology of the fauna is now fairly complete, it is possible to turn to a consideration of the various factors which influenced their life and development. Fortunately the presence of workable coal in the region has led to a large amount of exploration and exploitation of the beds in which the animals occur and it is possible to gain a clear idea of the conditions in which they lived.

The key to an understanding of this fauna was grasped by Newberry as is shown by the following quotations:

"In the descriptive portion of this volume, quite a number of species of the fossil fishes from the Coal Measures of Ohio are figured and described. A large part of these are from a single locality, which has already become somewhat celebrated for the number and interest of the fossil forms it has furnished. I refer to Linton, on the Ohio river, at the mouth of Yellow Creek. The fossils are found there in a thin stratum of cannel which underlies a thick seam of bituminous coal, that we have called Number 6, because it is the sixth workable seam from the base of the productive Coal Measures. Already about twenty species of fishes have been obtained from this deposit, and at least as many Amphibians; and all found here for the first time, although two or three species have since been met with in other localities, in this or adjoining States. On tracing Coal-seam No. 6, in various directions from Linton, the cannel at its base is found to thin out and soon disappear. We learn, from a careful study of the deposit, that there was in this locality at the time when the coal was forming, an open lagoon, densely populated with fishes and salamanders; and that after a time this lagoon was choked up with growing vegetables; and peat (which afterward changed to cubical coal) succeeded to the carbonaceous mud (now cannel)

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* This paleogeographic study is published by permission of the President of the Carnegie Institution of Washington.

† Moodie, R. L., Publication 238, Washington, 1916.

that had previously accumulated at the bottom of the water. The fishes of this pool were mostly small, tile-scaled Ganoids, belonging to the genus *Eurylepis.* Though here extremely abundant, they have not been found elsewhere. I have enumerated nine species of this genus, but possibly some of them should be considered as mere varieties. There were also in this lagoon two, or perhaps three, species of *Coelacanthus* (one of which is so closely allied to *C. lepturus* of the Coal Measures of Europe that they should not be separated, and yet this genus has been nowhere else recognized on the American continent). There are also found here the thin scales, from one to two inches in diameter, some ornamented and some plain, and also the lance-head teeth of *Rhizodus,* and the teeth and spines of *Diplodus.* On the whole, this must be looked upon as one of the most interesting localities of vertebrate fossils known on this continent ; and it is even doubtful whether *any* other equals it in the number of new species or in their zoological and geological interest."*

"The large number of species of fishes and amphibians (about fifty) found in one single coal mine at Linton indicates that the vertebrate fauna of the Coal Measures was much richer than has heretofore been supposed. The cannel coal of this locality was undoubtedly deposited in a lagoon of open water in the marsh where Coal No. 6 was formed. How extensive this lagoon was, we have not as yet learned ; but all the fossils found there have been taken from an area of a few hundred feet in diameter. We have probably now obtained representatives of most of the fishes and salamanders that inhabited this body of water, but certainly not all, for every considerable collection made there has contained something new ; and the fauna of the epoch in which this deposit was made must certainly have been very varied, since from this one spot have been taken the remains of fifty distinct species, less than a half dozen of which have been found elsewhere.

This coal mine at Linton may be regarded, therefore, as a kind of loophole through which we see, in all its details, the life of *one locality* in the great world of the Carboniferous age. Looking through that, we have before our eyes a little pool of water swarming with fishes of various kinds, some of them very large, clad in mail and provided with most formidable sets of trenchant teeth ; others, small but exceedingly numerous, covered with enameled and highly ornamented scales and plates. These latter, as we learn by coprolitic masses, were the prey of the larger ones.

With the fishes were a large number of aquatic, carnivorous salamanders, some of which must have been eight or ten feet in length, and as formidably armed as the larger fishes. Others were snake-like in form, yet several feet in length, bristling with spines, or protected by thick and bony scales. Others still were a few inches in length, very slender and delicate, and, as we

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* Newberry, J. S., Geol. Survey, Ohio, vol. i, Paleontology, pp. 284–5, 1873.

know by their mutilated fragments, served as food for the more powerful.

A remarkable circumstance connected with the Linton deposit is this: that in working up some hundreds of tons of the cannel coal which contains the fishes and amphibians, we have obtained not a fragment of an insect, and only a few small and imperfect remains of crustaceans. Mollusks, too, are entirely absent, no shell of any kind being found there, except those of *Spirorbis*, which is thought to have been an annelid. These occur, however, in millions, and we may infer from the multitudes of these delicate organisms that the water they inhabited was quiet, warm, and almost stagnant. Whether salt or fresh, we do not know, but it seems to me most probable that it was fresh.

Very few remains of plants have been found in the Linton cannel, and these, if leaves, are skeletonized, showing their long maceration in water. In this, as in many other respects, the Linton deposit is strikingly different from that of Mazon Creek, Illinois, which has yielded a large number of insects, crustaceans, and plants, and very few fishes and amphibians."*

The first step in the study of the Linton fauna was an attempt to determine whether Newberry was correct or not in his assumption that the Linton fauna was isolated in a pool of open water in the midst of a great swamp and that this pool was finally closed by the growth of vegetation causing the death of the animals. The attempt was made along two lines of evidence; first, the stratigraphy of the region around Linton and second, the method of formation of cannel coal.

1. *The evidence from the stratigraphy.*

The Linton fauna occurs in the Lower Freeport Coal of the Allegheny series of the Pennsylvanian. To test Newberry's idea an area of considerable size was selected surrounding the location of the fauna. This included Beaver, Allegheny, Washington, and Greene Counties in Pennsylvania; Hancock, Brooke, Ohio, and Marshall Counties in West Virginia; and Columbiana, Jefferson, Carroll, Harrison, and Belmont Counties in Ohio, as shown on the accompanying map, fig. 1. Many sections of the Allegheny series in this area were plotted and a few of the most detailed are shown in the columnar sections, fig. 2. The location of the sections is indicated by numerals on the map.

A study of sections 4, 3, 2, and 1, north and east of Linton, show a strong tendency for the Lower Freeport Coal and its accompanying beds to break up, indicating the edge of the local swamp. From Sprucevale, Columbiana County, Ohio (4 on the map), south of the mouth of the Little Beaver River,

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* Newberry, J. S., Geol. Survey of Ohio, vol. ii, pp. 179–180, 1874.

in Beaver County, Pennsylvania (3), then east to near the mouth of the Beaver River in Beaver County (2) and southeast to Sewickley in Allegheny County, Pennsylvania (1), the Upper Freeport Coal maintains a nearly uniform thickness of 2 to 3 feet underlain by a varying thickness of fire clay with a thin limestone at stations 4 and 2. Beneath this is a considerable thickness of sandy shales broken at station 1 by thin beds of sandstone and fireclay. The Lower Freeport Coal is very thin at these stations, represented by a carbonaceous slate only at station 1. Below the Lower Freeport Coal lie from 10 to 20 feet of sandy shales and then a heavy bed of massive sandstone, 50 to 75 feet, which at station 1 becomes a micaceous sandstone broken by the Upper Kittanning Coal.

FIG. 1.

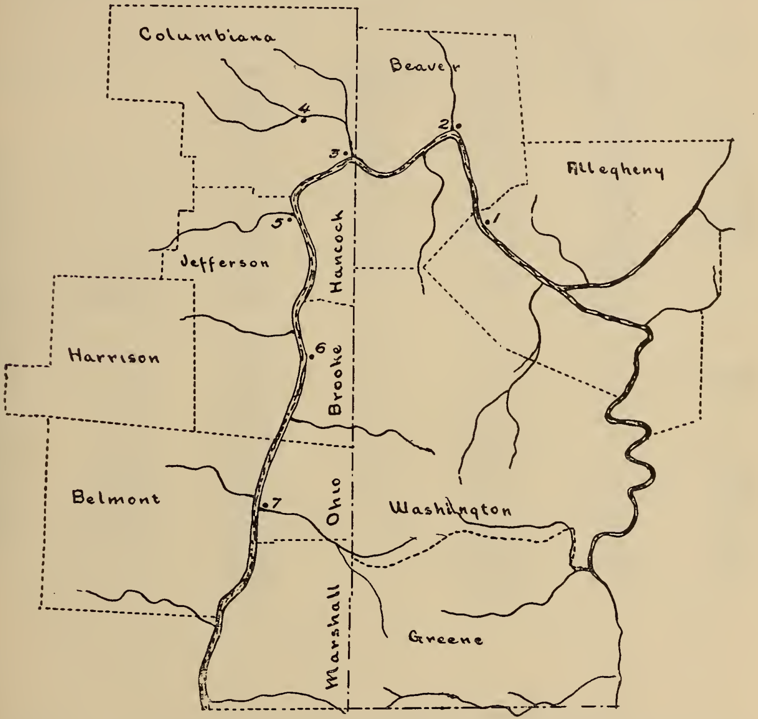

FIG. 1. Map showing the location of Linton, Ohio and the stations from which sections are quoted.

South from Sprucevale (4) the Upper Freeport Coal is 3 feet thick at Linton (5), underlain by fire clay but the limestone is absent, then follows 10 feet of shale and 5 feet of limestone, obviously not the upper bed at (4), and then 50 feet of shale and sandstone. The Lower Freeport is 7 feet thick, the lower part cannel coal, with 5 feet of fire clay and below this 7 feet of shale and sandstone with possibly thin layers of coal. At Wellsburg, Brooke County, West Virginia (6), the Upper Freeport Coal has been removed by erosion, but there are 40 feet reported as fire clay, 5 feet of Lower Freeport Coal, no cannel, and one foot of fire clay underlain by 60 feet of shale and slate. At Wheeling, Ohio County, West Virginia, the Upper Freeport is removed by erosion, but there are 50 feet of blue shale, then 7 feet of Lower Freeport Coal, without cannel or fire clay, lying above 96 feet of shale and sandstone. West of Linton the Lower Freeport Coal shows, in the adjacent counties at least, a decided thinning, with a corresponding increase in the accompanying layers. "The Lower Freeport Coal becomes locally important as the Whan Coal bed within

Fig. 2.

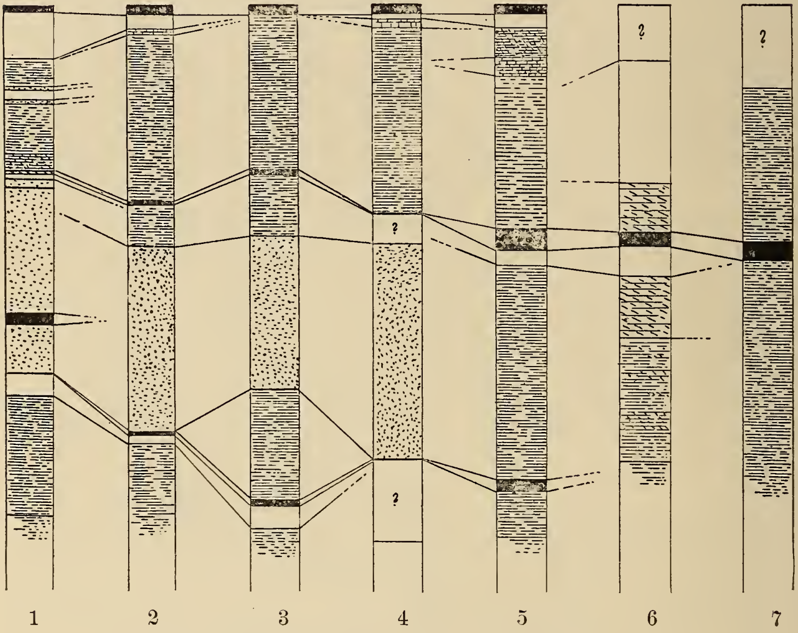

Fig. 2. Sections taken from the stations indicated on the map, fig. 1. Black, coal, Upper and Lower Freeport, Upper and Middle Kittanning. White, fire clay and unknown. Dotted, sandstone. Lined, shale and shaly sandstone. Obliquely lined, "slate." Vertically lined, limestone.

a small area in central Columbiana, but for the most part it is worthless."[*]

"The Freeport coals both thin. . . . Eastward the Upper Freeport is important, it can be followed from Yellow Creek in Columbiana County somewhat decreased in thickness, but in the southern part of the county is often 4 feet 6 inches and yields good coal. The chief drawback is the frequency with which it is cut out by the overlying sandstone. . . . The Lower Freeport is persistent, usually too thin to be utilized. It is rarely more than thirty feet below the upper."[†]

In Carroll County, Ohio, the following section has been given:[‡]

	Ft.
Upper Freeport Coal	2
Shale, sandstone, and conglomerate	40
Lower Freeport sandstone, massive	30
Concealed	50
Coal, Middle Kittanning	3
Fire clay	3
Slate	15
Coal	1
Slate	22

Near Sherodsville in Carroll County.

	Ft.
Upper Freeport Coal	4
Fire clay	6
Limestone	1
Concealed	40
Black shale	2
Lower Freeport Coal	3
Fire clay and modular iron ore	12

Newberry's generalized section for Stark County.

	Ft.
Coal, 7 (Upper Freeport)	1 to 3
Fire clay	1
Shale and sandstone with thin coal near the middle[§]	75 to 110
Coal, 6 (Middle Kittanning)	2 to 6

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[*] Stevenson, J. J., Bull. Geol. Soc. Amer., vol. xvii, p. 111, 1907.

[†] Ibid., p. 113.

[‡] Geol. Survey, Ohio, vol. v, p. 74.

[§] Includes Lower Freeport "a mere blossom."

Generalized section for Tuscawaras County.

	In North Ft.	In South Ft.
Coal (Upper Freeport)	3	4
Interval	70	35
Coal, 6a (Lower Freeport)	thin	2
Conglomerate, sandstone, and shale (Freeport)	50	52
Coal, 6 (Middle Kittanning)	4	4

Orton's section of northwest Guernsey County.

Upper Freeport Coal bed, Cambridge	thin
Clay, Upper Freeport limestone	10
Interval	50
Lower Freeport Coal bed	thin
Middle Kittanning	3

Stevenson remarks in the article quoted above, page 71, that the "Lower Freeport shows abrupt and extreme variations in thickness (in eastern Ohio) as well as in quality and occasionally carries on top a thick deposit of impure cannel."

A study of these sections taken in all directions from Linton shows that the Freeport Coal either becomes thinner, loses its fire clay (the leached ground soil of the marsh in which it was formed) or the accompanying layers become disturbed by intercalated beds. While it is admitted that the Lower Freeport Coal is variable in thickness and quantity, in almost every place where it is known, the peculiarity of the thickening at Linton, the presence of underlying cannel coal, and the undisturbed deposition of the accompanying shales and sandstones is at least strong confirmatory evidence of the presence of an open pool in the center of a great swamp.

Of the Lower Freeport sandstone, I. C. White says,* "It is one of the most persistent sandstone horizons in the Allegheny series. . . . The rock is usually quite hard, micaceous, and often pebbly, but does not split evenly." In the western part it is very uniform in character, running from 75 to 100 feet thick, but toward the east (station 1 on the map), it is broken by shale and a thin bed of coal (Upper Kittanning).

In the time before the deposition of the Lower Freeport Coal, the Linton area was evidently for a considerable time a region of deposit from moving water bearing the debris from a region undergoing rapid denudation, as is shown by the presence of undecomposed mica and the pebbles included in the matrix. This was one of the longer periods of depression in the region and the depression was extended over a wide area.

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* White, I. C., Geol. Surv. West Va., vol. xi, page 473, 1913.

2. *The evidence from the presence of cannel coal.*

Without going into the history of the discussion of the origin of the various kinds of coal, it is sufficient to state that it is now the generally accepted opinion that boghead, boghead-cannel, and cannel coals have been formed by the accumulation of algæ, spore exines, bits of resin, and other light, wind-blown materials which have grown in place in open water or have accumulated on the surface of open pools. Details of the discussion and the general conclusions may easily be found by following the references given by David White in his treatment of the origin of coal.* It is also of interest to note that the theory of the origin of cannel coal recognizes the necessity, or at least the advantage, of the presence of decomposing animal matter in its formation.

Accepting as a working basis that the stratigraphy and the presence of the cannel coal demonstrate the presence of an open pool in the vicinity of Linton, we may turn to the history of this pool and the other factors which influenced the development of the fauna.

East of Linton the Lower Freeport Coal lies directly upon the sandstone, but at Linton the section of the old Diamond Coal Mine shows several feet of fire clay beneath it. Fire clay is the result of the action of peaty waters, containing much CO_2 in solution upon an underlying soil. It is apparent that succeeding the long period of submergence during which the Lower Freeport Sandstone was formed there was a slight elevation, but a local depression in the vicinity of Linton retained a considerable body of fresh water in which accumulated the sediments of the adjacent land. The water at the edges of this pool was not deep enough to prevent the rapid development of an abundant flora. The roots penetrated the soil and the decomposition of the vegetal material furnished an abundance of CO_2 which deprived the soil of its alkalis, alkaline earths, and iron, reducing it to a fire clay. The bordering vegetation did not for a long time spread out over the surface of the pool in the middle of the swamp and during this interval there accumulated the material of the cannel coal and the amphibian and fish fauna developed large numbers both of individuals and species. The presence of a single form which must be placed with the reptilia indicates either a land at no great distance, from which the body of the animal was transported after death, or an aquatic habit for the reptile.

The physiographic environment of the fauna.

I. C. White has insisted upon the fact that though the beds of the Allegheny series are subject to frequent changes in the

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* White, David, The Origin of Coal, Bull. 38, Department of the Interior, Bureau of Mines, page 198, 1913.

material, due to minor changes induced by slight but repeated and rapid fluctuations of level, they maintain on the whole a homogeneity which speaks of widespread and long continued uniformity in the general aspect of the land and water. Perhaps the best picture that has been presented of the region is that given us by David White in Bulletin 38 of the Bureau of Mines, page 63:

"SUMMARY OF TERRESTRIAL CONDITIONS.

Coal formed on subsiding areas.

On the whole the criteria relating to the terrestrial conditions of deposition show that the formation of widely extended coals in series were regions of subsiding base-level coastal plains or filled basins. That the rate of subsidence was variable is shown by the varying character of the rocks of the coal measures; the presence of marine faunas in places immediately above the coal; the occurrence of shallow water limestones, of ripple-marked, rain-marked, or sun-cracked layers or of conglomerates or local unconformities: and in particular the occurrence of great thicknesses of coal covering large areas. The deposition of the great thicknesses of peat necessary for the production of a thick bed of coal, probably 10 to 20 feet of peat being required to produce a single foot of high-grade bituminous or semi-bituminous coal, could hardly have taken place except under such close adjustment of the rate of subsidence to rate of peat accumulation as to maintain a depth of water cover within limits that would permit the growth of peat-forming vegetation for an exceedingly long time. Too rapid a subsidence would have flooded the swamps so deeply as to kill the principal peat-forming vegetation, produce open water conditions, and allow the invasion of sediment-bearing water with its oversweep of mineral matter, or of oxygenated water which would have permitted the advance of decay (biochemical process), to the complete destruction of the superficial organic matter, unless the deposition of sand or mud were sufficiently rapid quickly to arrest the decay by exclusion of the sources of oxygen supply. The roofs of many coal beds bear evidence of the latter conditions. In most cases, however, the oversweep of clays and sands appears to have been so abrupt as to seal the underlying more or less aseptic organic mass from access of oxygen and to prevent its continued decomposition. On the other hand, if the subsidence of the region was too slow or there was warping of the region, the surface of the peat may have reached the upper limit of its formation and entered the zone of increasing exposure (insufficient water), in which the organic matter was reduced to 'humus' soil, and even destroyed, so that the formation of a thick bed of coal was impossible, unless the rise of the water level, usually by accelerated submergence, was brought about. The formation of a thick bed of coal is therefore seen to indicate in general the maintenance for a long period of an approximate balance between the rate of peat accumulation and the rise of the water, so as to maintain a depth of water favorable for the growth of the vegetation and its preservation as peat.

In confirmation of the views of many geologists the writer's observations of the horizontally extensive coal beds in the American fields lead him to conclude that the peat-forming vegetation, which was probably largely vascular, grew in place over nearly all of the areas of these coal beds and that it occupied these areas almost continuously during the deposition of the peat except at times marked by the inundation inwashes represented by the clay or shale partings in the coal. In other words, most of our commercial coal has been formed from plants that grew above the surface of the peat, and is of autocthonous origin. Coal that may be attributed to the mere accumulation of drift vegetation is, according to the author's observations, very restricted in area and variable in thickness, and much of it is too high in ash to be of value.

In certain regions in which the water was quiescent, but of too great depth for occupation by vegetal growth, bituminous shales and black carbonaceous muds, many containing marine or brackish water shells, seem to have been deposited in many places, the state of the organic material—that is, its stage of decay—being dependent largely upon the rate of accumulation of the vegetal debris and the supply of oxygen. At many points small areas of open water, temporary in duration, occurring in the midst of the swamps were marked by the concentration of spores, resins, waxes, etc., forming cannel layers or lenses, the more destructible matter being lost by decomposition, which here again is dependent on the oxygen supply and rate of delivery of the plant debris. In other cases very restricted areas of open water (not occupied by vascular plant growth) whose stagnant depths were more toxic seem to have favored the accumulation, without decay to the point of destruction, of plankton of various types, as well as of wind-borne spore materials forming boghead, and boghead-cannel coal. In none of the important and widely extended coal beds examined by the writer has he observed any lenses or intercalated bodies of coal that may be interpreted as masses, floating islands, or rafts of vegetation somewhat abruptly submerged, in accordance with the hypothesis proposed by numerous writers."

Elsewhere David White speaks of the region as "one vast peneplain."

The climatic environment of the fauna.

The flora of the region around Linton has been reported upon by David White. His list* of the plants of the Freeport group contains no forms differing especially from those of the whole Allegheny series, and all indicate the existence of a "singularly equable and humid but not tropical or even semitropical climate." There is no evidence either in the woody growth foliage, florescence, or fruition of any seasonal changes, either of temperature or of humidity. In other words, the animals lived in a period characterized by the extreme monotony of the climatic environment.

The organic environment.

The organic environment of any animal or group of animals may be defined as the group of contacts of that animal with other forms of life. Normally, the organic environment comprises both the flora and fauna, but in this instance the animals were not, so far as we can see, influenced by the vegetation more than that they profited by the shade of the umbrageous growths, sought refuge in the interstices of submerged roots, or possibly fed upon some forms of the algæ in the pool. None of these factors would have left any readable record in the morphology of the animals. The list of the flora occurring in the shales accompanying the coals of the Freeport group has been cited above.

The character of the contacts within the fauna.

The list of known amphibians from Linton as given by Moodie† includes 51 species. The genera are as follows :

Brachydectes
Cercariomorphus
Cocytinus
Ctenerpetom
Diceratosaurus
Eoserpeton
Erpetosaurus
Eurythorax
Hyphasma
Ichthycanthus
Leptophractus
Macrerpeton
Molgophis

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* White, David, Bull. Geol. Soc. Am., vol. i, page 154, 1900.

† Moodie, Roy L., Publication 238, Carnegie Institution of Washington page 18, 1916.

Odonterpeton
Œstocephalus
Pelion
Phlegethontia
Pleuroptyx
Ptyonius
Saurerpeton
Sauropleura
Stegops
Thyrsidium
Tuditanus

If we examine the animals as described and illustrated in Moodie's excellent monograph, we find that they were, one and all, provided with sharp, conical teeth, suitable only for a carnivorous or an insectivorous diet. This eliminates the vegetation of the period from consideration as a possible source, at least as an immediate source, of food, but introduces a most effective element of stress in the competition between the animals themselves, on the one hand to capture prey and on the other to escape the attack of predatory forms.

The possible sources of food were the fishes, the amphibia, and very probably the abundant arthropods, molluscs, and insects, though practically no traces of invertebrates have been found with the remains of the amphibians, except the casts of spirorbis-like forms. While there can be little doubt that some of the amphibians were carrion eaters and scavengers, the ultimate food supply must have been the invertebrate fauna of the waters and banks, and the very meagerness of the remains of such a fauna speaks eloquently of the crowded habitat and the eager search for every edible particle. Beyond this the diet was of flesh and the fauna was self-devouring.

From the description given it seems fairly certain that the amphibian fauna was isolated in a pool of clear water surrounded by a great stretch of swamp. The ordinary factors of environment which influence the development of a fauna were absent or ineffective, the physiography and the climate were monotonous in the extreme; the vegetation had only an indirect effect. The main stress upon the life was competition within the fauna. This stress became very high with the crowding of the pool, but as the monotonous environment afforded but limited possibilities for the formation of new habits, adoption of new habitats or the assumption of a new group of contacts in any form, it was not relieved by any over-specialization either in structure or habit. A study of the amphibia reveals only a very normal group of animals. They varied in size from ten feet to six inches in length, some were squat and sluggish, others lithe and serpentiform, some even so snake-like that they had lost their limbs. Some hid for safety in dark holes and corners, others lurked in the slime, feeding on carrion or the less active and well protected forms; still others flashed through the water in active pursuit of prey and dared give battle in their conscious strength. It was a fauna whose elements occupied all the possibilities of the pool to preserve their lives and propagate their kind, but there is an almost total lack of bizarre and overspecialized forms, none heavily armored and none with an excessive development of tusk or talon or spine, and none that could be called giants of their kind. There was a full occupation of all the reasonable possibilities of life but nothing that would indicate an extreme adaptation, either for offense or defense, to limited paths of life such as occur in other places and in other geological formations where the members of the faunas were very perfectly adjusted to each other. There was only the healthy growth induced by competition in a fauna which still retained all the resilience of its juvenile stage.

Such an assemblage existing under very powerful stress, if even from a single source, was full of the possibilities of development; ripe for the rapid and wide radiation in habits and structures long denied them by the monotony of their environment. For the animals in such a pool there were but two possible endings. Either the pool would become choked by the growing vegetation of the surrounding swamp, or in the many fluctuations of the land, channels would open whereby the animals could escape into other habitats and encounter a new environment. It was apparently the first of these fates which came to the Linton fauna. It was overcome in its full vigor before the ultimate adjustments of life to life had produced the extreme development of armor and weapons of attack seen in more mature or in senile faunas. Elsewhere in the same region similar faunas were released to expend in morphological advances and various adaptations to new conditions the stored up stresses of similar periods of isolation.

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Art. XIII.—*Some Fossil Beetles from the Sangamon Peat*; by H. F. Wickham.

Although the insect life of the North American Tertiaries has received considerable attention, that of our Pleistocene is relatively little known. Our ignorance of the exact distribution of insects in this latter period is due in part to the apparent scarcity of deposits containing reasonably well-preserved remains and, in almost equal degree, to the disinclination among entomologists to give the more or less fragmentary material the close study necessary for determination.

Most of the known North American Pleistocene fossil insects are from the clays, peats and asphalts. Nearly all of them, so far as recognized, are beetles, the hard exoskeleton of this group resisting destructive agencies much better than the comparatively delicate integuments of other orders. It is also evident, from the nature of the remains, that ground beetles and water beetles are much more likely to be preserved than those living upon plants, the result being that collections made in different sections of the country may have a similar physiognomy. While this renders the identification of new finds more difficult, it really gives a much better basis for comparative work than if the same number of species were scattered through many families. We are able, for example, to compare the Carabidæ, Dytiscidæ and Staphylinidæ of one location with species of the same families from other places.

During the past two years, I have received from Professor T. E. Savage sendings of Coleopterous remains which he collected in an exposed peat seam on the north bank of the Sangamon River near Mahomet, Champaign County, Illinois. This peat lies above the Illinoisan and below the Wisconsin drift. There is a slight development of loess or loess-like silt above the peat and below the Wisconsin, and Professor Savage considers that the reference of the bed to the Sangamon stage is rather definitely proven.

This collection allows us to make a comparison of two fairly widely separated North American faunæ which have been assigned to the same interglacial stage, since Doctor S. H. Scudder has reported quite fully upon a series of Coleoptera from the Scarborough beds near Toronto, Canada,* considered as belonging to the Sangamon interval. He recognized 76 species of 33 genera and 8 families. From these he reached the conclusion that the climate of Ontario, at the time of their deposition, was very similar to that of to-day or perhaps slightly

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* Contributions to Canadian Palæontology, vol. ii, part II, Ottawa, 1900.

colder, a considerable number of the recent allies of the fossils being known from a more northern habitat. On the whole, the fauna had a boreal aspect though by no means so decidedly boreal as one would anticipate under the circumstances.

Examination of the Illinois collection indicates the presence therein of ten determinable species belonging to seven genera and four families, the Carabidæ, Dytiscidæ, Staphylinidæ and Chrysomelidæ. These families contain, as well, the bulk of Scudder's Scarborough species, in the proportion of 36, 8, 19 and 2 respectively—that is, 65 out of the 76 which he has described. Five of the genera are common to both collections but all of the species appear to be quite certainly different. The basis for deductions as to climate is not very broad but, judging from the presence of *Carabus mœander sangamon* and *Chlœnius plicatipennis*, the general northern flavor of the remaining species and the entire absence of any without fairly close recent boreal allies, I think we are quite justified in assuming that conditions were, at any rate, more rigorous than in southern Illinois at present. Probably they were at least as severe as in Ontario at the date of formation of the Scarborough beds. It is true that all of the genera are now living in Illinois but they also occur very far to the north, extending in part to the shores of the Arctic Ocean and we must take into account the entire absence of anything characteristically southern. A glance at the notes following the descriptions will show that the near relatives of all the fossils in this collection are of northern range.

One might hope that the beetles would throw some light upon the identification of beds containing their remains and allow us to decide with some certainty whether or no the Scarborough deposit and the one now under investigation really belong to the same interval. The matter is complicated, however, by our ignorance of Pleistocene insects. Aside from the two collections noted above, we are acquainted, in this country, only with the probably more ancient Port Kennedy fauna, that of the widely distant Rancho la Brea asphalt deposit and an occasional scattering species from some other point. It has already been brought out that the species of the Scudder report are all different from those of the present paper, though in general closely allied. The differences are not great enough to indicate any wide dissimilarity in ecological conditions nor separation by a long period of time. On the other hand, the likenesses do not prove the deposits to be synchronous. It is apparently recognized that the Sangamon interval was of long duration (20,000 to 100,000 years*) and even if both Scarborough and Mahomet beds were laid down

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* Osborn, The Age of Mammals, p. 447, 1910.

during this stage their formation may be sufficiently remote in time to allow of some specific differentiation. We must take into account also the rather wide separation in space of the two places—but I very strongly question if ten species of the Carabidæ, Dytiscidæ, Staphylinidæ and Chrysomelidæ taken at random in a recent Illinois bog would all be different from 65 species of the same families collected during the same year and in similar surroundings at Toronto. I doubt if season has much to do with the divergence in character of the fossils since peat deposits would continue forming all through the warmer parts of the year and insect remains might readily be preserved at any time. The fact that there is no evidence of intrusion of southern types in the Mahomet collection would suggest that the deposit was perhaps formed when the Illinoisan glacial movement was well advanced on its southward route or at any rate previous to a far northward recession.

The species and varieties described in this paper are all new to science and are arranged by families as follows:

CARABIDÆ

- Carabus mæander sangamon
- Patrobus henshawi
- Platynus pleistocenicus
  - subgelidus
  - calvini
- Chlænius plicatipennis

DYTISCIDÆ

- Agabus savagei
  - prælugens

STAPHYLINIDÆ

- Olophrum interglaciale

CHRYSOMELIDÆ

- Donacia styrioides

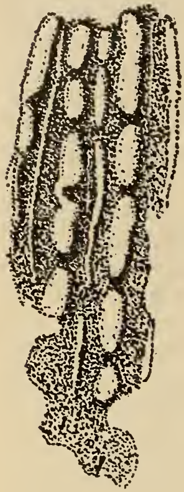
All of the types are to be found in the Museum of the University of Illinois.

CARABUS MÆANDER Fisch., var. SANGAMON new variety (fig. 1).

Represented by part of a wing cover, evidently the inner basal area of the left elytron, about $6{\cdot}90^{mm}$ in length by $2{\cdot}35^{mm}$ in width, more or less damaged on all margins. The sutural bead is like that of recent specimens; immediately exterior to it is a very fine, scarcely visible carina which corresponds to a similar line (of great variability in distinctness) on the living insect. The first row of tubercles has the basal one elongate, as usual in modern individuals, while in the second row those near the base are short as in most of the specimens in my cabinet. The third row is not well preserved. The carina between the first and second series of tubercles is interrupted instead of being entire and this carina, as well as the tubercles, is more irregular and less smooth than in any of my recent examples. The carina between the next two rows ef elevations is finer. Between all these raised sculpturings, the surface is roughened similarly to that of recent specimens but a little more coarsely.

The separation of this variety is based upon the rougher surface and particularly upon the breaking up of the carina. This character, in itself, is of small importance and does not indicate any radical change since the fossil was laid down in the Sangamon stage. To-day, *Carabus mœander* occurs in the north, from Maine and Labrador to Manitoba, south through the Rocky Mountains to Colorado and, probably as a relict from one of the interglacial stages, in the Chicago district of Illinois. Specimens from all of these places have been compared directly with the fossil. Several species of Carabus, part of them presumed to be identical with recent forms, others believed to represent extinct varieties or species, have been described from the Pleistocene deposits of Switzerland, Belgium and Galicia, one of which, *C. mœandroides* Lomnicki, from the last named locality, probably closely resembles the one above characterized.

Fig. 1.



Patrobus henshawi new species.

A single piece of peat carries the head, prothoracic episternum, pronotum and elytron, the last broken off behind the middle. Color black, shining. Head minutely punctulate (as viewed under a 9x hand lens), posterior transverse impression deep, roughened a little at bottom, frontal grooves strong, rugose and punctulate, the intervening convexity somewhat wrinkled transversely. Pronotum not very well preserved, the front portion being broken off. The disk is apparently very finely and sparsely punctulate, the median groove strong, wide and deep behind (as in the recent *P. septentrionis*), but fine at middle, a trifle stronger again anteriorly, basal foveæ moderately deep (less so than in *P. septentrionis*), strongly, closely and confluently punctured, connected by a punctate flattened area across the pronotal base. Prothoracic episternum quite strongly and closely but irregularly punctured anteriorly and posteriorly, the smoother submedian area less marked than in any of the four modern species of this genus (*P. aterrimus*, *P. longicornis*, *P. septentrionis* and *P. californicus*), with which I have been able to compare it. In general, the punctuation of this sclerite is rougher in appearance than in the recent form cited. Elytra moderately deeply striate anteriorly, about as in *P. septentrionis*, the striæ distinctly but not strongly punctate, both striæ and punctures becoming finer posteriorly, scutellar stria short and very oblique, interspaces convex near elytral base, flatter on the disk, finely wrinkled and minutely sparsely punctulate, these characters of intimate sculpture being possibly due to accidents of preservation. Length of elytral fragment, 5·00^{mm}. Width (entire), 2·25^{mm}.

Probably this species is most nearly allied to the recent *P. septentrionis* which it approaches in size and general sculpture, differing in the points brought out in the preceding diagnosis. It is not referable to any of the three species described by Scudder from the Scarbrough clays, being larger than *P. decessus* and with short scutellar stria; having a different prothoracic median line and basal foveæ from *P. gelatus*; and with unspotted elytra in place of the profusion of pallid dots seen in *P. frigidus*.

I take pleasure in naming this insect after Samuel Henshaw, Director of the Museum of Comparative Zoology at Cambridge, in recognition of his numerous and varied services to recent and fossil entomology.

PLATYNUS PLEISTOCENICUS new species.

Represented by a single practically complete elytron of shining black color without metallic luster. Striæ fairly deep and strong but not punctured, all attaining the raised basal elytral margin, the scutellar slightly interfering with the course of the first discal, throwing its base over towards the origin of the second. The scutellar and first discal are practically confluent at the apex of the former. The ocellate punctures of the outer edge are indicated towards the apical third but are not strong. None of the dorsal serial punctures can be made out with certainty, probably on account of the peculiar transverse, fine, apparently adventitious, wrinkling of the integument which gives the interstitial spaces the appearance of minute corrugation and, in places, of punctulation. The fifth and sixth striæ unite much farther from the elytral tip than in *P. subgelidus*. Length of elytron, 5·60^{mm}.

None of Scudder's descriptions and figures agree with this insect, but it would probably go nearest his *P. interitus* by the form of the scutellar and adjacent striæ, which, however, do not reach the elytral base in that species. The color is also different and the present insect is somewhat larger. Compared with recent North American species, the arrangement of the striæ in the neighborhood of the scutellum is very similar to that seen in some Colorado specimens standing in my collection under the name *P. propinquus* G. & H., but the surface gloss is entirely different.

According to Scudder's identifications, the genus Platynus was very abundant in the Scarborough beds, whence he has described eleven species. Six others, under the generic names of Platynus, Agonum and Anchomenus, have been characterized from the Pleistocene deposits of France, Germany, Schleswig-Holstein and Galicia.

PLATYNUS SUBGELIDUS new species.

Represented by a single practically entire elytron which is of a deep shining black color, the outer margin rather strongly curved, apparently much as in the recent *P. ovipennis*, extreme edge sharply and narrowly reflexed, humeral angle not fully exposed and, judging from the outline of the side, probably not very prominent. Striæ moderately deep and coarse basally and discally, finer apically, their punctures strong but of medium size, rounded or very little transverse and extremely close together. These punctures become much finer towards the apex, following the reduction of the striæ. Interstitial areas not visibly punctate but in some lights appearing very minutely transversely corrugate, this wrinkling becoming very strong apically (through folding of the integument in fossilization) so as to obscure the tips of the striæ. In consequence, it is not possible to say just where the fifth and sixth are joined, but this point is not far from the elytral apex. The scutellar stria is short, strongly punctured and not interfering with the first discal. The ocellate punctures of the outer margin, if present, are obscured by wrinkling. Length of elytron as exposed, $6{\cdot}00^{mm}$, in life possibly a trifle longer; greatest width, a very little over $2{\cdot}00^{mm}$.

A very careful comparison of this specimen with descriptions and figures of all of Scudder's species of Platynus from the Scarborough beds has convinced me that it is not referable to any of them though approaching (but exceeding) his *P. desuetus* in size. If reliance is to be placed upon the figure, *P. subgelidus* has much more closely punctate striæ. In comparison with recent species, *P. subgelidus* has elytral sculpture a good deal like that of *P. crenistriatus* Lec., but is larger. I do not venture to express an opinion as to which group it should enter.

PLATYNUS CALVINI new species.

Represented by a pair of partly overlapping elytra, shining black and moderately heavy in texture, the striæ impunctate, strongly impressed but not coarse, reaching the raised elytral basal margin. Scutellar stria a little less than half as long as the elytral breadth, free at apex. First discal strongly inflexed to base and almost joining the second at that point. Fifth and sixth confluent not far from the apical fifth of the elytra. Ocellate punctures outside of the eighth stria strong behind the middle of the elytral length but not reaching the apex. On the third stria, about one fifth from the base, is a strong puncture, while between the second and third striæ are two others, one a little antemedian, the other only a short distance from the apex. Interstitial areas flat or nearly so, extremely minutely punctulate and alutaceous. Length of elytron, 5·00^{mm}.

Very closely related in size and arrangement of striæ in the scutellar region to *P. interglacialis* Scudd., from the Scarborough beds, but evidently differs in color and texture. The closest resemblance that I can find among the modern species seems to lie with the *melanarius* group of Platynus, but here I do not find an exact duplication of the arrangement of the dorsal punctures. In giving the specific name, I have in mind my late friend and preceptor, Professor Samuel Calvin, who did so much to advance our knowledge of the Pleistocene formations in Iowa.

CHLÆNIUS PLICATIPENNIS new species.

Represented by a considerable portion of one elytron, of full width but with the base and apex broken off. Color black, surface moderately shining, no signs of pubescence remaining. The striæ are pretty deep but irregular, being composed of short, longitudinal, impressed dashes, much as in the recent *C. interruptus*. The intervals are alternating in height, as described for the modern *C. alternatus*, the punctures fairly deep, strong, so generally confluent as to form transverse irregular rugæ, occasionally broken up into granules. Length of fragment, 6·00^{mm}, greatest width, 3·00^{mm}.

Apparently this elytron represents the remains of a Chlænius allied to the modern *C. interruptus* Horn, occurring in Oregon, Manitoba and the Rocky Mountains of Colorado, and *C. alternatus* Horn, from the Saskatchewan district. It will be noted that both of these recent forms are decidedly northern types.

AGABUS SAVAGEI new species.

The type shows the upper surface of the head and prothorax with the two elytra detached and lying a few millimeters distant. All of these fragments are black, feebly shining. The head is finely but distinctly alutaceous, with a few small, scattered punctures, the lines forming the posterior and inner margins of the eye meeting nearly at right angles. Prosternum alutaceous, about like the head in minute sculpture, a narrow band of small punctures just behind the front margin becoming transverse rugosities in the angles, a similar but less pronounced band just in front of the prothoracic hind margin and a few scattered points on the disk. On the side which shows best, the lateral pronotal edge is beaded and very slightly reflexed. The pronotum as a whole is evidently rather strongly narrowed anteriorly, the margins nearly regularly but feebly arcuate. The front angles are sharp, strongly advanced, as shown by one which is nearly entire and the other which is somewhat more broken. The hind angles are not well uncovered but seem to be obtuse and perhaps a little rounded. Elytra alutaceous, with moderately strong punctures arranged in irregular longitudinal double series and a few inconspicuous scattered punctures in addition, marginal bead strong. Length of pronotum 1·45^{mm}; of elytron (not quite entire at tip) 4·60^{mm}; width of pronotum at broadest part, 3·45^{mm}; of elytron, not determinable on account of curling.

Six specimens are referred to this species, which I have named after Professor T. E. Savage. In the features shown, *A. savagei* is very much like the recent *A. seriatus* Say, common in the northern United States and in Canada. However, comparison of the present species with specimens of *A. seriatus* from the White Mountains and Newfoundland shows the fossil to be smaller, more strongly alutaceous and with deeper elytral serial punctures. Scudder has described *A. perditus*, fossil in the Scarborough beds, but calls particular attention to the lack of serial punctuation. Species of this genus are known from the Tertiary deposits of both continents and seven have been recorded from the European Pleistocene in addition to one from the Cambridge Peat. Today, Agabus is found commonly in swamp land, often burrowing in damp spots outside of the pools themselves.

AGABUS PRÆLUGENS new species.

The type is an elytron very similar to that of Colorado specimens of the recent *A. lugens* Lec., in my collection. It is of a deep black color, moderately shining, finely but very distinctly alutaceous, the rows of serial punctures double, quite deep but not large. The extreme apex of the elytron is broken off, but the remaining fragment is 6·40^{mm} in length. It differs from modern *A. lugens* in the entire lack of brassy reflections and in the texture of the surface sculpture. Four specimens are assigned here, all poor except the type.

OLOPHRUM INTERGLACIALE new species.

Represented by several elytra, 2·25^{mm} long, 1·10^{mm} wide, black, rather shining, subtruncate apically with the outer angle rounded off, punctuation confused, strong, moderately coarse, much of it confluent so as to form poorly defined transverse rugæ, no striæ visible, but the sutural bead shows faintly in some specimens. The outer margin is deflexed as in Olophrum, the line of flexure with a sharp edge.

While the generic reference cannot be made with any certainty, these elytra are apparently staphylinidous, judging from their form, size and sculpture. In all these respects they approach more nearly to *Olophrum obtectum* than to any other insect known to me, but are darker in color and even more strongly and closely punctate. Scudder has described three species of this genus from the interglacial clays of Scarborough, Ontario, but *O. interglaciale* appears to differ, by descriptions and figures, in being more strongly and closely punctured than any of these. In general, Olophrum may be considered rather boreal than otherwise in distribution. I find *O. obtectum* chiefly under bits of wood in damp places and have met with *O. rotundicolle* in swamp land near Leadville, Colorado.

DONACIA STIRIOIDES new species.

An elytral fragment, belongs to Donacia and resembles in fine strial sculpture a recent specimen in my cabinet collected at Cœur d'Alene, Idaho, labelled *D. pusilla* Say, var. *cuprea* Kirby. The fossil is flattened, the striæ fine but quite sharp, punctures small, not very well defined, interstitial spaces much wider than the striæ, relatively coarsely transversely rugose. The color is metallic blue or purple. As exposed, the piece measures 3·85^{mm} in length by 1·50 in breadth.

Two other small fragments are associated with the foregoing but may perhaps not be specifically identical. I cannot refer this fossil to either of the species described by Scudder from the Scarborough beds since his *D. pompatica* has deep striæ with larger punctures and *D. stiria* is said to have an excessively fine transverse rugulation. In North America, Donacia is much more abundant northward and *D. pusilla*, with which the present species has been compared, is more particularly characteristic of the country from Hudson Bay to Vancouver Island, southward to Oregon, California, Idaho, Colorado, and the Lake Superior district. The genus frequents swamp land and the shores of lakes, breeding in the vegetation common to such localities.

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Art. XIV.—*Granite in Kansas*; by Sidney Powers.

During the last three years granite has been occasionally encountered in wells drilled in Nebraska and in the east-central portion of Kansas over an area extending from near Eldorado, Kansas, to Pawnee County, Nebraska.* These wells, starting in the same Pennsylvanian horizon, encounter the igneous rock at depths of 550 to 2500 feet, while other wells within a short distance may be drilled to a greater depth and find only sedimentary rocks of the normal Paleozoic succession. The granite, a medium-grained, pink, biotite type, is not intrusive into the Pennsylvanian and must be of Early Paleozoic or of pre-Cambrian age.

In a recent paper, Twenhofel has called attention to granite porphyry, chert, and quartzite bowlders in (?) the Pennsylvanian strata near Rose, Woodson County, southeastern Kansas,† suggesting that the origin of the bowlders may be similar to the origin of the granite encountered in the wells. Twenhofel presents strong arguments to show that these bowlders were deposited contemporaneously with the LeRoy shales and sandstones of Pennsylvanian age. He also believes that the bowlders reached the positions where now found through the agency of ice, because "the sediments with which they appear to be associated were deposited in quiet waters—waters absolutely unable to transport bowlders of the size of those which are present."‡

If the bowlders are in Pennsylvanian strata it does not seem impossible that they were derived from a buried knob of igneous rock such as postulated below. The bowlders are on a low anticline but Twenhofel does not believe that they can have been derived from a granite mass in this region in Pennsylvanian time, because "the strata of the region are almost horizontal and if the 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."§ However, if granite is encountered in wells in Kansas at a depth of only 550 feet, it is quite probable that at places granite occurs still nearer the surface and it might have been undergoing erosion

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* E. Haworth, On Crystalline Rocks in Kansas, Univ. Geol. Surv., Kansas, Bull. 2, 1915. He describes some of the occurrences, but denies the *presence* of granite in the wells.

† W. H. Twenhofel, Granite Bowlders in (?) the Pennsylvanian Strata of Kansas, this Journal, xliii, pp. 363–380, May, 1917.

‡ Idem, p. 372.

§ Idem, p. 372.

somewhere in the vicinity of Woodson County during the deposition of the LeRoy shales.

A list of the wells which are known to have encountered granite follows, the first well being in Nebraska and all the others in Kansas. The depth at which the granite was first found is given and, where known, the total depth of the well is also given. It has been reported that the two wells in Nowata County, Oklahoma, three wells in Washington County, Oklahoma, and a well five miles east of Inola, Rogers County, Oklahoma, have also found granite, but it is possible that these wells were drilled through the Paleozoic series into the same pre-Cambrian granite which is found in the Ozark Mountains in Missouri.

Sec. 25, T 1N, R12E	Pawnee Co., Nebraska, near Dubois, depth 550–652 feet
SW¼ Sec. 27, T 2S, R12E	Nemaha Co., near Seneca. Two wells, depth about 600 feet
NW¼ Sec. 34, T 6S, R11E	Pottawatomie Co., near Onaga, Empire Gas & Fuel Co., No. 1 Albert Rokes, depth 920–1680
T10S, R 9E	Riley Co., ½ mile south of Zeandale, depth 958–1093
T10S, R 9E	Riley Co., 1½ miles southeast of Zeandale, depth 945–1200
NW¼ Sec. 26, T10S, R 9E	Wabaunsee Co., near Zeandale, depth 991–1093
SW¼ Sec. 1, T11S, R 9E	Wabaunsee Co., near Zeandale, Empire Gas & Fuel Co., No. 1 G. A. Root, depth 1169–1950
SW¼ Sec. 24, T15S, R 7E	Morris Co., near Kelso, Echo Oil Co., No. 1 Whiting, depth about 1970–2552
SW¼ Sec. 13, T16S, R12E	Lyon Co., Kansas Natural Gas Co., No. 1 Miller Ranch, granite reported 1360–1450
SE¼ Sec. 34, T17S, R 7E	Morris Co., Empire Gas & Fuel Co., No. 1 Moffitt, depth 1900–2500
NW¼ Sec. 2, T20S, R 7E	Chase County, near Elmdale, Empire Gas & Fuel Co., No. 1 Kaufman, depth 1873–3100
T20S, R 7E	Chase Co., near Elmdale, No. 1 Chase County Poor Farm, depth 1707–2501
NW¼ Sec. 14, T23S, R 5E	Butler Co., near Burns, Hoyt et al., No. 1 Libby, depth 2312–2502

With the exception of the well in T16S, R12E, all the granite wells listed fall into a line about 140 miles in length extending in a N.18°E. direction on the prolongation of a line of petroleum producing anticlines which includes Billings, Blackwell, Arkansas City, Augusta, and Eldorado. The principal petroleum production in Oklahoma–Kansas comes from an area of elliptical outline with the longer axis in a north-south direction 75 miles east of the southern extension of the granite axis. There is no doubt but that granite has been encountered in wells in Kansas, and possibly in Nebraska, other than those above listed, but this list will furnish some idea of the size of the area underlain by it.

Anticlinal structure has determined the location of most of the wells which have struck granite, yet two of the Zeandale wells and the Kelso well are not on anticlines. The large anticline at Eldorado, south of the Burns granite well, shows no granite at a depth of 3600 feet, nor does a well of the same depth 2½ miles from Burns. Therefore, the surface of this granite mass must have a relief of about 1300 feet in 6 miles.

Fig. 1.

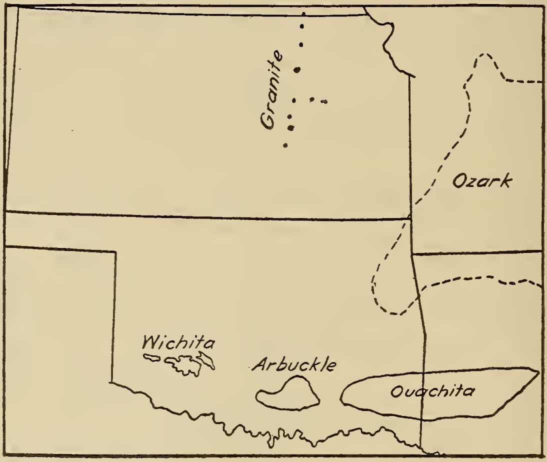

Fig. 1. Outline map of Kansas, Oklahoma and portions of adjoining states showing location of granite wells in Kansas and Nebraska with respect to the Ozark, Ouachita, Arbuckle, and Wichita mountains.

The total lack of metamorphism in the Pennsylvanian rocks around the granite knobs proves that the latter stood as islands in the Pennsylvanian sea and were gradually buried beneath the limestones and shales. In some of the wells red shale has been noted immediately above the granite, while in others, granite bowlders, sand, chert pebbles, and weathered granite above the fresh rock show that the knobs suffered erosion in Pennsylvanian time. In the first two Zeandale wells Professor

Haworth secured two varieties of dark-colored schists (evidently inclusions or dikes) and in the first well he found a one-foot bed of shale 32 feet within the granite (a fissure or cave filling or a dike).* Above the granite in both these wells, there is a bed of fossiliferous shale.

Pre-Cambrian granite is known in the Wichita, Arbuckle, and Ozark Mountains. The only Paleozoic granite in the region is the dike near Spavinaw, Mayes County, Oklahoma, on the edge of the Ozark Mountains,† the known extent of which is 1200 by 50 feet. It runs along the axis of a gentle anticlinal fold in a N.30°E. direction, cutting Ordovician strata, and yet these strata are described as being free from any special metamorphic action due to the dike rock. No similar dikes have been reported.

The local extent of the buried granite knobs and their lineal arrangement suggest that in the beginning of Pennsylvanian time they presented an appearance similar to that of the Wichita Mountains now or at the beginning of Permian deposition. These knobs must belong to a mountain system of pre-Pennsylvanian age and yet they are situated in a region which is supposed to have been covered at intervals and for varying lengths of time by Ordovician, Silurian, Devonian, and Lower Mississippian seas. The mountain system to which the granite belongs must have been formed either in the pre-Cambrian, the Lower Paleozoic (pre-Silurian), or in the Mississippian and is probably a part either of the Lake Superior or of the Appalachian folding—further drilling, especially in Nebraska and Iowa, should show which. A study of variations in the intensity of gravity in the region of the granite should also conclusively prove that the granite knobs are part of a large mountain structure and should delimit this structure. Up to the present time only one station in the eastern half of Kansas furnishes any data and the anomaly of this station according to the Hayford 1916 method is positive, agreeing with the anomalies of the stations in the United States situated on pre-Cambrian formations.‡

During the Lower Paleozoic, uplifts took place west and north of the present Appalachian system in two regions: the Cincinnati axis upon which rise the Cincinnati and Nashville domes; and the Ozark axis. If it be granted that the Ouachita, Arbuckle, and Wichita mountains represent the prolongation of the Appalachian system west of the Mississippi (see fig. 1), running in a N.75°W. direction, or

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* Op. cit., pp. 23–26.

† N. F. Drake, Proc. Amer. Phil. Soc., xxxvi, 338–343, 1698.

‡ Wm. Bowie, Investigations of gravity and isostasy, U. S. Coast and Geodetic Survey, Special Pub. No., p. 73, fig. 12, 1917.

making an angle of 125° with the main Appalachian trend, there is a rather striking arrangement of the Cincinnati, Nashville, and Ozark areas, and the Kansas granite, in an inner arc with a general axis from 100 to 300 miles west and north of the inner boundary of the main Appalachian axis.

The Kansas granite may therefore represent either an outlier of pre-Cambrian structure connected with the Lake Superior region, or a Lower Paleozoic uplift from the top of which the sediments were removed in pre-Pennsylvanian time, leaving only peaks of pre-Cambrian granite to be buried by Pennsylvanian sediments just as the peaks of the Wichita Mountains at the present time represent a formerly extensive mountain range now almost completely buried by horizontally bedded sediments.

Art. XV.—*A New Method for the Determination of Hydrogen Peroxide*; by George S. Jamieson.

The method to be described is based upon adding a measured volume of hydrogen peroxide solution to an alkaline solution containing an excess of standard sodium arsenite. When the reaction is completed concentrated hydrochloric acid is added and the unaltered arsenite is titrated with a standard solution of potassium iodate* using a chloroform indicator. The amount of arsenite found by titration is deducted from the amount taken, giving that oxidized by the hydrogen peroxide. In order to obtain a quantitative reaction with the hydrogen peroxide and the sodium arsenite it was found necessary to add sodium hydroxide in excess as directed below. It should be observed that this method is not influenced by the presence of organic preservatives as is the case with the well known permanganate method.† Also it has the advantage over the excellent Kingzett method‡ in that both the sodium arsenite and the potassium iodate solutions are remarkably stable. These solutions can be made of known strength without standardization and used immediately which is in marked contrast with the sodium thiosulphate solution employed in the Kingzett method. Furthermore, it has been found that the iodate method gives accurate results.

* J. Ind. and Eng. Chem., iii, 250, 1911.
† Analyst, viii, 36.
‡ J. Chem. Soc., 1880, 792.

In order to test the method, a solution containing 3·567 g. of normal potassium iodate in 1000^{cc} was used. The tenth normal sodium arsenite solution which had been made for another purpose over a year ago, was prepared by dissolving 4·948 g. of pure arsenious oxide in about 50^{cc} of water which contained 4 g. of sodium hydroxide. When the oxide had dissolved, 200^{cc} of a saturated solution of sodium bicarbonate were added along with enough water to make 1000^{cc}. The relationship between the arsenite and iodate solutions was obtained by titrating a measured volume of arsenite solution acidified with two-thirds the volume of concentrated hydrochloric acid.* 5^{cc} of sodium arsenite were found equivalent to $7{\cdot}5^{cc}$ of iodate solution or 1^{cc} of $KIO_3 \equiv 0{\cdot}667^{cc}$ of As_2O_3. If desired, the relationship of the two solutions may be calculated as follows: 1^{cc} of $KIO_3 \equiv {\cdot}003297$ g. of $As_2O_3 \div 1^{cc}$ of $As_2O_3 \equiv {\cdot}004948$ g. of $As_2O_3 = 0{\cdot}667^{cc}$ which is identical with the result obtained by titration.

The first hydrogen peroxide solution used to test the method was made by diluting 50^{cc} of ordinary commercial peroxide to 500^{cc}. Measured quantities of the arsenite solution which must be in excess of that required by the hydrogen peroxide taken for analysis, were placed in 500^{cc} glass stoppered bottles along with 10^{cc} of a 10 per cent solution of sodium hydroxide. A measured volume of the hydrogen peroxide solution was added from a burette while the contents of the bottle were gently agitated. After the solution had stood for 2 minutes, 40^{cc} of concentrated hydrochloric acid were cautiously added. The stopper was inserted and while holding it firmly in place the bottle was violently shaken in order to separate as much carbon dioxide as possible from the solution. Then the stopper was carefully released so as to allow the excess pressure of gas to escape without losing any solution. After adding $6\text{–}7^{cc}$ of chloroform the unoxidized arsenite was titrated with the potassium iodate solution with thorough shaking of the closed bottle after each addition of iodate until the end point, which is the disappearance of the iodine color from the chloroform, is reached. The amount of iodate used for the titration was converted into its equivalent of arsenite solution which was deducted from that originally taken, leaving that oxidized by the hydrogen peroxide. The following equations may be written to represent the reactions which take place:

$$As_2O_3 + 2H_2O_2 = As_2O_5 + 2H_2O$$
$$As_2O_3 + KIO_3 + 2HCl = As_2O_5 + ICl + KCl + H_2O$$

The following results were obtained:

$$1^{cc} \text{ of } As_2O_3 \text{ sol.} \equiv {\cdot}001701 \text{ g. } H_2O_2.$$

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* J. Ind. and Eng. Chem., iii, 250, 1911.

No.	ccH_2O_2 sol. taken	ccN/10As_2O_3 sol. taken	ccK10$_3$ sol. used	ccAs_2O_3 sol. used by H_2O_2	H_2O_2 found grams	Kingzett method
1	15·1	34·9	4·9	31·6	·0537	
2	15·0	34·9	5·02	31·55	·0536	·0536
3	20·0	46·0	6·0	42·0	·0714	·0710
4	20·0	45·5	5·45	41·9	·0712	
5	22·0	49·9	5·90	46·0	·0782	·0781
6	22·0	49·9	5·90	46·0	·0782	·0781

These titrations were made during a period of three hours after preparing the diluted hydrogen peroxide. It is important to titrate the hydrogen peroxide solution which has been diluted with ordinary distilled water of the laboratory soon after the dilution because it was observed that the hydrogen peroxide slowly decomposed. A diluted solution of hydrogen peroxide was prepared and analyzed. It was found to contain ·003639 g. of H_2O_2 per cc. After standing 24 hours it contained ·003551 g. of H_2O_2 per cc. and a week later it was found to contain only a trace of peroxide.

Another solution was prepared by diluting 55^{cc} of the commercial hydrogen peroxide to 500^{cc} which gave the following results upon analysis:

No.	ccH_2O_2 sol.	ccN/10As_2O_3 sol.	ccKIO_3 used	ccAs_2O_3 sol. used by H_2O_2	H_2O_2 found	Kingzett det's.
1	15·2	40·0	7·05	35·3	·0600	·0602
2	15·0	39·9	7·35	35·0	·0595	·0595
3	15·05	39·9	7·35	35·0	·0595	·0597
4	15·20	39·8	6·70	35·3	·0600	
5	15·10	39·8	7·00	35·13	·0597	·0598

The results obtained in each series of experiments show that the method gives accurate results. In practice, it would be recommended that a fifth normal sodium arsenite solution along with an equivalent potassium iodate solution (10·700 g. of KIO_3 per 1000^{cc}) should be employed.

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SCIENTIFIC INTELLIGENCE.

I. GEOLOGY.

1. *The Coral Reef Problem and Isostasy;* by G. A. F. MOLENGRAAFF. Kon. Akad. Wettensch. Amsterdam, vol. xix, No. 4, 1916.—Professor Molengraaff gives in this paper an interesting and ingenious hypothesis to account for the apparent submergence of oceanic islands, which has given rise to barrier reefs and atolls, without having recourse to those extensive subsidences of the ocean floor, which the Darwin–Dana theory postulates, and which has been held to be an objection to it.

He gives full weight to the idea of changes in the ocean levels during Pleistocene time by the piling of ice on the land and its subsequent melting, as recently urged by Daly, but following the views of Davis, he believes that to explain the topography of the oceanic islands surrounded by barriers, greater changes of level than could be ascribed to this cause must be accepted. This tends to strengthen the Darwin–Dana theory in its demand for actual subsidence.

To permit this without recourse to a general subsidence of the ocean bottom, he supposes it to be individual in each case, according to the following hypothesis.

He classifies oceanic islands and considers only those rising from abyssal depths as volcanic structures composed chiefly or entirely of basaltic material true oceanic islands. Other islands are to be regarded as those occurring in shelf seas, connected with continental masses, either wholly or partly submerged, and the coral islands found in these shelf seas are to be explained by the "glacial-control" hypothesis of Daly. The rocks composing these islands may be of diverse characters.

The material composing the earth's shell under the oceanic abysses is that of a basaltic substratum, called by Suess the sima, or barysphere, and upon this rests in relative flotation the continental masses of a more siliceous nature and lower specific gravity, or the lithosphere. He notes that isostatic equilibrium is general over the earth, but, since there are mountain masses where anomalies of gravity exist and isostatic compensation is not complete on the continents, he draws attention to the anomalies of gravity found on true oceanic islands and infers that none of these are isostatically compensated.

From this he draws the conclusion that, whereas on the continental masses anomalous mountain projections may be able to sustain themselves in virtue of a thicker, stiffer substratum, those rising from the ocean floor rest upon and are rooted in the more plastic basaltic substratum, or sima, and in the long process of time they must gradually sink down and be again welded into it. This gradual sinking down under the influence of gravity is regarded as the cause of the movement of large amount and long duration which is held to be necessary to explain barrier reefs and atolls in true oceanic regions.

The author suggests that a test of this hypothesis would be the finding of reef-crowned islands which had sunk to considerable depths, but admits that so far the evidence in this direction is scanty. He presents one case, however, in the Ceram sea which is held to be in the nature of the desired proof. It is obvious also that the hypothesis should apply to all volcanic islands that rise from the oceanic abysses wherever they may be found. In the Atlantic only Bermuda is held to fill this definition, and to be in the area of reef-building corals, and the fact that reef limestone was found in a boring on it to extend to the depth of 245 feet below present sea-level is viewed as agreeing with the hypothesis.

The reviewer, who desires to say at the outset that he has no bias toward any particular theory as to the formation of coral islands, offers the following comments on this hypothesis. In the first place the work which has been done in recent years upon the strength of rocks in resisting deformation precludes the idea that a basaltic cone could flatten out by its own weight. There might be some lowering by the compacting of fragmental or vesicular material, but this effect should take place largely in measure as the cone grew and would soon cease. A volcanic cone of itself must be regarded as a competent structure. If the sinking takes place it must be by a yielding of the foundation on which it is placed and of the cone as a whole.

It cannot be supposed that a yielding basaltic stratum can immediately underlie the sea. Moreover, a distinction must be made between material that is rock, that is a rigid solid, and that which is in any sense liquid or initially plastic. The floor underlying the sea must be of rock and it cannot be plastic until a depth has been reached where the resistance to deformation has been overcome. The experiments of Adams show that under laboratory conditions the crust increases in strength with depth. Or, on the other hand, if plasticity is to be referred to a change of rock from the solid to the liquid condition, this also can only occur at a depth where increasing heat is sufficient to overcome the effect of pressure, and this can be no relatively slight one. It is clear from this, therefore, that if the volcano sinks bodily into the sima, large underlying masses of the crust on which it stood must also be involved in the movement. It is also questionable whether a mass of tightly fitted earth blocks resting either on a liquid substratum, or one rendered plastic by deformative stress, would not be competent to sustain the volcanic load under the static conditions posed in the hypothesis. In order to have subsidence, it would seem as if differential movements in the yielding substratum must occur. But if these took place on a small scale they would be attended by outflows and quick readjustment, while the hypothesis does not permit us to assume undertow movements on a large scale leading to orogenic processes. It is difficult to see how such subsidence as is demanded could occur without diastrophism.

In regard to Bermuda it may be said that since the coral rock only extends about 250 feet (nearly 75 meters) below the present sea-level, this is practically within the limit of the glacial control theory, or not allowing more than 50–60 meters in change of level according to that theory, would indicate a very minute subsidence from Eocene time. Molengraaff noticing the total thickness of the coral limestone at Bermuda of 380 feet (110 meters nearly) and that 135 feet of this is now above water, assumes both up and down movements of these dimensions but this is unnecessary, for that part of the limestone now above sea-level is everywhere remarkably and very strongly cross-bedded, indicating a pronounced dune structure. It is difficult to imagine such strongly inclined cross-bedding occurring on a small isolated island except by atmospheric action. No upward movement seems, therefore, needed and to obtain a just thickness of the limestone deposited as a marine formation the part now above water should be subtracted from the whole, leaving 245 feet. Considering the situation of the drill hole on the outer edge of the island it would seem to the reviewer that the atmospherically weathered deposits encountered below the coral rock are most naturally explained by their being the washed-down products of land-waste lying on the outer slopes of the island below sea-level, that is a wave-built terrace, rather than as indicating soil in place, carried under by subsidence. Also the rounded forms of the pebbles in this deposit indicate much wear and transport of the material. It is difficult to see how over 300 feet in depth of soil could accumulate on a small island without being washed off.

It would seem to the reviewer, therefore, that Bermuda, standing as it has since, at least, Eocene time, and no one knows how much longer, is an example of the stability of true oceanic islands rather than the reverse.

One cannot avoid the impression on reading the paper and noting expressions used by the writer like these: "From this it follows that the continents must be considered as flows of salic composition, floating in the sima in the same way as ice bergs do in water, being submerged with about 85–95 per cent of their mass," and "the whole sima has been called by Daly basaltic substratum," along with similar ones, that the writer conceives of the shell immediately underlying the ocean floor as being in a liquid state or possessing at all events a much higher degree of plasticity than the continental masses. To be sure he quotes from others to support his view and seems to feel that its assumption is demanded by recent researches on isostasy, but it would seem as if this were pushing the idea of isostasy to a rather extreme limit. It would at all events be of interest to test the hypothesis which the writer has so interestingly presented by the results of what recent investigations in the fields of seismology and astrophysics have taught us regarding the physical properties of the outer shell of the earth.

L. V. P.

2. *A Study of the Magmatic Sulphide Ores;* by C. F. Tolman, Jr., and A. F. Rogers. Leland Stanford Junior University Publications, 1916, 76 pp., 20 pls., 7 figs.—The authors define "magmatic deposits" as those segregations of ore-minerals that take place under the influence of, or closely connected with, the molten stage of the parent rock. Ore accumulations accompanied by destructive pneumatolytic action, or those formed by hydrothermal solutions, are not to be classed as magmatic deposits. Typical magmatic deposits are confined to the basic rocks. Their study has led to the hypothesis that "the magmatic ores in general have been introduced at a late magmatic stage as a result of mineralizers, and that the ore-minerals replace the silicates. This replacement, however, differs from that caused by destructive pneumatolytic or hydrothermal processes in that quartz and secondary silicates are not formed at the time the ores are deposited.

It is conceived that the process of formation of plutonic rocks consists of stages and that rock differentiation and ore formation are the results of an orderly series of events. The stages in the norites and gabbros which contain the magmatic sulphide ores are as follows:

(1) The first minerals to form are olivine, pyroxenes and feldspars.

(2) Magmatic alteration of the silicates, as the change of pyroxene to hornblende, often takes place prior to the formation of the ore-minerals.

(3) Later magmatic products include interstitial pegmatite material, interstitial quartz, tourmaline, garnet, analcite, epidote and calcite.

(4) The introduction of the ores by mineralizers is later, in general, than the minerals of group (3) and is unaccompanied by any secondary silicates.

(5) Pegmatite dikes often come later than the magmatic deposits of the basic rock itself.

(6) Hydrothermal alteration, subsequent to magmatic ore deposition and which in general is insignificant, includes the development of chlorite, tremolite, anthophyllite, sericite and serpentine.

(7) Lastly downward enrichment and oxidation may take place.

The second part of the paper is taken up with a discussion of various deposits of magmatic ores and the third part contains the summary of the characteristics of magmatic ores and various theoretical conclusions. W. E. F.

3. *Origin of Massive Serpentine and Chrysotile-Asbestos, Black Lake–Thetford Area, Quebec;* R. P. D. Graham, Econ. Geol. xii, 154–202, 1917.—The author presents a summary of the geological structure of this important asbestos field and examines in detail various theories concerning its history. Some of his more important conclusions follow. The serpentine area has been derived from the alteration of original peridotites. A cross-section

from unaltered peridotite to the chrysotile may be divided roughly into four zones as follows: (1) unaltered peridotite; (2) partial serpentinization of the olivine, with pyroxene more or less unaffected; (3) olivine completely, and pyroxene partially, serpentinized—this zone constitutes the massive serpentine "bands"; (4) complete serpentinization of both olivine and pyroxene—this zone forms the chrysotile "veins." The serpentinization has proceeded outward from joint planes, etc., through the agency of siliceous solutions which, permeating the walls on either side of such fissures, have first acted on the olivine content of the rock and from the resulting concentrated aqueous solutions of olivine, serpentine has been deposited in the form of microscopic fibers. The expansion attending this reaction tended to render the rock more porous and permit the solutions to reach fresh zones of the rock and carry the change further on. The result has been that in the zone immediately bordering the fissures the serpentinization of the rock has been complete, while beyond this there is a more or less gradual transition until the unaffected peridotite is reached. The structure of the rock has changed progressively with the serpentinization. Even in the massive serpentine the structure of the original rock can at times be seen, and where, further, more or less unaltered pryoxene crystals yet remain and the magnetite is disseminated much as it occurs in the original peridotite. It is only in the chrysotile vein that the original structure is entirely lost, even to the extent that most of the iron ore has here collected along certain definite zones. The chrysotile of the veins is believed to be the result of the parallel position and transverse attitude assumed at the very outset by the minute fibers, and of their subsequent growth in only one direction. The ultimate length of the fibers is limited only by the width attained by the completely serpentinized zone. W. E. F.

4. *Contributions to the knowledge of Richthofenia in the Permian of West Texas;* by EMIL BÖSE. Bull. University of Texas, 1916, No. 55, 52 pp., 3 pls., 1 text fig.—A long and detailed description of the brachiopod genus *Richthofenia* and the two Texas species *R. permiana* and *R. uddeni.* The author, after a review of the geographic and geologic distribution of the species of the genus, concludes that they are characteristic of the Permian and were especially common in the early middle Permian. C. S.

5. *Contributions to Geology;* reprinted from the Johns Hopkins University Circular, March, 1917, 129 pp., figs.—The first paper in this set is by Professor W. B. Clark, who gives a short history of the rise of geological surveys. E. B. Mathews treats of "The use of average analyses in defining igneous rocks," and J. T. Singewald of "The rôle of mineralizers in ore segregations in basic igneous rocks." F. Reeves writes on "The origin of the natural brines of the oil fields." The other seven papers, by Berry, Gardner, Woodring, Thom, Wade, and Dorsey, deal with Mesozoic and Cenozoic stratigraphy and faunas. The pamphlet is replete with new and important information. C. S.

6. *Geological Survey of Alabama.* EUGENE A. SMITH, State Geologist.—The following bulletins have been issued:

No. 17. Second report on the Water Powers of Alabama; by BENJAMIN M. HALL and MAXCY R. HALL, Consulting Engineers. Pp. 448; with map, plates and text figures.

No. 18. Preliminary Report on the Crystalline and other Marbles of Alabama; by WILLIAM F. PROUTY. Pp. 212; 40 pls., 20 figs.

No. 19. Statistics of the Mineral Production for 1915, compiled from the Mineral Resources of the United States by EUGENE A. SMITH. Pp. 87.

7. *Bibliography of the Geology and Mining Interests of the Black Hills Region;* by CLEOPHAS C. O'HARRA. Bulletin No. 11, South Dakota School of Mines; Department of Geology. Pp. 216, with map. Rapid City, South Dakota, May, 1917.—The obvious value of this bibliography is increased by the fact that in most cases brief digests are given of the papers noted. There is also a map of the Black Hills Region.

8. *Story of the Grand Canyon of Arizona: a popular illustrated account of its Rocks and Origin;* by N. H. DARTON. Pp. 81. Kansas City, Mo. (published by Fred Harvey).—An interesting account of the Grand Canyon, made instructive by the clear exposition and sections of the writer; it is very attractive in the large number of well-chosen illustrations.

9. *Bulletin of the University of Texas, 1916, No. 66.* J. A. UDDEN, Director of the Bureau of Economic Geology and Technology. Pp. v, 93; 7 pls. (including map), 7 figs. Austin, Texas.—This bulletin is devoted to the Thrall Oil Field and includes a chapter on this general subject by J. A. Udden and H. P. Bybee; another on the ozocerite by E. P. Schoch; and a third on the chemical composition of the Thrall petroleums by E. P. Schoch and W. T. Read.

II. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Food Poisoning;* by EDWIN OAKES JORDAN. Pp. 115. Chicago, 1917 (The University of Chicago Press).—This is a very readable summary of the evidence and probabilities relating to the responsibility of certain articles of food for those physiological disturbances which are frequently designated as "ptomain poisoning." It also deals with sensitization to protein foods, poisonous plants and animals, mineral or organic poisons added to food, food-borne pathogenic bacteria, animal parasites, poisonous products formed in food by bacteria and other micro-organisms, and poisons of obscure or unknown nature, including the so-called deficiency diseases. The judgment of the author appears to be sane and well balanced on many topics which are still within the range of debate. The little volume is not too technical to pre-

vent anyone having a moderate acquaintance with the biological sciences from reading it with profit. L. B. M.

2. *Principles of Agricultural Chemistry;* by G. S. Fraps. Easton, 1917 (The Chemical Publishing Co.). 2d edition. Pp. 501.—A volume dealing with the principles and practices of scientific agriculture from the standpoint of the chemist. It includes such topics as the essentials of plant life, soils, fertilizers, the composition of feeds, and the feeding of farm animals. Most of the subjects are dealt with in exceedingly summary fashion, so that no one could profit adequately by the perusal of the book without considerable preliminary training in the sciences of chemistry and biology. Historical matter is introduced into some of the chapters. The treatise serves as a guide rather than an exhaustive presentation of a very large group of modern agricultural themes. It is unfortunate that the term "proteid," now generally abandoned in favor of "protein," has been retained in the new edition. L. B. M.

3. *The Secretion of the Urine;* by Arthur R. Cushny. London, 1917 (Longmans, Green and Co.). Pp. ix+241.—No one familiar with the author's contributions to physiological literature need be told that a volume by Professor Cushny on kidney functions is almost certain to present something of more than conventional interest. The present is one of a new series of monographs on physiology intended, as the editor, Professor Starling, expresses it, not to give an exhaustive account of previous writings, but rather to afford "an appreciation of what is worth retaining in past work, so far as this is suggestive of the paths along which future research may be fruitful of results." Accordingly we find Cushny departing from the traditional controversy on the theory of renal secretion and advocating what he terms "the modern view," in which considerations of physical chemistry and physical physiology are employed to combat so-called vitalistic hypotheses. Something of the viewpoint may be inferred from this quotation: "One part of the kidney filters off the plasma colloids, another part absorbs a fluid of unchanging composition. The kidney exercises no discrimination, but continues these activities through life, just as a muscle exercises no discrimination. The kidney loses somewhat in dignity and romance when it is thus represented as merely a hard-working organ, which is admirably fitted to remove the waste products of the blood, but which is so devoid of judgment that in some conditions it acts to the prejudice of the organism by removing the diluent instead of the poison" (p. 56). The chapters cover the following topics: anatomy and histology of the kidney, the chief constituents of the urine and their concentration, the work, gaseous metabolism and blood supply of the kidney, theories of renal secretion, direct evidence on the functions of the tubules and glomerulus, blood supply and kidney secretion, the reaction of the urine, the action of diuretics and other drugs, glycosuria, perfusion of the kidney, albuminuria, notes on nephritis and other

renal disorders. An elaborate bibliography completes a stimulating monograph. L. B. M.

4. *Field Museum of Natural History;* Frederick J. V. Skiff, Director. *Annual Report of the Director for the Year 1916.* Pp. 75–146; with numerous plates and a frontispiece portrait of the late Seth E. Meek, assistant curator of Zoology, 1897–1914.—The energies of the Field Museum staff in 1916 were chiefly devoted to the work involved in preparation for the exhibition halls of the new Museum. Although this has necessarily involved some confusion and while expeditions and field-work have been practically suspended, the ultimate result will doubtless bring a full compensation for the inconvenience now experienced. There have been a large number of notable new accessions.

5. *Chemical and Biological Survey of the Waters of Illinois.* December 31, 1915. Edward Bartow, Director. University of Illinois Bulletin, Water Survey Series, No. 13. Pp. 381; with numerous illustrations.—This bulletin contains a general account of the work done by the Water Survey of Illinois in 1915, with summaries of the chemical, biological and engineering work. There are also included several special investigations, relating to bacteria in well water; typhoid fever epidemics; methods of water purification, etc. H. P. Corson shows that manganese, ordinarily considered uncommon in waters in this country, is present in a number of water supplies in the state; at Mount Vernon it had formed a serious incrustation in the city water pipes which contained 4·4 to 8·8 per cent.

6. *British Museum Publications.*—Recent publications are the following:

Instructions for Collectors; No. 13.—Alcohol and Alcoholometers; by S. F. Harmer. Pp. 8.

Guide to the British Fresh-Water Fishes, exhibited in the Department of Zoology; by C. Tate Regan. Pp. 38; 23 figs.

Report on Cetacea stranded on the British Coasts during 1916, by S. F. Harmer. No. 4, pp. 1–13, one text-figure and one map.

OBITUARY.

Dr. T. McKenny Hughes, Woodwardian professor in the University of Cambridge, died on June 9 at the age of eighty-five years.

Horace T. Kennedy, of the Geological Survey of Ireland, was killed in action on June 6.

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SCIENTIFIC INTELLIGENCE.

Established by BENJAMIN SILLIMAN in 1818.

THE AMERICAN JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

FOURTH SERIES

VOL. XLIV—[WHOLE NUMBER, CXCIV].

No. 261—SEPTEMBER, 1917.

WITH PLATE I.

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1917.

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Specimen 1½″ x ⅞″; one crystal embedded ¼″ in diameter and projecting 3/16″. $20.

Specimen 1¾ x 1¼″; one large crystal laying on the matrix ½″ long and 5/16″ in diameter, doubly terminated and with some pyrites. $25.

Specimen 1¾″ x 1½″; two crystals embedded, one crystal 5/16″ in diameter, the other ⅜″ in diameter; both projecting about ⅜″. $35.

Specimen 2 x 2″; one large crystal embedded, 9/16″ in diameter, projecting 11/16″; crystal is of parallel growth of good color and fine termination. $45.

I also have a few other fine specimens up to $200.

Crocoites, Dundas, Tasmania. I just received a fine lot of matrix specimens priced at from $6 to $10.

ALBERT H. PETEREIT

81-83 Fulton St., New York City

Halemaumau, the lava pit of Kilauea.

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XVI.—*Volcanologic Investigations at Kilauea*, with Plate I (frontispiece)*; by T. A. Jaggar, Jr.

Contents

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* For explanation of Plate I see bottom of p. 162.

INTRODUCTION: MAGMATIC GASES.

THE immediate work of the Hawaiian Volcano Observatory since it was established in 1912 has been concerned with recording rather than theorizing. Confirmation or refutation of existing theories is greatly dependent on a knowledge of habits and of the sequence of changes which happen in the course of time and the comparison of charts showing these sequences, with other charts that show such changes as those of rainfall or numbers of earthquakes, or the tides or movements of the sun and moon. It is by comparison of time changes that such great sciences as astronomy and meteorology have been built up. Volcano science has had no such records and our observatory is trying to supply the defect.

Fortunately, however, five colleagues who have worked at Kilauea have written important articles suggesting theoretical possibilities concerning the mechanism and chemistry of the gases and the lava. Three of these papers deal with the ancient problem of water vapor as a cause of volcanic activity. Dr. Albert Brun* of Geneva believes that water is unessential, Professor Daly† of Harvard and Mr. F. A. Perret‡ of Naples believe that gases rising from heated magma in the depths are the main heating and liquefying agents in liquid lava, without being prejudiced as to the amount or origin of the hydrogen and oxygen which undoubtedly exist among these gases. Drs. Day and Shepherd,§ of the Carnegie Institution, after chemical work at Kilauea for two seasons, published results showing that steam certainly exists in the gases blown out from flaming cones on the Halemaumau floor, but the proportion by volume of water among the gases collected was only about four per cent, while the dominant ingredients were sulphurous acid,

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* L'Exhalaison volcanique, Paris, 1911.

† Proc. Amer. Acad. Arts and Sci., xlvii, No. 3, 1911.

‡ This Journal, vols. xxxv–xxxvi, 1913.

§ Bull. Geol. Soc. Amer., vol. xxiv, pp. 573–606, 1913.

EXPLANATION OF PLATE I (fig. 1) frontispiece.—General views, interior of Halemaumau, the lava pit of Kilauea volcano. (*a*, upper view) Aug. 26, 1915, 9 A.M. Upper surface duplex lava column, Halemaumau pit, from S.W. rim. Diameters 780 by 730 ft. (238 by 222 m.). Length liquid lake 700 ft. (213 m.), maximum width of same 220 ft. (67 m.), and depression of lake 410 ft. (125 m.). Bench clinging to wall left 18 ft. (5 m.) and general floor level 6 ft. (1·8 m.) above lake. The clinging bench marks lava level of 1914, mossy appearance due to mat of Pele's hair. Western conduit pond on left, sinkhole niches middle and right. Streaming left to right; minimum incandescence, fountaining and fuming left; maximum right. Rising activity, crags of bench magma crust tilted and fissured on the right by weight of overflows shown. Panchromatic photo by Jaggar, camera inclined forward.

(*b*, lower view) Jan. 31, 1917, 5 P.M. Depression 45 ft. (13 m.). Diameter 1200 ft. (366 m.). Halemaumau from S.E., showing islands and benches on the left, overflow floors on the right. Swift current around South Island in foreground. Strong overflow in progress, culmination of winter rise. Compare map, fig. 2, p. 168. Photo, Morihiro.

carbon dioxide and nitrogen, with a residue of about seven per cent rather equally divided among the inflammable gases sulphur, carbon monoxide and hydrogen, the latter predominant among these. There was in addition less than 0·1 per cent in all of fluorine, chlorine and ammonia.

All of these workers agree that rising gas achieves the work known at the surface of the earth as volcanic activity. I think that they all agree that the gases rise from deep sources, and so far as the water problem is concerned, they all agree, in opposition to the older geological text books, that gases other than water in large measure heat and operate the volcanic engine. In this they verify a conclusion reached many years ago by Dr. Wm. T. Brigham,* Director of the Bishop Museum, and Mr. Wm. Lowthian Green.† Their differences of opinion concern the extent to which the combinations with oxygen above listed are original gases or products of union with air, and more especially the extent to which surface heating, by chemical combination among these unstable mixtures, is responsible for the liquid lava pools and flows.

Brun believes that original carbon in the form of hydro-carbons exists in lava, and nitrogen combined with hydrogen in the form of ammonia. He insists that there is no original water from deep-seated sources emitted by lavas. Perret believes that the oxides and hydrates which come forth as gases are the result of union with superficial air and water but that the unadulterated gas from the deep region is more elemental and is frequently quite breathable in great volcanic explosions, whereas the oxidation products are disagreeable or poisonous. In some cases, such as Vesuvius and Stromboli, he has breathed the rush of gas from great explosions and perceived no chlorine, sulphur or poisonous carbon compounds. This agrees with some recent observations of the writer in Hawaii, when a few feet from and immediately to leeward, of the Halemaumau lava lake on its shore (fig. 12), of a pahoehoe overflow on its border and of an *aa* flow on Mauna Loa, he found no difficulty whatever in breathing the intensely hot products of small bubblings all over these glowing surfaces and perceived almost no sulphur odors; whereas at a greater distance to leeward of a positively flaming grotto or cone, the bluish fume which condenses is full of intolerable compounds of sulphur with oxygen. The Selby commission determined that one ten-thousandth part SO_2 in air is intolerable to human beings. It hardly seems probable, therefore, that as much as *50 per cent* of the magmatic gas rising directly from fresh lava can be SO_2‡ (see below).

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* Kilauea and Mauna Loa, Mem. Bish. Mus., 1909.

† Vestiges of the Molten Globe, Honolulu, 1887.

‡ Bull. Haw'n. Vol. Obs'y., Sept. 1914, p. 121.

Mechanism of Heating.

Is Lava Lake Hotter Below Surface?

Daly points out that a volcano may be a true furnace in that heat-producing chemical reactions necessarily take place where free hydrogen is present. Nevertheless he considers that the heat, generated partly from reaction between the gases underground, is continuously distributed by "two-phase" convection with a cooler liquid phase of the melt sinking while a hotter and lighter gas-bubble phase is rising. The rising gas by expanding would have a strong cooling effect, so that if there were no compensatory heat reaction, Daly calculates that a bubble rising at the surface at a temperature of 1200° C. would at depth of 37 meters (120 feet) have a temperature over three times as great or 3700° C. He finds that the loss of heat at the surface of the lava lake is vastly greater than the heat lost by conduction into the wall rock enclosing the volcanic pipe. Accordingly the heavy surface lava, losing its dilating gas and growing denser for that reason and by cooling, sinks at the grottoes and fountains, and pours in subsurface currents downward. This hypothesis necessarily makes the lava lake hotter and less dense below the surface for several hundred feet of depth, if the lake is over the conduits.

Perret also clearly expresses belief that the lava lake is hotter below for he conceives the islands as floating and extending "to a considerable distance below the surface where the temperature and the chemical activity of the lava are much greater." With reference to chemical activity Perret writes: "These gases which issue from the liquid lava of a volcano are not to be considered as juvenile gas in its primal state, but that which, expanded into and worked over with the lava in the volcanic edifice, is subjected to the action of air, water and oxidizing and transforming processes of the most complicated kind resulting in the formation of those oxidized and hydrated compounds of sulphur, carbon, chlorine, etc., which constitute the gaseous emanation of ordinary volcanic activity.*

Day and Shepherd, on the other hand, reached the conclusion that such oxidized gases as water vapor and sulphurous acid are primal, and that chemical action is still going on among the gases, that at these temperatures free sulphur could not remain inactive in presence of carbon dioxide nor free hydrogen in presence of both of those and sulphur dioxide in addition; "the heat generated . . . . may well be much more than sufficient to counteract the cooling effect of the expansion within the rising lava column, which may thus become hotter and not cooler as it approaches the surface."† The absence of

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* Loc. cit., this Journal, xxxv, p. 146, 1913.

† Loc. cit., p. 600. The present writer has measured the thermal gradient of the lava recently (Jour. Wash. Acad., July, 1917). There is hot surface reaction, a sub-surface cool zone, and rise of temperature next below that, until the bottom lava is reached.

equilibrium among the gases at the surface of the lake is shown by great variety in proportions of the individual gases in different tubes collected at the same time, and by increase of maximum temperature in the fountains at those times when the quantity of gas is greater. Discussing the water which condensed abundantly in the tubes, these authors believe it could not have come from reaction of hydrogen with air because such a quantity of hydrogen would produce explosion. But this was all on the stated assumption that the flaming gases had met no atmospheric air below the surface cracks where they were collected.

Atmospheric Oxidation of Magmatic Gas.

Without entering here upon an exhaustive discussion in criticism of these several writers, I would point out that, except for the statement quoted from Perret, these investigators seem to me to take no sufficient account of the certain and obvious reaction of the volcanic gases with oxygen of the air, nor of the extent to which sulphur, hydrogen and carbon may by less obvious mechanism be brought into contact with air within the edifice of highly porous rock that encloses the lava conduit for some thousands of feet above sea-level. Day and Shepherd, however, point out that in the gas reactions there is an enormous store of volcanic energy "which reaches its maximum temperature at the surface itself."* The abundant flames† through cracks in crusts over the lake, over the grotto fountains and central fountains, through the border cones, and the blowing cones which form above cracks in the floors, and the myriad flaming orifices even at the fronts of some of the flows (block lava of Mauna Loa 1916),‡ are the obvious evidences of reaction between gas and air. A second method of indraught of air downward into the lava is produced by downflow at the grottoes, and in times of subsidence at the sinkholes, when violent cascades rush down border pots from the lake, the cataracts tumbling vertically 30 or 40 feet (9 or 12^{m}) into a boiling, flaming and fuming cauldron (fig. 9*b*), carrying down the surface crusts, and obviously engulfing air by downsuction as in a waterfall. A third mechanism which carries air downward into the liquid lavas of lakes and flows

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* Op. cit., p. 600.

† Dr. Wm. T. Brigham was the first to point out these flames, which were never positively seen by Professor Dana, though they were eventually accepted by him. (*Characteristics of Volcanoes*, 1891.) The insistence by Brigham on flames, and by Green on absorption of air, against geological opinion which would have it that steam must be the active agent, illustrates the great advantage in science of continuous observation over closet theorizing. Brigham, Green and Coan lived on the field and knew their volcano; the foreign geologists came for short visits, intent on seeing, with preconceived opinion for a guide.

‡ Lava flow from Mauna Loa, 1916, by T. A. Jaggar, this Journal, xliii, pp. 255–288, April, 1917.

is furnished by the cracking, streaming and foundering process (fig. 12*d*) whereby great quantities of porous hardened lava crust carry air down into the gas-charged melt and probably discharge it rather slowly, owing to the sealing of the pores by chilled glass as the slabs first sink in the liquid just below the surface. This liquid is at a temperature so low (see experiments hereafter) as to be solidified by such contact, and has no power to melt up the deeply chilled crusts which are several inches thick. A fourth mechanism which brings oxygen and volcanic gases into contact beneath the surface of the lava column is furnished by all those cavings-in and crackings of the older rock whereby avalanches (fig. 4*a*) or single blocks are precipitated into the liquid lava, or where the liquid lava by percolation through newly-opened crevasses, or by "stoping," gains access to broken surfaces of fragments filled with air. A fifth process, not at all obvious but possibly very effective, is the indraught of air from the wall through the pores of the lava column, creating a blast furnace and incessantly compensating a tendency to vacuum created by chemical reactions,* or by convectional gas pumping, within that column.

It is interesting to note that Wm. Lowthian Green in his "Vestiges of the Molten Globe" held that the fountaining of the lava at places of descent was due to air being carried down with the lava and expanded. He lays great stress on the quantities of air carried down in the lava and even insists that vesiculation is due to air. Expansion of air would not account for the flames observed, and the temperature is not high enough for dissociation of water vapor, which Green insisted on. Neither will quiet foundering of crusts, however, nor a lowering of the general level by escape of gas, as suggested by Perret and Daly, account for the violent downsucking at the fountains and grottoes. This action is frequently sudden, or graduated from slow to fast in a very short distance. Continuous or spasmodic disturbance of equilibrium of the lava by oxidation of gases with devesiculation would account for the phenomena observed.

The chief gases collected at Kilauea in 1912 from a flaming cone on the floor by Day and Shepherd had the following approximate average composition† by volume for 1000 liters of gas which was pumped:

Water	4%
Sulphur dioxide	50
Carbon dioxide	25

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*Dr. Shepherd informs me that in the reaction $2H_2 + O_2 = 2H_2O$, the volume shrinkage is one-third even at high temperatures.

† Kindly estimated for the writer by Dr. A. L. Day. The SO_2 is doubtful, much of it being probably free S. Assuming derivation from air, this partly accounts for the excess of combined O for the N present.

Carbon monoxide	2
Hydrogen	3
Sulphur	2
Nitrogen	14

These are in two groups of three each, namely carbon monoxide, hydrogen, and sulphur, all inflammable, and the three products of the combustion or oxidizing of these, namely carbon dioxide, water vapor, and sulphur dioxide. The only other abundant ingredient is nitrogen (14 per cent), which is a constituent of air.

The lava was splashing within the glowing spatter cupola whence the gas was drawn. This lava was below the level of a porous "shattered floor" made of lava shells. A channel "just below the surface crust" connected this pot with the lake directly. The roof of this channel collapsed to a chasm a few days after the gases were collected. "As the larger bubbles rose and burst from the liquid lava within the dome, the jar could be felt on the floor where the collectors stood and a splash could be plainly seen through the cracks."* In other words, very hot gas only 7 per cent of which was combustible and 79 per cent of which was a combustion product, was rushing out through the cracks of the dome above the level of a tunnel leading to the open, cooler air above the lake and all the surrounding floor was porous shattered rock shells full of air above the liquid level and doubtless communicating through scores of openings with the tunnel and the dome which throbbed and jarred. And in addition, the lake, consisting of the same gas-charged lava as that in the dome, was incessantly engulfing air-filled crusts and skins and doing so with especial vehemence, by streaming in the direction of this grotto channel, and thereby also pumping air through the tunnel.

Under these circumstances it is impossible for the writer to conceive of the 79 per cent of oxidized gas as having had no contact with air before emerging from the blowing cone. There is no question but that this was the most perfect experimental collection of volcanic gas ever made, but I do not believe that any apparatus at the surface of the volcano can collect uncontaminated juvenile gas. The writer does not wish to be understood to imply that *all* the oxygen compounds in the gas are atmospheric combustion products, but that a larger proportion of them are so than these authors have admitted. The facts demonstrated, however, by the Day and Shepherd collection, of the presence of the three combustibles and the three combustion products, and the argument which they present of heat reactions that reach a maximum at the surface, make a contribution to volcanology which bids fair to revolutionize the science.

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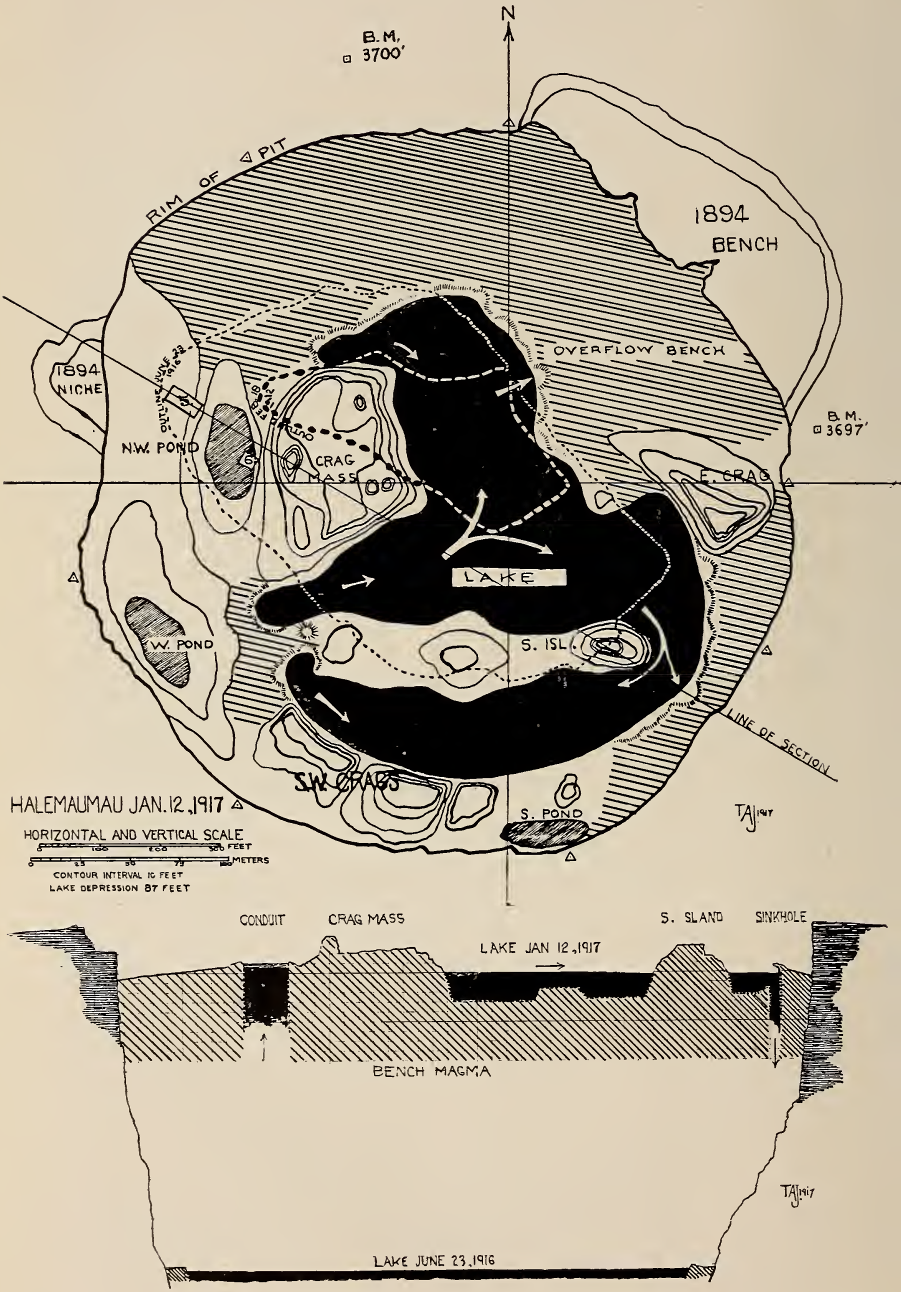
* Loc. cit., p. 588.

Fig. 2.


N
B.M. 3700′
RIM OF PIT
1894 BENCH
1894 NICHE
OUTLINE JUNE 23 1916
FEB. 18
FEB. 12
5
6
N.W. POND
CRAG MASS
OVERFLOW BENCH
B.M. 3697′
E. CRAG
LAKE
W. POND
S. ISL.
LINE OF SECTION
S.W. CRAGS
S. POND
TAJ 1917
HALEMAUMAU JAN. 12, 1917
HORIZONTAL AND VERTICAL SCALE
0 100 200 300 FEET
0 25 50 75 100 METERS
CONTOUR INTERVAL 10 FEET
LAKE DEPRESSION 87 FEET
CONDUIT
CRAG MASS
S. SLAND
SINKHOLE
LAKE JAN 12, 1917
BENCH MAGMA
TAJ 1917
LAKE JUNE 23, 1916

EVIDENCES OF CONVECTION ; THE DUPLEX LAVA COLUMN.

Daly terms "two-phase convection" the mechanism whereby deep gases rise as bubbles with increased rapidity toward the surface of a lava column and the liquid, released by surface collapse of the bubbles and loss of the gas, tends to sink because it is heavier than the rising froth.

Both he and Perret made diagram sketches* showing the lava basin in the Kilauea pit to be shallow and saucer-shaped with one conduit beneath smaller than the visible pool. If conduit remains small and saucer remains shallow, the pool being bordered by a bench of overflow within the pit, how is it that the bottom of the saucer is built up while the lava surface rises 600 feet in six months? (See section, fig. 2.)

As will be shown below, there is every evidence that just this relation, but with several tubular conduits, existed from June to December, 1916, and that the lava lake remained continuously shallow. The bottom of the lake builds up by accretion of the relatively cooled and denser sinking surface layers of the convection, step by step with the building up of the shore bench or "floor" by the spasmodic overflow which takes place from time to time owing to the inflation of the liquid part by the rising gas-bubble currents of the convection. The obvious surface evidence of such convection lies in the persistence of deep wells at certain fixed sites from which vesiculated lava springs up and streams outward across the surface of the lake, while on or near the opposite shores the solidified crusts and skins founder in the grottoes and the fountains. There have been such source wells or spring holes at the west and north sides of Halemaumau for many years and the dominant convectional streaming has been away from them. That they are definite wells in the fresh bench lava has been repeatedly demonstrated at times of faster lowering of the level of the lake, when they were revealed as local small pits. The inflow pits frequently persist for long periods as separate ponds of lava (fig. 6*a*).

*Loc. cit., Daly, p. 77 ; Perret, p. 345.

FIG. 2. Map and diagrammatic section of Halemaumau, Jan. 12, 1917. Lava lake in black, crusted conduit ponds shaded, overflow benches diagonal lines, raised crags contoured. Coarse dotted outline lava lake of Feb. 18, 1912. Fine dotted outline June 23, 1916. Rectangle (5) site of lava spring of June 5, 1916. Rectangle (6) west corner of pool June 6, 1916. Note that N.W. corner has been conduit source on all these dates. Slight slope lake surface from conduits W. to overflow bench E. Bench magma elevated on conduit side W.S.W., subsided on sinkhole side E.N.E. Section without vertical exaggeration, lower profile shows simple rising pool of June 23, 1916. Shoal shown in lake bottom, upper profile, was revealed by subsidence February, 1917. Depths from soundings and subsidence records. Note progressive shoaling from W. to E. Diagrammatic sinkhole E. shows ridge of accretion on lake bottom margin which produces cascade ledge when subsidence takes place. Surveys with transit by T. A. Jaggar. Bench marks (B.M.) U. S. Geological Survey, trig. stations Hawaiian Volcano Observatory. Meridian approximately 155° 17′ 8″ W., lat. 19° 24′ 33″ N.; 10-foot contours above lake as datum plane.

Variable surface Radiation.

It has been said that the maintenance of the lava lake in a fluid condition is product of an incessant struggle with cold.* The two-phase convection hypothesis imagines a lagged system like a hot-water heating plant with circulation evenly maintained by rising of hot fluid to the radiator (crater) and unobstructed sinking of cooler fluid to the furnace. Daly has not discussed the possibility, which seems to me a certainty, that uneven radiation of the system at the surface is what builds the annular bench around the lake and the semi-solid hot lava column within the pit and under the lake, with perforations through it at the wells of uprising foam. The uneven radiation is due to shifting and changing radiators, the craters, which vary continuously in size, shape and debris accumulation as the lava rises, overflows, falls or shifts its vent; and which themselves occasionally by gas reaction become localized heaters.

In other words, the downflow material of the convection becomes very viscous near the surface and actually hardens *at* the surface in the form of overflow benches and islands. When the net effect for a given period is a rising in a crater which widens upward, the downflow column, plastic but stiff within, may build by accretion under and around the hot froth column, and either encroach on the latter or the reverse according as the heat supply and the cooling are balanced or not (Plate I and fig. 2).

It is evident that if this view is correct, then a profound subsidence of the entire lava column, induced at Kilauea by an extraneous cause, like rock tide stress or the relief by overflow of connecting tubes at Mauna Loa, should carry down the semi-solid lava body as well as the more liquid lava lake. This is just what happened at the time of the great sinking in Halemaumau which took place June 5, 1916, simultaneously with the conclusion of the lava flows on Mauna Loa. The lake for two days resolved itself into a shallow streaming puddle, and remained so for 400 feet (122 meters) of subsidence. The supporting floor of the liquid lake and the islands which protruded through the lake, sank steadily and undermined the peripheral bench, which tended to cling to the outer funnel walls of the rock pit, so that the bench and lower walls crashed inward in great avalanches. The bench rock was incandescent and semi-solid; the old walls of the encompassing pit were not. For two days of subsidence, the talus slopes from such tumbling were always supported by the sinking lake bottom. When avalanches fell into the lake its shallowness was instantly revealed by the wave which carried all of the liquid up the far slope and by distribution congealed it. The

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* Daly, loc. cit., pp. 68, 71 and 92.

islands, mere crusted summits of irregularities on the main lava column, were eventually buried under the talus. The foaming gaseous member of the column appeared towards the end as a lava spring, trickling down the western talus like a mountain torrent (fig. 2, loc. numbered 5), and within a few days this and other springs cascading into the lake restored to it its central position in the pit (fig. 2, loc. numbered 6 west corner lake June 6) surrounded by debris slopes (fig. 4*a*).

There is reason to believe that during the progress of a complete eruptive cycle of Kilauea between two repose periods, like the interval 1907–1913, the adjustment of rising gaseous lava to sinking viscous lava becomes most perfect at the culmination of the eruption, when effervescence is general and uniform, surface heat is distributed and at a maximum, and border benches are absent. Such a culmination was reached in December–January, 1911–12, when the lava lake extended from wall to wall of the pit, and the subsidence thereafter for eighteen months involved a very rapid dwindling in the size of the liquid phase (fig. 2, heavy dotted outline) and a final retirement of the entire column to the depths amid the wreckage of the solidified portion.

Evidences of Shallowness of Liquid Lava Lake; the Bench Magma.

Lava Islands.

The writer has studied the formation of islands in the Halemaumau lava lake repeatedly during the last five years, and has determined that they are capable of extraordinary shifting of position both vertically and laterally in the course of twenty-four hours. He has never, however, seen any evidence that they floated as independently buoyed objects in the liquid part of the lava column, after the fashion of an iceberg in water. That they could not be so buoyed is shown by the facts that they do not equally rise and fall with the risings and fallings of the lake, that they tend to acquire and retain fixed positions, by survey, while the convection currents stream about them, and that movements of tilt in the island escarpments have been repeatedly diagnosed, the tilt according in direction with a place of overloading of the border bench with lava flows. They are thus integral with the shore and bottom of the lake. Their horizontal shiftings are rare, when they move pivotally as crust blocks of the bench magma.

Also these islands pass by gradations into craggy scarps in or partly in the border bench where all stages of their formation have been photographed in sequence. Here the relation to weighting by overflow has been repeatedly demonstrated. The effect is strikingly like the supposed relation of sedimentation to isostatic uplift. On this small scale, moreover, the mechanism is indeed isostatic, for the uptiltings and upheavals of bench blocks and lake bottom in Halemaumau are nothing more than adjustments of the crust of the semi-solid lava column, in which the lake is a saucer, to the mobile matter beneath which tends to flow and rearrange the surface features whenever overweighting takes place locally.

Thus heavy flows repeated on the bench northwest for weeks, August to October, 1916, heaved up out of the shallow bottom of the lake a large crag mass, which eventually stood as a hill 70 feet (21 meters) above the lake, but began as a small flat islet (Pl. I*b*, figs. 3, 4, 5). Later a similar islet suddenly appeared in the southeast corner of the lake immediately opposite a shore of continuous overflow, and this rapidly rose until it was a pulpit rock 40 feet (12 meters) high (Pl. I*b* and fig. 7). The border bench itself on the east, fissured off from its southeast extension, rose gradually for five months after August, 1916, its surface tilting to the northeast where there was ceaseless overflow, and finally lifted a pinnacle corner clear above the edge of the pit while its back slope was inclined at forty-five degrees (figs. 8*a* and 10). Most remarkable of all was the adjustment of February 18, 1917, when after a fortnight of subsidence of other features, this crag suddenly parted from its supports against the old wall and in the course of twelve hours or less subsided 30 feet (9 meters) upon its viscous foundation, and at the same time opposite to it in the lake a low flat island of the previous day rose 40 feet (12 meters) above the lake to become a towering, flat-topped, steep-sided mass (fig. 8*b*, see also S.W. islet fig. 5). In appearance this mass was like the lava dome of Tarumai in Japan, which rose in 1909.* The conclusion was inevitable that deep flow from beneath the crag became inflow beneath the island, the distortion affecting, not the lake, but the lake bottom. Other rising features corroborated this by survey. The cause of this reverse movement was the unloading of the lake bottom by the faster sinking away of the liquid. The equilibrium, which had balanced lake bottom versus border bench while the basin was full, was disturbed when the lake sank differentially to its saucer.

Shoals, Sinkholes and Conduits.

Other evidences that the lake of liquid lava is at all times shallow, whatever its depression within the pit, were furnished by the afore-described subsidence of June 5, 1916, and by relatively sudden subsidences at other times. On June 5, 1916, a shoal appeared of glistening black lava flats, not infallen debris, after sudden subsidence of 60 feet (18 meters). In early February of 1917, rapid subsidence from depression 45 feet (14

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* See article by Simotomai in August number.

meters) to depression 94 feet (29 meters) revealed shoals over the whole southern arm of the lake (fig. 9). In the midst of these shoals was a circular sinkhole 60 feet (18 meters) in diameter, which became the scene of a spectacular downpouring of the liquid part of the melt, through a river-like channel from the remainder of the lake, across the shoals. This revelation of sinkholes, often with vortical whirling (fig. 3), is a common feature of sudden subsidence. Eight minor pits were revealed by the subsidence of February, 1917, four of them known orifices of inflow for nine months previous, three at known grottoes of downrush, and one a sinkhole under the bottom of the lake. The downflow holes were in general at the opposite end of the pit from the inlet tubes. At times of rapid rise, however, downflow is not persistent in the same holes, and the circulation becomes stagnant or reversed. Moreover, during rapid subsidence an inlet tube may become a sinkhole (fig. 2).

FIG. 3.

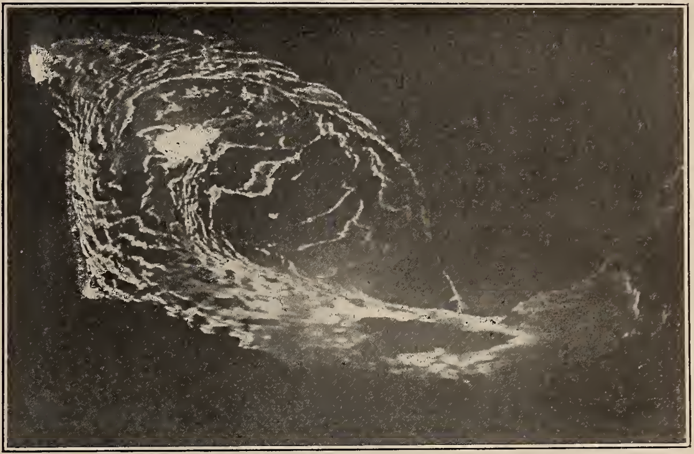

FIG. 3. Feb. 2, 1915, 8.30 P. M. East pool of Halemaumau, dimensions 500 by 200 ft. (153 × 61 m.), from the S.E., looking down. Depression 440 ft. (134m.). Lake converted into whirlpool of subsidence over "Old Faithful" sinkhole, the supply torrent following a circuitous channel from a northern conduit, and entering the sinking pool tangentially as a cascade from the E. Blocks of crust on surface of torrent, "Old Faithful" bursting in center of whirl. Photo Jaggar.

There appears to be no escape from the conclusion, fully borne out by the accounts of the older writers,* that the lava

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*Dana Lake, New Lake, 1880 to 1890, Brigham, loc. cit., Hitchcock, "Hawaii and its Volcanoes," 1909.

[*Text continued on p. 183.*]

FIG. 4.

a

b

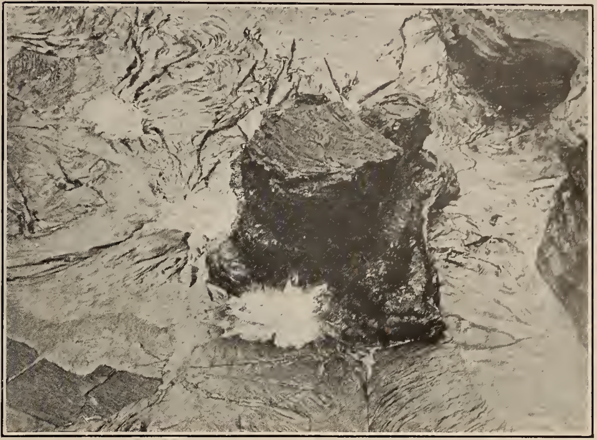
FIG. 4. 1916-17. Stages in development of great crag mass. Photos Jaggar.

(*a*) North margin lava lake, June 24, 1916. First stage bench terraced by uplift. Talus slopes from collapse of June 5 emerging through bench magma at borders. Depression 592 ft. (181 m.).

(*b*) Same scene on Aug. 16, 1916, terraced bench raised and fissured. Islets in foreground from raised shoals beginning of crag-mass. Depression 390 ft. (119 m.).

FIG. 4.

c



d

FIG. 4. (*c*) Telephoto of northern islet Sept. 13, 1916, looking down from N. Depression 326 ft. (99 m.). Same as tiny islet seen as mere dot in *b*. Note crust wrinkling, and cracking and foundering blocks in lower left hand corner. Fountain against islet.

(*d*) Same viewpoint as *a* and *b*, Feb. 24, 1917, after great crag-mass had passed its maximum. Note main tilt of upraised surface to W.S.W. Depression lake 106 ft. (32 m.) Summit knob identical with island in *b*.

Fig. 5.

a

b

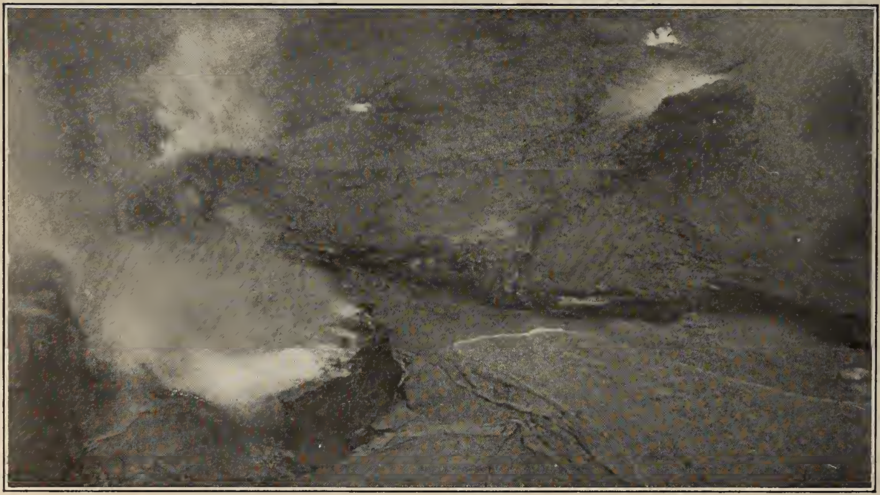


Fig. 5. Growth of the crag-mass and uplift of southwest islet, September, 1916.

(*a*) Sept. 14, 1916, 10.30 a. m., from S.E. Depression of lake 326 ft. (99 m.), crag-mass 52 ft. (16 m.) above lake. North islet on right attached to crag-mass, lifted suddenly since day before (fig. 3, *c*). The S.W. islet, shown on the left, was formed on Sept. 5 from a collapsed promontory; it was submerged during a rise Sept. 8; it reappeared again, along with rise of neighboring bench, as shown, on Sept. 9.

(*b*) Sept. 26, 1916, 3 p. m., from S. Depression of lake 312 ft. (95 m.). N.W. pond with two fountains in background, outward streaming from crusted channel in foreground. Southwest islet now 20 ft. (6 m.) high and rising. Its high walls, now wholly without shore-line markings, due to upthrust as semi-solid mass through lake bottom shell, here shallow. Photos Jaggar.

Fig. 6.

Fig. 6. 1916. Relations of conduit pond N.W. to lake streaming and growth of crag-mass. Photos Jaggar.

(*a*) Aug. 23, 1916. Interior of Halemaumau from the north. N.W. pond overflowing on the right, rising crag-mass in middle, outward streaming of lake from W. arm on the left. Note Y form of the lake and tilting of crag-mass toward the region of overflooded bench. Depression 345 feet (105 m.). Left photo with deep yellow filter, showing bright lines.

(*b*) Dec. 15, 1916. Mature crag-mass looking W. The summit pinnacle is identical with larger islet in fig. 3*b*. Lake depression 138 ft. (42 m.)

Fig. 7.

a

b

Fig. 7. 1916–17. Development stages of S. island in lava lake. Photos Jaggar.

(*a*) Nov. 7, 1916. South island and beginning of E. point, from S. margin Halemaumau. Depression 193 ft. (59 m.).

(*b*) Jan. 5, 1917, from E. rampart at lake level looking S., showing E. point left, S. island right, and fresh overflow in foreground. Depression 101 ft. (31 m.).

FIG. 7.

c

d

FIG. 7. (*c*) Feb. 3, 1917. S. island above rim of pit, looking eastward. Depression 45 ft. (14 m.). Culmination of rise.

(*d*) Feb. 28, 1917. S. island and S.E. cove after subsidence, looking S.W. through gulch in tumbled benches. Depression 115 ft. (35 m.).

FIG. 8.

a

b

FIG. 8. Jan.–Feb., 1917. Showing conditions before and after sudden uplift of E. island. Photos Jaggar.

(*a*) Jan. 27, 1917. Upraised E. crag from rim Halemaumau looking N.N.W., summit 1 ft. higher than rim of pit. Lake depression 50 ft. (15 m.).

(*b*) Feb. 22, 1917. On right subsided E. crag 30 ft. (9 m.) below rim of pit and on left upraised island of bench magma 40 ft. (12 m.) high which rose 40 ft. from a shoal in the lake in a single night, Feb. 17–18, 1917. Lake depression 106 ft. (32 m.).

FIG. 9.

a

b

FIG. 9. Feb. 1917. Bottom of lava lake abandoned by subsidence, showing sinkhole cascade. Photos Jaggar.

(*a*) Feb. 28, 1917. Bottom of lava lake of previous month looking S.W. from S.E. margin Halemaumau. Depression 115 ft. (35 m.).

(*b*) Feb. 14, 1917. From S. looking down at sinkhole pit 60 ft. (18 m.) in diameter. Channel from lake in background, cascade deflected by obstruction and falling 40 ft. (12 m.); condensation from rising sinkhole gases on left. Depression 94 ft. (29 m.). Great banners of flame rising above sinkhole visible only at night.

FIG. 10.

FIG. 10. Jan. 23. 1917. 12.15 P. M. Halemaumau during sounding test, looking N.W. from S.E. rim of pit. Lake depression 60 ft. (18 m.). Mauna Loa and outer rim of Kilauea crater in background. Shows sounding party at work with long pipe on E. point making first immersion. The second immersion was made on left side of large spatter hummocks shown beyond and to the right of E. point. The pipe was immersed in a fluid glow line similar to those shown in foreground Pl. I*b*, lower view; that plate also shows E. point during strong overflow, and violent bombardment of spatter hummocks in evening light. Photo J. J. Williams.

lakes of Kilauea are truly shallow pools, with feeding conduits beneath of small size. Where these lakes are confined in the cylindrical crater of Halemaumau and within it are surrounded by or include benches and crags of solid lava developed by overflow and accretion, these latter are merely subaërial extensions of the semi-solid lava column, which forms the bottom of the lake, and through which feeding conduit tubes are maintained open. This lava column is incandescent within, graded in viscosity from high to low in transition to the liquid lake through its bottom, from high to solid in transition upward to the crags, and probably from high to lower viscosity in depth where the convectional circulation must become adjusted to a uniform and relatively slight radiation outward into the retaining walls.

It might be asked, how do the inner bench overflows, as a part of and contributory to the upward growth of this non-liquid lava column, differ from any other surface lavas? The answer is that they are surface layers of a continuously mobile body; that by their weight they subside and displace the mobile incandescent matter into which they grade downward; away from them this semi-solid paste actually pushes upward locally so as to maintain a balance among islands, crags, benches and lake bottoms; there is hence a slow circulation, itself essentially convectional, in the matter which supports the liquid lake, in addition to the much more rapid convection continuously stirring the lake itself. Where such overflows become buried for hundreds of feet of such compensated subsidence, under other flows of the same kind, remaining integral parts of the lava column and reheated within it, in marked contrast to the older rock walls adjacent, they must be considered a part of the live lava column and of the mechanism of its circulation, and quite distinct from surface lavas which become frozen and dead. (See description of collapse of June 5, 1916, above.)

Summary, Duplex Lava Column.

I have attempted above to develop proof that there are two phases of the mobile lava column generally visible within Halemaumau, the one apparently liquid, the other apparently solid. Investigation has shown that the liquid lake is largely a gas-charged froth, and that the rocky benches are only a surface hardening or crust upon a stiff but mobile and incandescent column of lava. The liquid phase maintains a shallow saucer, fed by a few spring holes beneath, in the top of the semi-solid phase. Both phases are in circulation. Heavy crusts founder with much effervescence in the liquid lake while quiet upwelling of lighter lava goes on on the opposite side, and surface streaming pours from the locus of upwelling to the locus of foundering. In the case of the semi-solid bench lava, overflooded occasionally by the liquid, there is tendency to incessant but very gradual subsidence of the flooded plains, and elsewhere to uplift, especially near the inlet vents (fig. 2, section). The places of flooding shift, however, and in the course of a long term of rising lava in Halemaumau pit, the net effect is a subsidence of the bench region compensated by an inward flow under the lake bottom saucer, keeping the latter shallow, and even lifting islands above the lake surface. I shall speak of the two phases as the lake magma and the bench magma.

Consistency of Bench Magma.

When the lava column subsided 400 feet (122 meters) suddenly as above described, from depression 300 feet (91 meters) within the pit to depression 700 feet (213 meters), after months of building up by repeated risings and overflowings, there was revealed incandescence throughout the bench and island magma. This substance fell inward by opening narrow vertical fissures back from the edge of the bench, until the slabs so loosened tottered and descended crumbling to the slopes below. There was always revealed a bright red luminous fracture surface and the larger slabs, many tons in weight, would flex outward slightly and then fall, disintegrating to a glowing talus whence arose great billows of chocolate-brown dust. These avalanches were noisy but less so than might have been expected, owing to the peculiar consistency revealed by the arching out and crumbling, for which the writer can think of no better simile than that of hard cheese breaking. The entire absence of heavy quaking at the upper rim of the pit, even when a whole quadrant of the bench fell immediately below the observer, showed that the attachment to the side walls was slight. I have elsewhere seen a very small remnant of an older rock bench, long firmly attached, produce a strong earthquake on falling.

It was evident in this collapse of June 5 that the piled up overflow strata of months previous were a uniformly incandescent and mobile stiff magma throughout, and that burial preserved the inner heat of the flows and reheated the crusts. These crust layers of flows are of thicknesses varying from a few inches to several feet (fig. 17*a*, foreground), like other pahoehoe flows *and are full of air in vesicles.*

A phenomenon, occasionally seen during such subsidence at orifices in this bench magma, is an outflow which also is like crumbled cheese, and incandescent, but starting out like a liquid and falling like gravel or sand. It trickles out from fresh vertical breaks in falling benches. This substance appears to be identical with or very like *aa* lava on cooling, but I have never had access to it for verifying the resemblance.* Some of this fell from the glowing wall shown in background of fig. 15*c*.

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* See "Live *aa* lava at Kilauea," by T. A. Jaggar, Jr., Jour. Wash. Acad. Sci., vol. vii, No. 9, May 1917, pp. 241–243.

EVIDENCES OF HEAT FROM GAS OXIDATION.

Considering what a poor conductor porous basalt is, as illustrated by the outer walls of the pit, and granting greater radiation at the lake surface than laterally, and particularly if the lake is at its hottest near the surface, as suggested by Day and Shepherd, this reheating of flow crusts and buried crags demands special consideration. Furthermore the whole question of a special mechanism of oxidation heating would seem to be worthy of examination, in view of the new facts concerning bench magma and lake magma. The difficulty of introducing water vapor from meteoric sources into a lava column has been found insuperable. Does the same difficulty apply to air, an uncombined mixture of fixed gases, and among them oxygen?

In the early part of this paper the writer has indicated five methods by which air may be brought into contact with sulphur vapor, with hydrogen or with carbon gas in the volcano, and the first two of these are not hypothesis but fact, for surface flames are abundant, and suction at grottoes and sinkholes is unquestionable.

Types of Flames.

It is singular that geologists who saw Kilauea active could have disputed the existence of flames. They are generally invisible by day and they vary greatly in visible abundance by night. Their color by night is of two distinct kinds, blue-green and yellow. The common banners of flame over the grottoes, seen against a dark background, appear from bluish-green to violet. The sharp flame spears which burst out and play only a few seconds, when crusts on the lake are rent apart over accumulated gas, are bright blue, sometimes appearing in series like jagged saw teeth. These bluish or blue-green flames are very common above spatter cones built over cracks in the benches, and at wall chimneys where the lava froth has percolated into high talus or cliff cracks and developed a flaming aperture, sometimes a hundred feet (30 meters) or more above the lake.

It is a question of great interest whether such climbing vents are only the differential mounting of the froth by gas expansion, favored by small size of the crevice selected, or whether the heat of oxidation itself, by a sort of blowpiping, fuses and lines its way with a melt re-fused from the rock penetrated. If such refusion by oxidizing gases is possible amid talus openings, for example, it is possible on a considerable scale amid the interstices of the crusts of the still hot bench flows, buried by subsidence and overflow, and full of air cavities large and small.

[*Text continued on p. 192.*]

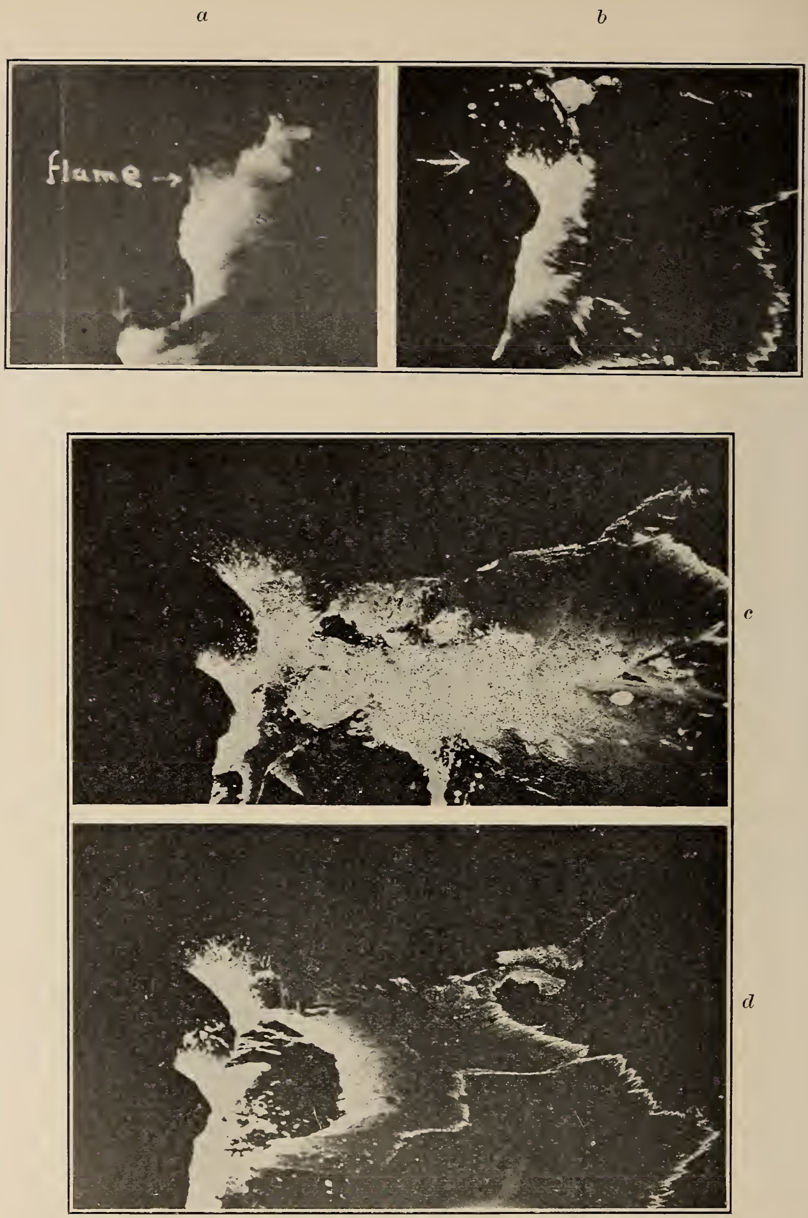

FIG. 11. Sept. 14 and 18, 1916. Telephotographs of S. grotto at night, looking down from S.E. rim, bench on left, lake on right (see fig. 5*a* extreme left). Depression 326 ft. (99 m.). Arrows on bench point to flames (blue-green variety) which were rising through recesses among spatter lumps. Dallmeyer lens of 11·4$^{\text{cm}}$ diameter, 43$^{\text{cm}}$ focal length, working at F 3·8 (Series B). Wratten "M" plates.

(*a*) Deep blue filter Wratten C. 24, aperture F 4, two seconds, 8 P. M. Sept. 14. Shows stalactite drip. Grotto flaming, blue rays.

(*b*) Bright green filter Wratten B, aperture F 5, one second, 7 P. M., Sept. 18. Note incandescent splashes on bench, and jagged edge of crust on lake, from which there was inrush to grotto. Grotto flaming, green rays. Visually the continuous spectrum of the melt shows much green, but almost no blue. Hence the rendering of the lines and splashes in contrast to (*a*).

(*c*) No filter, aperture F 3·8, 1/50 sec., Sept. 18, 8 P. M. Crusts downsucking with multiple fountaining migratory to the left toward grotto.

(*d*) No filter, aperture F 3·8, 1/50 sec., Sept. 18, 9 P. M. Hexagon of crust being engulfed at grotto. Note in *c* and *d* graded incandescence to centers of gas oxidation. Photos Jaggar.

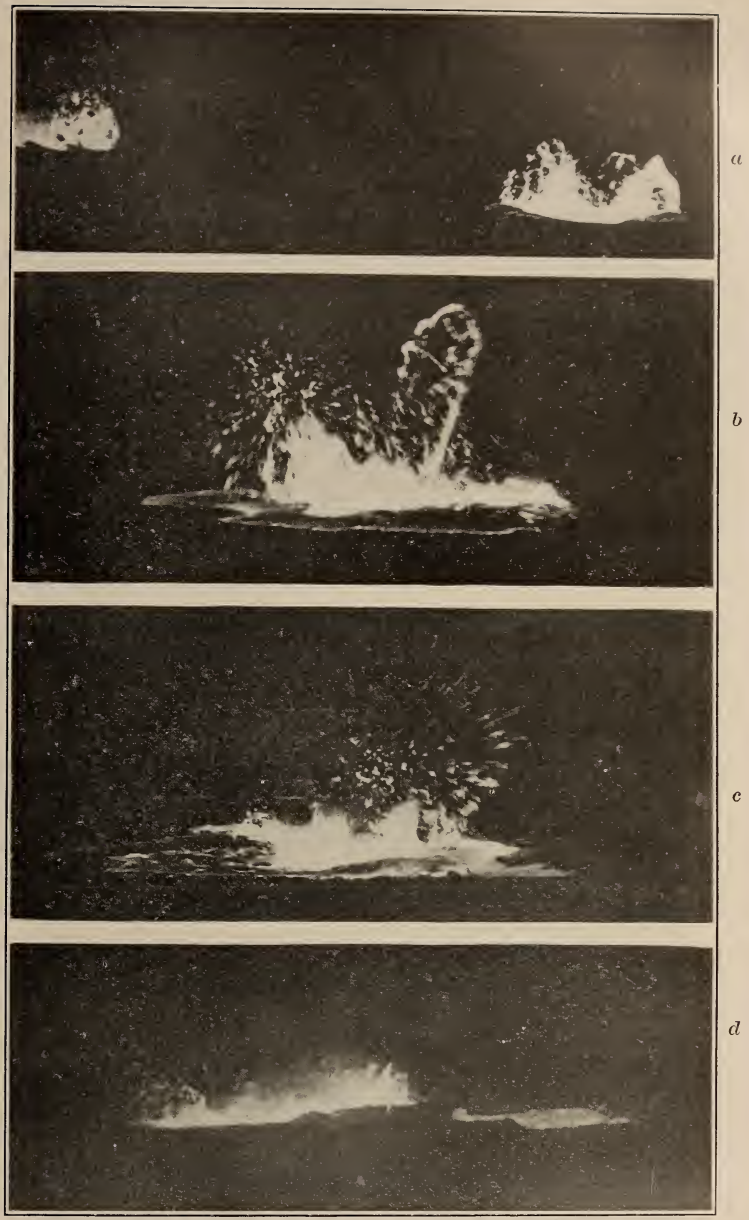

FIG. 12. Jan. 26, 1917, 6 P. M. Series of photographs, Wratten Panchromatic plate, aperture F 6·3, exposure 1/35 sec.: lava fountains 100 ft. distant in N. cove of Halemaumau, observer standing on E. point (see fig. 2). Prolonged migratory type of fountaining. Depression 50 ft. (15 m.).

(*a*) Shows sub-crustal explosions breaking surface; note high viscosity and depression in crust.

(*b*) Second stage, flinging and spraying, area elongated with migration to the right, actual fountain 40 ft. (12 m.) long.

(*c*) Blowing and flaming, with increased elongation, diminished viscosity, and down-suction.

(*d*) Termination of fountaining against wall in background, with expulsion of gas, flames, and much production of filamentous glass. In taking these pictures the writer was at the edge of the lake to leeward of its whole central region, but was not at all inconvenienced by the gas from its smaller bubblings. Photos Jaggar.

Fig. 13.

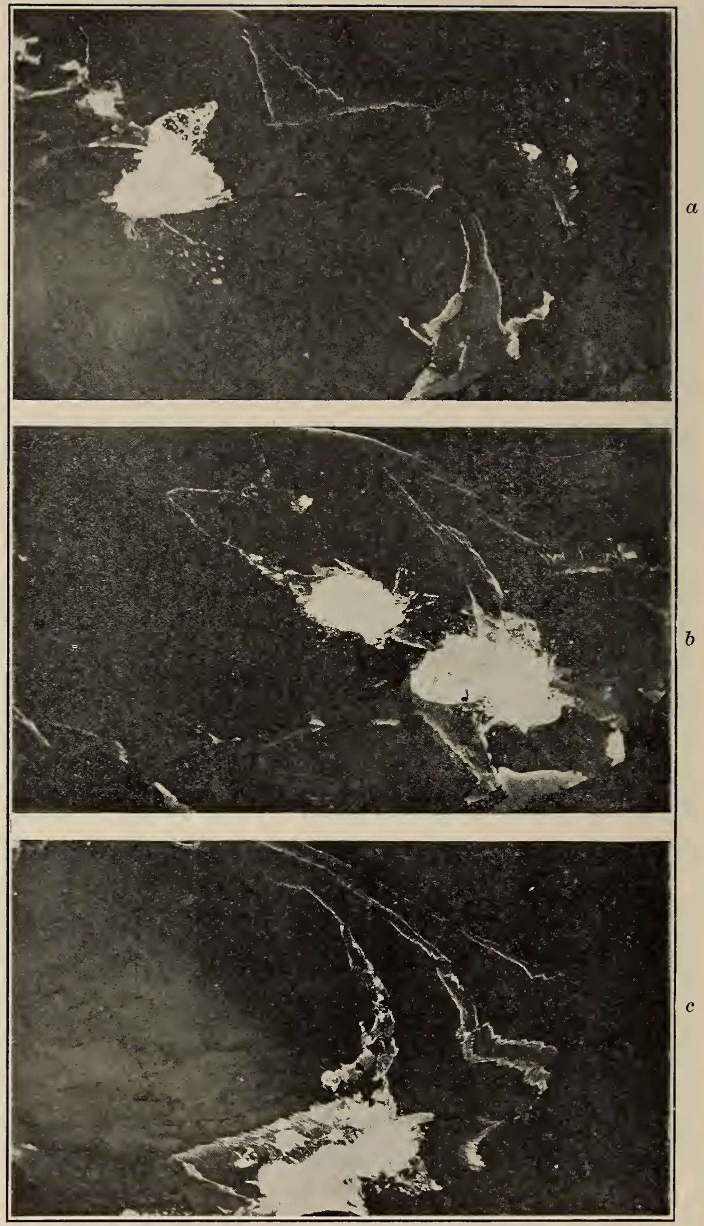

Fig. 13. Oct. 5, 1916, 12 noon. Telephotographs of travelling fountains in N. cove, from N. rim of Halemaumau, looking down. Depression 283 ft. (86 m.). Fountains migrating from left to right, conflicting currents meeting and crusts foundering along conflict line. Large Dallmeyer lens, aperture F 5, exposure 1/20 sec., red filter Wratten F. Photos Jaggar.

(*a*) Skins downfolding, line of fountains, crusts drawn to explosion center.

(*b*) Second stage, fountains have moved to right and enlarged. Crusts forming behind them.

(*c*) Last stage, fountains expending themselves against bank, chiefly in one great explosion center.

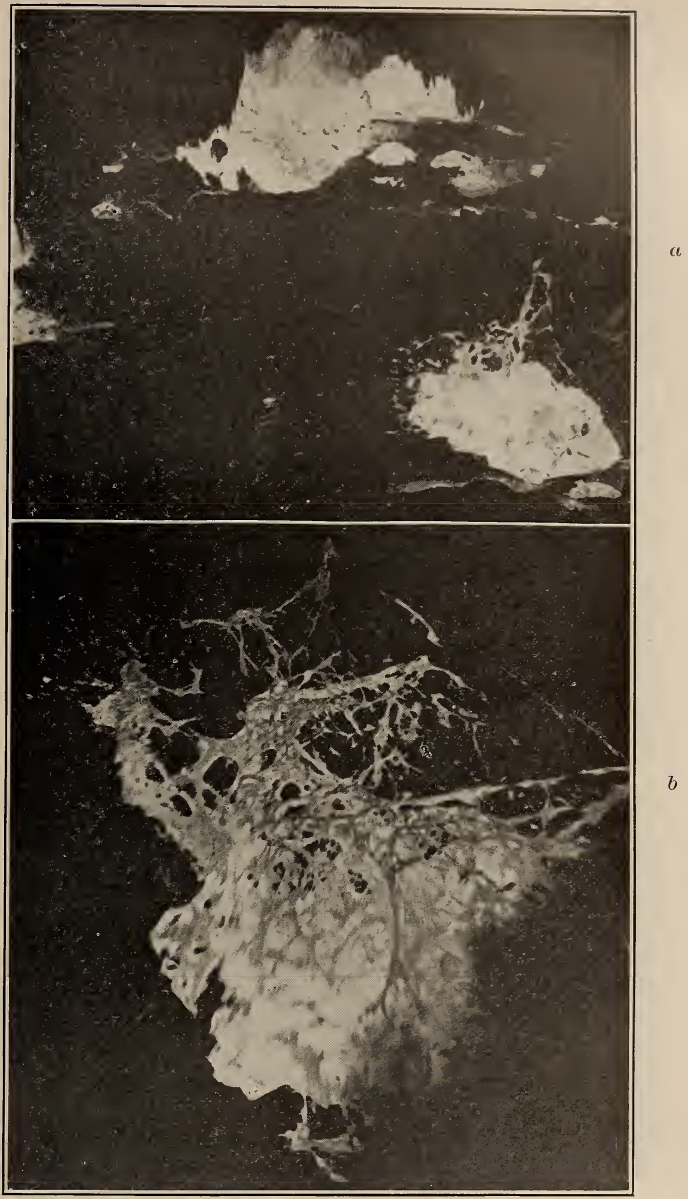

FIG. 14. Aug. 23, 1916, 8 P. M. From the north. Grotto, dome, and openwork fountains. Telephotographs with large Dallmeyer lens, aperture F 3·8, 1/50 second exposure. Lake depression 345 ft. (105 m.). Photo Jaggar.

(*a*) Night view of distant shore shown in fig. 6*a*, magnified. Central and border dome fountains, and in background interior of very large half-dome grotto overhung by spatter rampart, with curtain of stalactites on each side. The hazy interior above is flame. The central fountain slowly migrated to the grotto.

(*b*) Openwork of nearer large fountain, bursting in north cove. Shows multiple expanding bubbles of glass, not detectable by eye. Fountain approximately 30 ft. (9 m.) high, seen from above at a high angle. Note decrease of blurring motion and of luminosity from center of explosion below to upward limit of fling. Solidification in air is taking place. Such bubbles do not explode to fragments but expand within a ropy network.

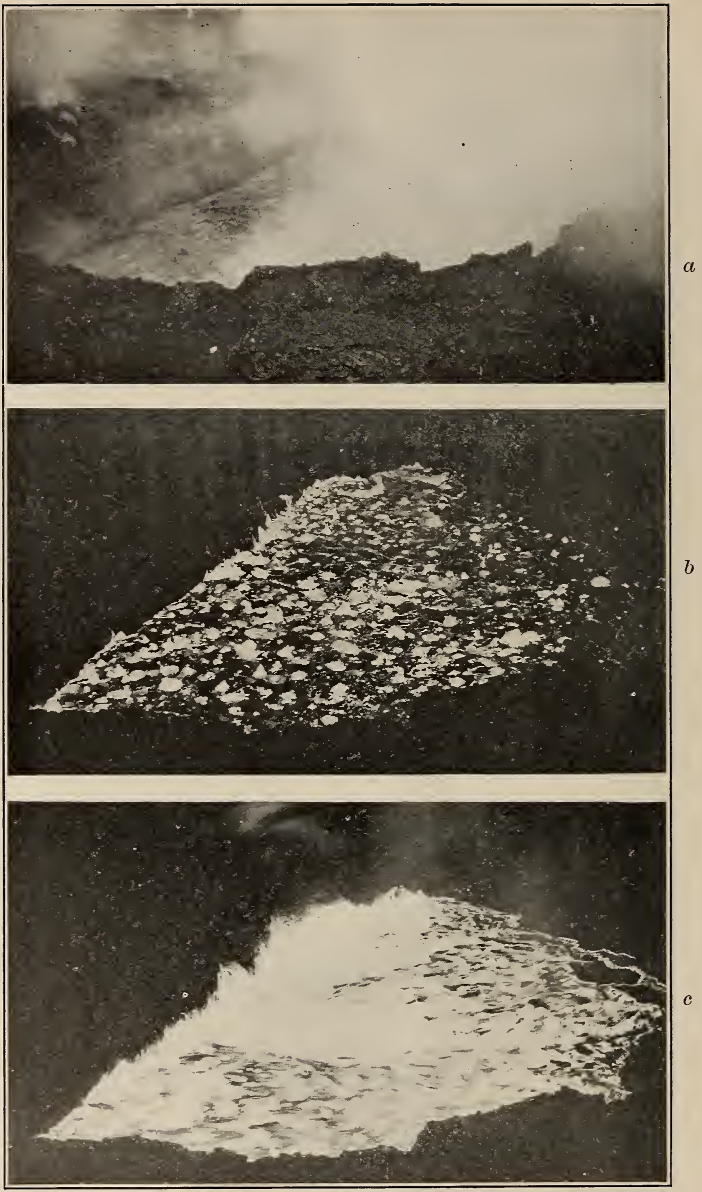

Fig. 15. Intense multiple fountaining of Halemaumau July 17–20, 1912, looking W. From maximum depression of 329 ft. (100 m.) June 22, there had been strong rising to minimum depression 192 ft. (58 m.) July 12, followed by subsidence to depression 273 ft. (84 m.) July 20. Thereafter subsidence continued.

(*a*) Daylight July 17, 1912, 9 A. M., shows inner pit of violently effervescing lake magma, surrounded by floor of bench magma which was fuming and collapsing. Photo Jaggar.

(*b*) Shows same scene at night, July 20, 1912, 10 P. M., exposure 1/5 sec., streaming from right to left; note increase in size, height and numbers of fountains from right to left. Length of straight shore on left 510 ft. (155 m.), width of lake 325 ft. (99 m.). Larger fountains 25 ft. (7·62 m.) in diameter.

(*c*) July 20, 1912, 10 P. M., same as (*b*) but longer exposure 2 sec., shows rapidity of streaming towards left, down-suction at line of shore grottoes and at zone of travelling fountains across middle; crusts parting at right shore; spatter, stalactite curtain, flame, and bombarded incandescent wall; fume above. The same violent turbulence was present in (*b*) but short exposure arrests motion. Photos J. T. Warren, Eastman film, aperture F 4·5.

FIG. 16.

a

b

FIG. 16. Jan. 16, 1917. Details of lake surface and rampart grotto at time of experimental work. Depression 78 ft. (24 m.). Photos Jaggar, taken from lake shore.

(*a*) Heavy crusts of lake surface folding downward along line of small fountains 50 ft. (15 m.) away.

(*b*) Rampart grotto with splashing fountain 30 ft. (9 m.) from observer. Iron pipe for experiments shown in lower left corner both pictures.

The second type of flames is comparatively rare and is distinctly yellow in color like an ordinary coal-gas flame. I saw this first in 1912, flaring out from an aperture in the tumbled high east benches, far above the lake level, and lasting the greater part of a minute. Twice in 1916 during the long rising spell of the summer, I saw a yellow flame suddenly burst through the crusts of the lake, and then flitter a short distance as a flaming foam or spume, dividing into several smaller flaming masses before going out. The yellow flames, luminous possibly with hydrocarbons or other impurities, are so rare in the present epoch that they must be considered curiosities.

On the other hand, the blue flames are very common and on certain nights when streaming is slow and crusts are heavy, they play in gigantic banners or blankets above blowing grottoes, or out horizontally from overhanging spatter margins of the lake, under which the gas from beneath crusts is escaping with a rush against the bank, and so is deflected outward. I have seen such blankets of flame for a length of 20 feet (6 meters) of shore jetting over the lake surface out from the shore for a distance of from 10 to 15 feet (3 to 4 meters), as though from a great flat-mouthed Bunsen burner. Frequently such flaming orifices jet lava spray to great distances, and the evidence of gas pressure is shown further by puffing noises and ceaseless variation in the length of the flame banners. Ordinary flames shoot up three to four feet (one meter) above the fountaining border grottoes (figs. 14*a*, 12*d*, 11*a*, *b*).

I am unable to agree with Mr. Perret that visible flames always occur above bursting dome-shaped fountains, which break through the crusts in the middle region of the lake surface (figs. 14*a*, 15*b*, 13*b*). I have stood on the spatter rampart at the lake margin a few feet from such fountains, and have watched and photographed fountains for years, and made special efforts to photograph the flames with color screens (figs. 11*a*, *b*, 13). My experience is that shooting blue flames break out just as crusts part at the beginning of fountaining, but that when the doming and spattering phases of large or small fountains occur, a flare of flame sometimes is visible, but quite often is not so. It does not seem probable that this observation is due merely to differences of seeing, for the same fact is in less measure true of the border fountains which sometimes are without visible flames. The central fountains most addicted to flaming are the continuous or "perpetual" kind (fig. 12). I am inclined to attribute the absence of flames above some fountains to the fact that the gases inflating them are more completely oxidized than in the flaming cases. This would of course mean that the combustible gases are variously oxidized in depth.

With reference to the composition of the gas burning in the blue flames, as contrasted with that of those smaller bubblings of the liquid lava which emit gas without flame, there is in daylight a distinct yellow-brown fume at the places where the blue flames occur (fig. 9*b*, over sinkhole), and higher there is a condensation of pale blue fume which expands above into a larger cloud faintly blue. This blue smoke is very hot and may be nearly invisible, but it is the most irrespirable of the Kilauea fumes, and the odor is that of sulphur dioxide. It probably contains also the trioxide. The gas from the smaller bubblings makes no perceptible fume and has very little odor, but is sometimes oppressive as though with carbon dioxide. The white smoke that rises from cracks in the benches and crags is weakly sulphurous but quite respirable, and appears to be in the main a mixture of moist air and unburned sulphur. In working to leeward of Halemaumau one learns to dread the intolerable blue fume from the sustained continuous fountains; at night these are seen to be surmounted by flames, so that the conclusion appears warranted that the surface oxidation which they represent is mainly that of sulphur vapor.

Gases Responsible for Flames.

It thus appears that of the three combustible gases hydrogen, carbon monoxide and sulphur, the last is most in evidence as surface flames, the second, along with impurities, may be represented by rare flames but mostly achieves its combustion below the surface, while the first, namely hydrogen, flashes to water vapor in depth, and is not (unless by spectroscopic means) to be diagnosed by itself as flame at the surface. A residue of both gases is mixed with the sulphur.

By its stronger affinity for oxygen, hydrogen would certainly be the first of the combustible gases in the mixture to achieve oxidation below the surface if oxygen were available; we find it in the Day and Shepherd analysis of even the surface gases in larger amount than the carbon monoxide. In view of the evidence that some oxygen reaches the lava column below the visible lake surface from downward suction and from engulfed talus slabs and crusts, and that in the gas-collecting apparatus water vapor condensed abundantly, it seems hardly admissible that none of the water should be produced by combination of hydrogen with atmospheric oxygen. If any of it is produced by sub-surface combustion of hydrogen, then we have in such combustion a formidable heating agency to be reckoned with for whatever depth air enters the lava. In less degree but in like fashion air would at these high temperatures (850° to 1150° C.) react powerfully with carbon monoxide and sulphur vapor to produce heat.*

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*Dr. Shepherd suggests (oral) that silicon hydride ($SiO_2 + 4H_2 = SiH_4 + 2H_2O$) is a combustible unstable gas formed at high temperature, possibly present at Halemaumau, and that he has detected the odor of carbon oxy-sulphide (COS) there. The latter is a lower temperature product, also inflammable, and might be expected in the bench magma.

Distribution Crusting and Fountaining.

On the lake surface over or near the inlet conduits, and hence at the points of departure of the surface streaming, a very marked cooling effect is generally observed in the form of dark crust which remains stationary over the uprising gas-charged melt (figs. 5*b*, 6*a*, 15*c*, on the right, 3 on the right, 18 on the left). Effervescence and incandescence are both at a minimum at the locus of fresh rising lava. Radiation cooling and expansion cooling both achieve their maximum immediately over the inlet vents. This was profoundly puzzling to the writer during several years of continuous record and close observation, when he supposed that rising juvenile gas was the main source of heat, and hence the inlet wells should yield high incandescence and much bubbling. Such multiple bubbling of bright luminosity occurs in fact (1913) over the inlet region only when the lava is subsiding, and convectional outletting is greatly dominant over inletting—when a shallow rapid circulation mixes air with the volcanic gases. During rising periods the whole lake surface is apt to be quiet and crusted. (Contrast fig. 10 rising, with fig. 15 sinking.) These facts imply that the rising magma and gas from deep sources are only moderately hot, the gas is evenly distributed in small bubbles, and such lava is quickly solidified and crusted on exposure to atmospheric temperatures.

Let us now watch what happens as the crusts form, thicken and stream across the lava lake to founder with sudden tearing, downsucking, flaming and violent effervescence at a border grotto, or to be engulfed at a central fountain. Such a fountain forms, first, by conflicting currents tearing a crust asunder; then a spurt of flame appears, followed by a little bubbling; then a general downsucking of skins takes place toward a point, frequently tearing a symmetrical hexagonal opening in the crust, fifty feet (15^m) across or more (fig. 12, *a* and *b*). The crusts are heavy, tough, membraneous bodies like a doormat (fig. 16*a*) and when they rift, the stiff vesicular slag below wells up in the wake of the block which is foundering and draws out variously cooling shreds of its own substance from the solid jagged edge of the mother crust, a glassy, veined membrane of great toughness forming instantly over the newly exposed lava through shades of cherry red to purple and black (fig. 11, *b*, *c* and *d*).

Cool air is incessantly circulating in contact with the crusts to replace the hot uprush from the whole lake. The crusts are three to four inches (eight to ten centimeters) thick (fig. 17*a*), vesicular above, frequently folded or festooned and so involving large cavernous space, and their under sides, when they are seen to turn up edgeways and sink, are covered with

Fig. 17.

Fig. 17. Jan. 1917. Experimental work on E. rampart of lava lake in Halemaumau pit.

(*a*) Jan. 4, 1917. Looking northwestward across fresh overflows in foreground at rampart. Part of crag-mass and N.W. outer wall in background. Dipping up liquid lava from lake; 20-foot (6 m.) pipe with iron pot attached. Fountain splashing over rampart on the right. Note thickness of broken crusts in foreground; these are like the crusts which cover lake. Lake depression 101 ft. (31 m.). Photo Stotts.

(*b*) Jan. 11, 1917. First measurement of temperature with Seger cones. Shows bend in pipe where heated most at lake surface; straight below and above. Cylinder with cones on end of pipe. Lake depression 87 ft. (26 m.). Photo Jaggar.

(*c*) Jan. 16, 1917. Third test with Seger cones. Pipe immersed in lava on left, anchored with rope right. Lake depression 78 ft. (24 m.). Photo Jaggar.

a porcellanous glaze which is stalactitic and impervious. It is gas-tight, for the crusts are frequently ballooned upward by gas. Doubtless the blocks become completely encased in such a glaze when they sink. There can be no question, to the writer's thinking, but that such up-ending blocks, spongy in their vesicularity, exposed to sweeping winds, are filled with air. Green was of the same opinion. The mechanism of their solidification implies a cooling interstitially by air which replaced the hot gases of the unsolidified state. The persistence of those hot gases in tension in the vesicles is unthinkable, particularly as the crusts, after reaching a certain thickness, always acquire the impervious glaze beneath, and are openly porous above.

Simultaneous with the foundering of the crust area, a dome-shaped mass of bubbles, or "fountain," bursts having quite the appearance of an ebullition center in boiling milk; this dome may end the explosion, or it may be continued with a series of high flings of drawn slaggy openwork (fig. 14*b*), or prolonged gushes of spray and flame, the noise being like surf accompanied with puffing. Lava fountaining is not the expansion of a single great bubble, but that of a swarm of bubbles, a true effervescence, and as it progresses the fluid heats and loses viscosity markedly, flinging small droplets of glass such as the normal lava never makes. While the fountain lasts, engulfment and inward sucking to its center continues, and the surface currents set towards it, increasing in speed at the center, from some distance away. Foundering at the spot does not always precede fountaining, and fountaining may occur abortively without downsucking, raising convulsively the surface without breaking it, or merely throwing back a flap of crust without exploding through the under layer.

Great balloons of crust are sometimes blown by quiet gases, the bellying mass finally tearing at the end, when the gas escapes and burns. For an instant a glowing cavern is seen within with a bubbling liquid floor, and then the skin collapses. The true fountain, however, doming and spurting, is always followed by indraft of crusts. A continuous fountain is always a place of rapid downsucking and engulfment.

I have said that a fountain forms where currents conflict. Such conflict may be of three kinds, surface meeting of two or more streams, deflection of a current against the shore, or sub-surface meeting of currents following down opposed bottom slopes with the convection. This last case reaches a maximum when such submerged downstreaming meets from various directions at a sinkhole where the united flowings descend. A fountain over such a sinkhole reappears from time to time in the same place, and if the streaming process down the sinkhole is constant the fountain will be rhythmic

This is the case with "Old Faithful," a rhythmic fountain which, with occasional lapses, has been frequently seen in Kilauea. The fountaining border grottoes are places where there is conflict of a current or currents with the resistant shore, and commonly also these are over submerged sinkholes.

The meaning of a conflict of streaming currents will be apparent when we remember that convection is the motive power. At x holes a lighter fluid is rising; at y holes below a shallow lake a denser fluid is sinking; atmospheric cooling, radiation and gas expansion change the x fluid into the y fluid; and a more viscous, partially cooled magma descends. Such is normal convection, and some such convection progresses in Halemaumau. Solidification increases weight. The lighter fluid rises through the conduits west: crusts form rapidly over it: these are drawn toward the several sinkholes east: they are heavy and founder in the lighter magma just beneath them, when two currents, developed by this sinkhole distribution, bring crusts together and rend them or bend them so as to release the gas accumulated beneath and start an engulfment, which progresses rapidly edgewise when once a portion of a sheet of crust is submerged. This engulfment is often a flexible downfolding (fig. 16*a*). The result is to draw away along a fissured line a wide sheet of crust, and hot magma wells up the fissure and itself quickly crusts over. This cracking and foundering process is seen in flexible skins, heavy blankets and hard brittle crusts according to their thickness, the supporting power of the fluid next below, and the length of time that the crusts are allowed for solidification without disturbance. The surface streaming is maintained as a part of the convection by this mechanism, with accelerations at the fountains. Maximum speed of surface streaming is attained during general subsidence, when sinkhole mechanism is dominant over conduit mechanism; when the x holes lose pressure of rising magma and the y holes themselves subside and downflow through them is at a maximum, uncompensated by any tendency of inflow to add y holes to the x group.

Problems of Fountain Mechanism.

Why should fountains burst at all, and why at points of interference of currents? Furthermore why should *accelerated* streaming rush centripetally with engulfment to the fountains? Why should continuous fountains emit banners of flame? And why should the fountains be places of highest incandescence and highest apparent liquidity? (Fig. 18.) This is evidenced by their spatter which is a perfect glass, often drawn into filamentous floss. (See glisten of fresh lava, Plate I*a*, upper view.)

It has been stated above that some fountains *do not* burst through the surface, but merely heave it in a sudden abortive effort without breaking the crust or emitting gas. These indicate that explosion takes place below the surface with such balance of reactions that the gas product replaces the re-agent gases. There is no evident ballooning over them, the crust is simply heaved suddenly and sinks back and the gas produced is disseminated below.

There is no evidence from artificial stirring of the surface that a condition of general tension exists immediately under the surface crusts. Stirring with an iron pipe does not generate a fountain. A fall of rock tumble into the lake carries down great quantities of air in vesicles, and fountaining immediately results. A log of wood thrown into the lake end on remains below the crust, carbonizes, produces jets of red flame and induces fountaining. In both of these last cases reaction between the hot gas of the magma and an oxidizing agent is responsible for fountaining.

FIG. 18.

FIG. 18. Mar. 10, 1916, 6 P. M. Night view upper surface lava column Halemaumau from S., rising and overflowing lake, strong activity, depression 450 ft. (137 m.). Dimensions and conditions extraordinarily like those of six months before (Pl. I*a*, upper view), though a marked subsidence of lava column had intervened. Western conduit pond on left crusted over and dark, middle region moderate luminosity and fountaining, maximum oxidation shown on the right by flaming, sinkhole fountaining, breaking up of crusts, and fuming. The luminous line on the extreme right is a cascade rivulet pouring down from the lake among tumbled crags. Photo Jaggar.

Mechanism of Different Types of Fountains.

With great quantities of air-filled crust ceaselessly foundering in a gas-charged melt cooler than their fusing point, the gases of the melt including hydrogen, carbon monoxide and sulphur at high temperature, explosive reactions are inevitable, and these will be a local, temporary and incomplete oxidation, or a general, definitely situated, prolonged and flaring blast-furnace effect, according as the supply of oxygen is temporary and inadequate, or continuous and effective. The conflict of streaming convection currents which determines foundering, will thus produce subsurface oxidation of gas, more or less complete, according as the downrush of air and air-filled crusts is rapid or slow, general or sporadic, localized or shifting, continuous or temporary.

It must be borne in mind that the only significance of current conflict is as an observable and measurable evidence of crust breaking; and that this breaking of crusts by convectional interference is not limited to the surface, but takes place wherever the glazed and air-charged blocks are subjected to fracturing or erosion, as when they are drawn down sinkholes in the bottom of the lake.

On this analysis it will be seen that fountains should burst where violent oxidation is produced by contact at high temperature of magmatic gas and air.

Thus central fountains may commonly be attributed to such accumulation of air-filled crust beneath the surface, as to start the oxidation reaction; this involves violence and a consequent further breaking up of the air-filled block; the reaction may involve condensation and devesiculates the melt, consequently downsucking from the surface ensues, which supplies more oxygen; localized heat is liberated, inducing localized convection and expansion, and vertical escape of combustion products. The two processes are opposed and produce the opposed effects seen at a normal lava fountain, namely violent upward discharge of more or less burned gas and convulsive downward indraft of crusted magma.

It will be seen that when two surface currents of different velocity come together at an oblique angle and along the line of meeting continuous downfolding of huge blankets of crust ensues, the two currents merging into one and carrying along the submerged foundered skin in the new direction, the condition is ideal for generating a line of travelling fountains (fig. 13). And just such travelling fountains are there generated, the explosions migrating with the line of meeting, accelerating the inrush of the skins along the line, sucking down free air with them in the violence of the reaction, and increasing in vehemence of fountaining until raw glowing air-free melt has been exposed on both sides, the fountain usually ending its career at some permanent grotto on the bank. The two currents streaming at different speeds in this case furnish erosion mechanism to break up the crusts under the surface along the line and so liberate imprisoned oxygen for union with the magmatic gas.

Rhythmic fountains like "Old Faithful" have commonly at Kilauea intervals between explosions of from thirty to ninety seconds and occur immediately over sinkholes in the bottom of the liquid lake some 50 feet (15 meters) below the surface. They are particularly in evidence during a term of prolonged and continuous subsidence when the sinkhole is steadily acting as such, but their regularity may continue during rising. The crust material which founders at the lake margins of the cove in question sinks to the bottom and on being drawn into the sinkhole is broken up in contact with the gases of the lava. The reaction is continuous in supply of materials. The excess of combustion products and localized heat effect extend to the surface of the lake vertically in spasms, instead of continuously, because the excess of uncombined oxygen is insufficient to maintain a continuous stack or furnace through the 50 feet (15 meters) or so of liquid melt above. Such central fountains occasionally become continuous. What factors are dominant in contributing to the rhythm of the surface explosion is as yet unproved, but it seems probable that the sinkhole itself acts rhythmically in its downflow, becoming clogged at intervals. The greatest amount of oxygen, heat, expansion and local convection would be produced during its more rapid downsuckings, and these times would surely upset the surface equilibrium of the pool above and produce a fountain.

Continuous fountains, at the lake margin especially, form grottoes of spatter glass in beehive, or half-dome, form, open as glowing caverns on the side toward the lake and frequently perforated with small flaming crevices, the walls of which are incandescent (figs. 14*a*, 16*b*, 10 right center). Usually such grottoes surmount border sinkholes of some permanency as revealed by sudden subsidences, and there is reason to suppose that the mechanism of a prolonged building up of the bench lava, with persistence of such a grotto, constructs such a sinkhole by upward growth of the cavern in the bench and of the floor of the lake by accretion (fig. 2, section) under the cavern's mouth. Towards such a grotto there is continuous suction, within there is continuous but variable fountaining and spraying from outrush of gas, through the apertures and above the entrance cavern there are continuous but variable spears and banners of flame. Still higher appears the bluish fume which retains its heat for hundreds of feet above and to leeward and is painfully acrid with SO_2 and SO_3 in its effect on the human mucous membrane. The temperatures in these grottoes are very high as shown by their luminosity, the magma within them is at minimum viscosity as shown by its mobility, and the glassiness and freedom from vesicles of the spatter product are remarkable. Moreover the linings and stalactites of such grottoes indicate refusion, and oxidation of the iron to the ferric condition. The variability in fountain action at grottoes may be from zero, when all is quiet and crusted, to tremendous spraying and blowing with towering banners of flame (fig. 20) and an inrush which amounts to a cascade from the lake to a cauldron within the cavernous dome. Times of extreme quiet are characteristic of rising, times of extreme activity are characteristic of sinking. This last antithesis is true also of all other fountains.

The grotto fountain appears to be a true case of a stack or furnace built at the margin of the lava lake remote from inlet conduits. The furnace is fed by relatively continuous downflow of lava vesiculated with combustible gases, and supplied with oxygen by continuous downsucking with this magma of large quantities of air. The reactions are quite as in the other cases cited, but the recess constructed by spatter around the margins permits a concentration of the blast at one point. It is quite probable also that chemical activity of gas with lava, reheating the substance of the grotto walls, adds to the heat supply in these specialized edifices. The opening of a confined glowing cavern toward the air over the lake, with continuous indraught of that air induced by the downflow, brings about very complete combustion of the less active gases such as sulphur vapor at the orifice of the stack, and prevents the condensation of free sulphur which elsewhere appears as a white smoke or kind of gaseous emulsion when the vapor rises gradually cooled through border cracks in the bench lava.

Construction upon Lake Bottom.

The great quantities of air-filled crust sucked under the lake margins at the border grottoes probably descend to the bottom with much of their oxygen unconsumed and with their relatively cool and heavy substance incessantly adding, by a backward or eddying subsurface circulation, to layers of more or less comminuted material on the bottom of the lake increasingly viscous downward (fig. 2). This subsurface crustal material is what builds up shoals in those portions of the shallow lake least eroded by streaming and least heated by oxidation. Comminution, by destroying the buoying effect of vesicles, accelerates sinking.

We should thus expect shoals to be built out at the sides of inflowing fresh lava from the conduits, where fountains are absent, and where quiet eddies would permit construction upward from the bottom to join with the thickening crusts at the surface. There has been repeatedly demonstrated a tendency for the lake to grow from the western conduits eastward during rising, in the form of a Y with arms curved outward, the stem being the current from the source. This is what happened in the summer of 1916 when a simple oval lake developed powerful streaming outward from the west side, then shoals appeared and peninsulas were built out (fig. 5) on both sides of the current, until the Y or T form was produced (fig. 6*a*).

Sinkhole Cascades.

The extreme case of the grotto fountain is the sinkhole cascade such as was described on pp. 172, 173 above. Such cascades from the lake into holes at its border, or in its bottom, have repeatedly appeared when general subsidence began. Commonly the place of cascading is a border pot which may have been a place of rising lava pouring out into the lake during a previous rising spell. When sinking begins the magma in the smaller tube sinks lower than the lava in the lake with the result that a torrential fall is precipitated from the lake into a glowing void, intense effervescence or fountaining is in progress in the depths of the pot which receives the fall, great sheets of crust from the lake are drawn over the rim, and break up in the abyss, and a column of flame and fume rises above with great heat and much sulphurous acid gas (fig. 9*b*). All the phenomena of such a cascade are those of a border grotto exaggerated (fig. 11*d*).

For a long time in watching such cascades the writer was in doubt whether the lake lava actually poured over a ledge or whether the appearance of such an edge were not merely the more rapid fall of surface layers over the slower liquid beneath where the magma in the border fissure, open on the lake basin side, sank as a froth by loss of gas faster than the magma of the larger lake body. I am now convinced that commonly there is an actual lip of bench magma which the lava of the lake pours over, and this lip is usually the margin of the lake bottom, revealed by reason of the sinking of the liquid lake within its basin in the bench magma.

There has recently (February 21–28, 1917) been a remarkable case of such cascade action after 46 feet (14 meters) of subsidence of the lava lake—just sufficient to uncover much of the bottom and leave the lake a very shallow body coursing like a river. At the northeast margin under the cliff of bench lava there was revealed a cavern in the wall into which the lake lava cascaded for seven days and longer. The fall was shaped in plan like an obtuse V with the point toward the lake; the cascade poured over both arms of the V, while in one place an outcropping of ledge rose through the fall and divided it. This clearly indicated that the liquid was cascading over a solid or semi-solid obstruction. And this was just at the level where the irregularities of the margin of the lake bottom of the previous higher stand of the lava might be expected to appear. Incidentally the cavern was at a location of large and continuous border grotto building for many previous months.

During the progress of such cascading the lake may maintain its level, or even rise, showing that the cascade is not an outlet. It merely reveals during excessive shallowness, convectional mechanism commonly concealed by greater depth in the lake. That the violent downrush during cascading, however, is swifter than at other times, is shown by the fact that when such a cascade is in action, it is apt to satisfy completely. or nearly so, the fountaining requirements of the lake mechanism, for almost all other fountains cease playing while the cascade is falling. This might be expected, as the rest of the lake at such times is very stagnant and crust foundering is largely limited to the one place where crusts and air are being sucked down in prodigious quantities and the heat and flaming are excessive. Probably excess of downward convection over inflow or some equivalent mechanism in the relation of bench magma construction to lake magma effervescence, brings about the cascade phase of downflow. If, however, it is maintained by an extreme phase of oxidation of gases, which keeps the level of lava in the sinkhole 20 to 50 feet (6 to 15 meters) lower than the level of the lake, then we have to make careful inquiry as to how this could be brought about.

Condensation by de-vesiculation.

In the above discussion of oxidation fountaining, it was pointed out that two opposed processes would operate in opposite senses, when foundering crusts along with convection downflow mixed air with explosive gases, and so induced oxidation, excessive heat, consequent gas expansion, and consequent localized upward gas convection. Mention has been made in addition of condensation resulting from the explosion of unstable mixtures of oxygen with hydrogen, carbon monoxide and sulphur vapor. Whether there would be such condensation at the high temperatures prevailing in molten lava is a question for the physical chemist. We know that two atoms of hydrogen uniting with one of oxygen produces a molecule of water which in its liquid state occupies greatly diminished space in contrast to its gaseous progenitors. In the case of water vapor at 850° C., however, condensation would be less, and the same is true of the transformation of sulphur with oxygen to SO_2 and of CO with oxygen to CO_2. If in the heated condition there is less change in the vapor tension resulting when these reactions take place, it is evident that the violent downsucking at the grottoes and fountains must be accounted for by some process other than chemical condensation.

The only conceivable process other than gas condensation, in view of the obviously excessive discharge of gas and liberation of heat which occur at these places, to account for the loss of volume which produces downward suction, is a partial de-vesiculation of the lava, a loss of gas which decreases its bulk, and to that extent increases its density. It is plain that if the furnace of a grotto stack could reheat the *vesiculated* lava for any depth, we would have our convection reversed and so would become involved in paradox.

It is evident that the reheating does not prevent convectional downflow of the liquid, and this would clearly not be the case if we had to deal with mere thermal convection, rather than two-phase convection. But in the union of the oxygen of crust vesicles, with the combustible gases of viscous lava vesicles, to induce violent reactions which expel great quantities of burned and unburned gas vertically, the hard crusts must be comminuted, and the melt must be largely robbed of its vesicles. The burned gases escape in large bubbles, while the local heating and lowering of viscosity favor expansion and escape of the small bubbles. Therefore loss of gas plays an important part in shrinking the heated lava of the grottoes and sinkholes. The expansion of the combustion products, moreover, is a cooling effect. All of this may account for the lowering of the level in the sinkholes, when extraordinary oxidation is maintained by the cascading process. Furthermore, the faster the shrinkage within a sinkhole, the heavier the cataract resulting and the more voluminous will be the direct suction of air downward. This in turn increases oxidation and so the process of acceleration is self-propagating to the limit of combustible gases available.

Multiple Fountaining of 1910 to 1912.

Before leaving the question of fountaining, mention must be made of the very remarkable distributive fountaining, generally accompanying subsidence, in Halemaumau lake in 1910 and 1912. This may be considered a time when the lava column had reached its highest level and was entering upon a general decline that reached its lowest in 1913. There was a sudden spurt to nearly the 1910 level in December–January, 1911–12, and there was another rise to a lower level in July, 1912. The characteristics of this extreme activity were abundance of bubble fountaining and numerous large fountains, rushing and streaming surface currents in changing directions, and frequent lines of traveling fountains when two or more such currents would meet and oppose each other. In July of

1912 this process reached its maximum, when in a small oval lake about 600 feet (180 meters) long, depressed 200 feet (60 meters) below the rim of the pit, there were several hundred large fountains and many more small ones (fig. 15). All of these were playing at once with a roaring noise, intense incandescence, tumultuous rush of surface currents, and bombardment on the bank, first on one shore and then on the other.

To account for this phase of activity we must suppose that convectional downflow was dominant, a shallow, air-filled and superficial convectional circulation was very rapid, and that accordingly oxidation was at a maximum. This was the summer when the Day and Shepherd gas collection was made and excess hydrogen was found among the combustible gases. Temperature measurement with Holborn-Kurlbaum pyrometer gave 1185° C. This was the time when Day and Shepherd found *greatest emission of gas* (maximum fountaining) to coincide with highest measured temperatures. There had been repeated inward tumbles of great quantities of air-filled bench rock in 1910, 1911 and 1912, the lava each time recovering so as to rise and submerge this talus debris. It seems likely that the excessive fountaining during the season of sinking of 1912 was due to the breaking up by subsidence of this submerged air-filled debris, and this, coupled with and contributing to extreme rapidity of two-phase convectional circulation, as outlined above, brought about an admixture of much oxygen with combustible gases. Vast quantities of air were drawn down directly with downflow currents, under the banks and at the traveling fountains, owing to the speed of the torrents, which increased to cascades in August. It is possible that at certain seasons the supply of some unstable gases such as hydrogen is larger than at other times, and the heating effect greater. Routine photospectroscopic work on flame spectra might prove this.

Disappearance of Liquid Lava during Low Levels.

These terms of violent effervescence coincided with culminations of rising and the beginnings of sinking. With the low levels of September, 1912, and of the entire year following May of 1913, gas pressure dwindled to a minimum and the pit at some 700 feet (213 meters) of depth was floored with frozen lava surrounded by talus slopes. There was much sulphur fume and water vapor, but even the hissing of confined gas at times ceased completely. This condition, merely because the lava column had retired topographically to a depth one-sixth of the height of the mountain above sea-level, could hardly be attributed to depression alone. Why, in other words, should depression induce inactivity? Why should not the same violent fountaining, and vast discharge of gas and heat, go on within the mountain at 700 feet of depression, if the phenomena of streaming and fountaining in the liquid lake were functions independent of the form of the higher lava pit, and of contact with the atmosphere? The lava was sluggishly present in the depths of the pit for it would occasionally begin puffing and glowing, and its sulphur smoke was always rising.

The answer to these questions would seem to imply that lake magma convection at these low levels becomes very sluggish or stationary, owing to lack of stimulation with oxygen, and that at the higher levels with increasing sinkhole suction of free air, larger area of surface crusts, and assimilation of air-filled talus blocks, the lava gradually acquires an increased fluidity in proportion as its upper edifice becomes increasingly a furnace. Meanwhile the bench magma, matrix for the furnace of the liquid lake, remains always a sluggish, heavy and stiff substance such as lay dormant in the depths during the intervals of low level.

Heating Mechanism in Bench Magma.

The heating mechanism by oxidation of combustible gases which has here been outlined, was first mentioned in relation to the heating of the bench magma. The discussion so far has been directed chiefly to the rapid engulfment of air in the liquid lake. We have seen that an excess of air engulfed in glazed crusts becomes built into the viscous bottom of the lake and that heavy crusts and talus blocks, full of air in vesicles, become buried and incandescent, by a gradual subsidence under overflows, in the mass of the bench magma column.

The maintenance of this inner heat in the bench magma column is accomplished by the slow circulation of its lava, by conduction from the conduits and sinkholes which perforate it, by the burial of incandescent lava flows within it, by the burial of hot bottom layers of the lake upon it, and lastly by actual percolation through it of the volcanic gases under pressure. It is probably this last process which discovers buried air cells, and the gases, uniting with the oxygen so encountered, set up a distributed liberation of heat. This reduces viscosity and so aids the slow circulation of the mass, which as before mentioned, proceeds by peripheral depression under weighting, and central upflow under the lake.

It is difficult to prove this, for the interior of the bench magma is rarely under observation. This much, however, is certain, that the rock of the islands and bench crags, when revealed by collapse only a few weeks after it has solidified, is intensely oxidized. The ferrous iron in the basalt and the magnetite crystals have gone over to masses of earthy brown limonite and red hematite. The lava when it solidified was on the surface black, glistening and glassy, while within it was gray-black and lithoidal. Such rapid decomposition through and through for scores of feet one month from the time when live lava was overflowing, as in the collapsed west pit of February, 1917, points to profound and rapid oxidation with strong evolution of heat. Moreover, on March 14, 1917, in this same region, after subsidence of the lake of 84 feet (26^m) in six weeks, the weathered pahoehoe flow surfaces, dead since January, began in places to glow with red heat, though 70 feet (21^m) above the lake and quite remote from any live lava. This reheating appeared to be gas oxidation through small crevices.

The writer as yet has no clear vision of the gradation downward of temperature and viscosity in the bench magma nor of its transition stages downward to where bench and lake magma are one. A two-phase convection in the deep region complicated by such opposed processes as adiabatic expansion and gas fluxing, or the assumptions on the one hand of increased temperature in depth from a heated substratum and, on the other, of decreased temperature owing to incomplete gas reactions, are too difficult for the student of observable facts. Apparently the bench magma and the lake magma in Halemaumau, with their respective circulations, are definite facts, and for the present, speculation as to what is beneath may be postponed. That the lava column is a stiff body with its gases in solution, and at no great depth, appears extremely probable.

EXPERIMENTS TO DETERMINE DIFFERENTIAL TEMPERATURES.

Queries Concerning Temperature.

There have been hitherto presented in this paper evidences from observation at Kilauea volcano of a duplex lava column, of convection, of shallowness of the liquid lava lake, of heat supply and of oxidation of gases. The evidence from five years of recording, summarized above, necessarily leads to queries, answerable in part, at least, by some very simple experiments, if opportunity offer for direct contact with the lava lake, grottoes and blowing cones through the agency of simple instruments thrust into them. Such an opportunity of easy access to the fire pit was first presented to the writer in January, 1917, and for three weeks, while the lava remained high, a series of rough experiments was made with a view to answering leading questions.

Such questions are concerned primarily with temperature, viscosity and depth. Would experiment show the lava lake to be hotter or cooler below the surface crusts, than the recorded temperature of about 1000° C. measured with thermoelement by Perret and Shepherd in 1911 in the "Old Faithful" fountain region? Would the grottoes give temperatures higher or lower than the maximum 1185° C. recorded with optical pyrometer by Day and Shepherd at the time of intense multiple fountaining in July, 1912? Is the temperature below the surface crusts high enough to melt those crusts when foundered? How are the temperatures graded from lake to grotto, or to blowing cone on the bench? How hot are the burning gases? Are they hot enough for refusion of the basalt?

Reconnaissance and Method.

The floor of Halemaumau around the liquid lake was reconnoitered from the east by a steep trail, and from the west with rope ladders, on January 3, 4, 5 and 7, 1917. The northeastern rampart, a place of repeated overflow and largely built by spatter over grottoes, was found to be a favorable location for work at the actual edge of the liquid lake. We were here standing on the bench magma, and could thrust iron pipes into the lake magma. On January 4 an iron pot of lava was dipped up from the lake (fig. 17*a*), with three immersions, in the hope that such a pot might imprison the volcanic gas. This pot was sent to the Geophysical Laboratory. On January 7, the high western crag mass (fig. 6*b*) of the bench magma was climbed to its summit, and photographs made in all directions from this central position. It became evident that Seger cones enclosed in series in the ends of common "galvanized* iron" (rolled steel) pipes, would be serviceable for determining approximate temperatures, and as the temperature in the lake magma was expected to be at least 1000° C., the first Seger cones used were of fusibilities near that figure (fig. 19).

The conditions of this sort of experimentation are arduous, and the thrusting of a one-inch ($2{\cdot}54^{\mathrm{cm}}$) steel pipe into the lava and withdrawing it, are by no means simple operations. The floor or bench was covered with pahoehoe lava flows freshly overflowed nearly every day, crusted with shells three to five inches (eight to thirteen centimeters) thick, and red hot beneath (fig. 17*a*). Several times I crossed flows which had poured out within four or five hours. The rampart was three to eight feet (one to two meters) high, built of glossy fling from the fountains, which incessantly spattered over it, with changing locations of activity. Consequently the surface of the rampart was hot enough to burn shoe leather, but one could stand on it with hob-nailed boots, by keeping in motion. The high lake when near to overflowing (Pl. I*b*, lower view) was most favorable for access and on account of its quietness, brimming close to the rampart edge and above the level of the floor behind. Work at such times, however, had to be rapid, as at any moment sudden rising might start overflow, or the rampart might collapse, or fountaining might begin at the

* Zinc oxide would act as flux and make readings too high. Black steel was used later.

place selected (fig. 20). The heat radiating from the lake surface at the rampart was very great and could be endured for a few minutes, but not for an unlimited time. On the surface of the lake, drifting with the current slowly along the bank, were heavy crusts like elephants' hide (fig. 16*a*), which wrinkled and crackled and were hard stiff bodies several inches thick. No pipe would penetrate them and it was always neces-

Fig. 19.

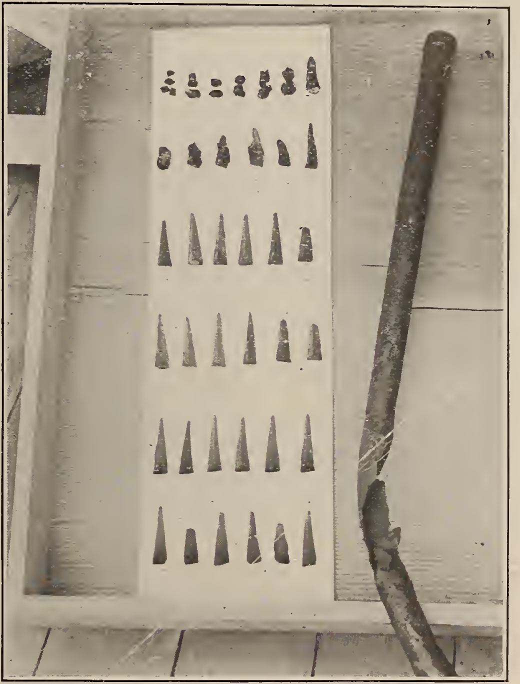

Fig. 19. Seger cones and partially fused one-inch steel pipe used in temperature experiments. Pipe as described for Jan. 26, 1917, fused through at bend, which was at flaming entrance to gas cupola. Fusion progressively less to end of pipe, which was farthest within the cupola. Cap over end destroyed. The upper row of Seger cones was fused in this pipe. The six rows of Seger cones numbered from above downward are those resulting from tests; the short cones of the lower four rows are mechanically broken but not fused; the fusibilities in degrees centigrade from left to right in each row are as follows:

1st row (uppermost), Jan. 26, 1917, 620, 710, 800, 870, 970, 1090, 1130.
2d row, Jan. 22, 1917, 590, 680, 770, 870, 970, 1070.
3d row, Jan. 18, 1917, 2d test, 590, 680, 770, 870, 970, 1070.
4th row, Jan. 18, 1917, 1st test, 590, 680, 770, 870, 970, 1070.
5th row, Jan. 15, 1917, 770, 800, 870, 950, 970, 990.
6th row, Jan. 11, 1917, 990, 1030, 1070, 1110, 1130, 1150.

sary to wait for a rending of the crusts, which revealed the viscous glowing slag beneath, or to find a place, otherwise convenient, where one of the ragged glow lines of upwelling was maintained (fig. 11*d* and 20). It was necessary, moreover, for such a liquid place to persist for some minutes, in order to leave the pipe submerged long enough to insure thorough heating of the Seger cones within, and then it was problematical as to whether the pipe could be withdrawn, as heavy crusts were apt to pile against it and to freeze around it. It commonly took the united strength of four or five men to withdraw a pipe (fig. 17*c*), and on two occasions the pipe was lost. Fortunately the surface current proved shallow and while the heated pipe always bent during immersion, it was commonly held by border crust at the lake surface, so as to prevent its being swept along.

Fig. 20.

Fig. 20. Jan. 31, 1917, 6 p. m. Depression 48 ft. (15 m.). Looking N.W. Violent fountaining, blowing, flaming and overspatter in grotto under S.E. rampart. Shortly after time of Pl. I*b*; when quiet overflow had ceased and depression had begun. Note trajectory of flying spray, in the midst of which were great banners of flame. Wide glow lines under S. island in contrast to Pl. I*b*: indicates incandescent overhang at lake margin due to temporary subsidence. This glow rim appears all around lake. General subsidence and fountaining follow intervals of quiet inflation. Photo Morihiro.

Temperature of Lava Lake.

The first three tests with Seger cones were directed to determining the temperature of the liquid lava just beneath the surface crusts, with immersion of about three feet (one meter) of pipe. Six Seger cones were used in each test, of fusibilities differing progressively by about 40° C. The following were the results of these three tests (fig. 19):

Jan. 11—Six Seger cones of fusibilities 990° C. to 1150° C., immersed 6 minutes, 3 feet (1^m) below crust of lake; cones blackened but no trace of fusion (fig. 17*b*). Highest glow and sharpest bending of steel pipe were at point of immersion, where *gas burned in air*, showing zinc flame coloration from galvanizing on pipe.

Jan. 15—Six Seger cones of fusibilities 770° C. to 990° C., immersed 11 minutes, 3 feet below crust of lake; cones blackened but no trace of fusion.

Jan. 16—Six Seger cones of fusibilities 770° C. to 990° C., immersed 30 minutes, 3 feet below crust of lake; (fig. 16*a*) apparatus frozen into crusts and incandescent pipe rent asunder in the effort to recover apparatus by twisting. Cylinder containing cones lost (fig. 17*c*).

In all these tests the cones were held by their bases in a special riveted iron container so that the tips were free within a three-inch (eight centimeters) steel cylinder eleven inches (28^{cm}) long, covered with a screw cap at the lower end and screwed on a one-inch galvanized steel pipe at the upper end. This pipe, 20 feet (6 meters) long, was open at its upper end and was used as a handle for thrusting the cylinder beneath the lava. A rope was attached to the upper end of the pipe so that several men could pull in recovering it.

These tests were surprising, especially that of January 15, when a cone, of fusibility 770° C., wholly failed to fuse though immersed three feet beneath the surface in the quiet streaming lava of the lake for eleven minutes.

On the same day, January 15, two temperature readings were made with Bristol portable pyrometer, a commercial thermo-element. The element, without covering, was thrust directly into the liquid lava at the edge of the lake and left there until the recording needle of the galvanometer came to rest. The first trial gave maximum temperature 860° C., the second trial 910° C. The upper end, or "cold junction," of the apparatus was necessarily hot exposed in air to the radiant heat from the surface of the lake and the rampart. The makers furnish no correction chart for this source of error, and hence the actual temperatures, if the instrument is accurate, were somewhat higher than the figures recorded. But the range exhibited by the thermo-element, though higher than that of the Seger cones, is still much lower than was expected. And probably the Seger cones afford the more reliable data. The writer recalls assisting Dr. Daly in 1909 in some temperature readings on the *fountains* of Halemaumau, made with Féry pyrometer, when a temperature of 940° C. was registered, and this was believed at the time to be much too low. In general these first experiments of 1917 show that the lake magma is much cooler than has been supposed.

Temperatures of Grottoes and Flames.

The next temperature tests with Seger cones January 18, 22 and 26, 1917, were devised with a view to determining the relative heat of the lake magma twenty feet (6^m) from a grotto, of the lava inside a grotto, and of the burning gas from a blowing cone. Supposing that possibly the three-inch (8^{cm}) cylinder of the first experiments made too large an air space around the Seger cones, and also because such a cylinder was awkward for recovery when it became clogged with crusts, a simpler device was used for holding the cones. The six Seger cones were placed end to end in a spiral of steel wire nineteen inches (48^{cm}) long and this was inserted directly in the end of the one-inch pipe which was closed with a screw cap. The upper end of the pipe was open. From the results of this second series of experiments, which for the lake lava showed the same tendency to low temperatures, but elsewhere fused the Seger cones abundantly, the writer is convinced that the air space in the larger pipes somewhat invalidated their results. The following are the records of the second series (fig. 19):

Jan. 18—First Test. Six Seger cones of fusibilities 590° C. to 1070° C., heated close to lake surface 30 minutes, then dipped under lava one minute. Dipping was not complete, so that three upper Seger cones of low fusibilities were less blackened than the three lower ones. The three lower cones which were blackened were of fusibilities 870° to 970° C. Only the cone of 870° fusibility showed any fusion effect and this was very slight on the angular edges of the cone. As the pipe became involved in crust and the zinc galvanizing of its outer surface burned with a bright greenish yellow flame, it is possible that this fusion of cone 870° was induced by an artificial reaction.

Jan. 18—Second Test. Repetition of first test, six Seger cones of fusibilities 590° to 1070 C. heated 30 minutes close to lake surface, then dipped completely for one minute so that all the cones were immersed in the lake. Again the pipe was entangled in crusts, bent and recovered with great difficulty. All of the cones were blackened, but none of them was fused, *not even that of fusibility 590°*.

Jan. 22—Six Seger cones of fusibilities 590° C. to 1070° C. in the end of a pipe 40 feet (12^m) long were placed in the interior of the northeast grotto (like fig. 16*b*) 20 feet from the locality of immersion of Jan. 18. The terminal was just over the boiling lava for 10 minutes; then 5 feet ($1{\cdot}5^{m}$) of the pipe was submerged in the lava for 5 minutes. The pipe was drawn down violently and recovered, much bent, with great difficulty. The Seger cones were all fused in some measure, that of fusibility 1070° least so. The temperature of the grotto was thus at least 1100° C.

Jan. 26—Seven Seger cones of fusibilities 670° to 1130° C. were placed in the glowing interior of a blowing dome (fig. 21) which had been built over the northwest inlet well or pond above a roof of arched lava flows. About 3 feet (1^{m}) of the end of the pipe was thrust for 9 minutes in a flaming orifice 10 inches (25^{cm}) in diameter in the side of the dome. The flame was under pressure and of the blue-green variety. The pipe was of ordinary commercial galvanized steel covered with a screw cap of annealed cast iron, and the Seger cones within were in a spiral of "spring steel" wire. Lava was splashing in a cavernous space 12 feet (4^{m}) below. The galvanizing first burned off the pipe, then the surface of pipe was seen to be continuously dripping with molten incandescent drops, especially at the window, and after 9 minutes the pipe was eaten through, *apparently fused*, for a length of about 9 inches, just at the window orifice where the visible gas flame began (fig. 19). The incandescence was highest opposite the window, a strong yellow heat; that inside the dome was orange. The pipe was at once removed. The molten drops appeared to have been molten iron. The cast iron cap was almost completely gone. The pipe showed gradations of fusion from a maximum at the flaming window to a minimum at the inner end. The spring steel spiral inside showed no sign of fusion. The Seger cones were all fused, that of fusibility 1130° C. least so, indicating a probable temperature over 1200° C. It was at first thought that the corrosion of the pipe was oxidation, but in view of the dripping fusion and the differential effects on three classes of iron, and the fact that after the cap was destroyed, the inner spiral had every opportunity to oxidize, but did not do so, it seems that actual fusion took place. Annealed gray cast iron (the cap) fuses at 1220° to 1275° C., rolled steel (the pipe) fuses at 1325° to 1375° C., and hardened steel (the spiral) fuses at 1425° to 1500° C. Wherefore we may conclude that the temperature of the burning gas at the flaming window was close to 1350° and that inside the cupola near 1250°. Even if the metallic reaction was largely oxidation, these figures would not be materially changed, as the Seger cone 1130° was greatly fused *within the dome*, and the incandescence of the pipe at the window was much higher. The dripping melt in such case was an iron-sulphur oxide flux of fusibility probably near 1250° C.

Summary of Temperatures.

By summarizing the results of these two groups of tests it appears that the lake magma immediately below the surface glow lines has a temperature range from 750° to 850° C.; that the lava in the fountaining grottoes has a temperature range from 1100° to 1200° C.; and that the oxidizing gases in the blowing cones have temperatures ranging from 1250° C. within the cones to 1350° C. or higher at the flaming orifices.

Reverting now to the queries asked at the beginning of this section, it would appear that the temperature range measured by Perret, Day and Shepherd, namely 1000° to 1185° C., is correct for the fountaining lava, but that the temperature of ordinary lava beneath the crusts is not the same as that of the fountains, but much lower. As the melting point of the basalt is near 1100° C., the lake melt would rank as superfused, or fluent and unsolidified below its fusing point, if it could be treated as a pure melt. Furthermore it becomes plain, on the other hand, that the hot gases rising through this same lava become vastly hotter, when confined in a spatter cupola above the lava, and hotter still when liberated for complete combustion in air. The conclusion seems justified that the heating effect is due to union with oxygen, and that this union begins below the fountains, increases within the blowing cones, and culminates in the visible flames.

Fig. 21.

Fig. 21. Jan. 7, 1917. Looking W. at blowing cone built above arched lava flows roofing N.W. conduit pond. A similar roof was seen to fall in suddenly a few weeks before. The middle figure is looking into flaming orifice, 3 ft. (1 m.) across, in summit of cone and 12 ft. (3 m.) below could be seen the fountaining lava. This cone, built higher by spatter, with lateral window instead of summit orifice, was the scene of temperature measurement which fused steel pipe Jan. 26, 1917. Photo Jaggar.

Refusion.

Two deductions may be made at once from the temperature distribution in a blowing cone:

First, that the more slowly oxidizing gases at 1250° C. inside the cone are well above the melting point of the lava walls of the cone, and are also able to oxidize the ferrous iron of the interior surface. The results are seen in the secondary glazes, often brown or silvery with ferric iron, found in the interiors of caverns; they are seen also in the peculiar cavern stalactites; these glazings mark a refusion of cavern linings so as to destroy the visible vesiculation of a rough surface and to coat the whole with a smooth mantle of porcellanous aspect. These secondary linings are found everywhere on Kilauea, where the pahoehoe lava has withdrawn from its crusted portions and left cavernous spaces. The linings and stalactitic forms are in great variety of color and texture, and it has been for years apparent to the writer that nothing would account for them satisfactorily except a mechanism of refusion, because of their lithologic distinction from the molten rock. When refusion in a blowing cone goes far enough it results in the glowing "filagree" cone, fused through from within, which may collapse and reform, during rising of the lava, again and again. The rising lava is cooler and constructs; the gas chamber of subsidence is hotter and destroys.

Furnace effect.

Second, that a blowing cone is an excellent furnace stack for creating a draught of air into the interior from below, the hottest portions being at the orifices in the summit. This would create a strong updraught, and as all blowing cones contain gas chambers over lava connected in some way with a larger pool, and commonly at the pool level, there would always be an air channel to supply oxygen to the base of the stack, during the temporary subsidences of the liquid column, which from hour to hour alternate with risings. Therefore rising lava in the stack would yield the purest magmatic gas; sinking lava should produce more combustion within the edifice. The puffing which has given these cones their name may be a combustion phenomenon; it is sometimes strikingly like the noise made by a locomotive.

Relative Coolness of Lake.

As to the normal lava lake temperatures, it is clear that foundering crusts in a melt of 800°, 900° or even 1000° C. would have no chance for refusion (melting point 1100° to 1200° C.). On the contrary, in a superfused pure melt their tendency, if not opposed by reheating mechanisms, would be to start solidification. They would pile up on the bottom, were they not disintegrated by explosion and local reheating, through the union of magmatic gases with the oxygen in their vesicles. As has been explained above, in view of the fact that great quantities of crust have been seen foundering without immediate fountaining effect, there is probably such piling up along with storage of the oxygen through gas-proof glazing, which coats the exterior of foundered blocks. This would be especially expectable if the lake is shallow, and more viscous near the bottom, in places removed from the sinkholes.

EXPERIMENTS TO DETERMINE DEPTH AND CONSISTENCY.

Queries concerning Depth and Consistency.

In order to settle this point with reference to the liquid lake, shallowness being a seemingly indispensable condition to account for the facts observed, an experiment was devised having in view the bold project of actually sounding the lava pool of Halemaumau. The preliminary work with iron pipes and Seger cones had shown that the crusts are heavy and stiff, the lava beneath sufficiently plastic to be dipped up in an iron pot, but by no means as mobile as molten lead, while the lava of the grottoes seemed much more liquid when stirred with an iron pipe. The grotto lava which solidified around the pipe terminal exhibited dull oxidized surfaces, smaller vesicles, finer texture, and a dense selvage next the iron, while the accumulations of normal lake lava were lustrous, lighter, glassy and coarsely vesicular. The streaming currents in the lake are neither strong nor deep in contact with the submerged pipes, but in the grottoes they are very powerful.

The queries suggested concerning viscosity and depth, possibly answerable by experiment, are as follows: (1) when the lake is at a high level, at what depth would a sounding rod strike bottom? (2) Is the lake magma stiffer or more liquid in depth?

Measurement of Depth.

On January 23, 1917, with the surface of the lava lake depressed only 50 feet (18 meters) below the rim of Halemaumau the writer tried sounding with the aid of half-inch ($1·27^{cm}$) "black iron" (steel) pipe. A total of 200 feet (60 meters) of piping was screwed together and this was laid out across the northeast floor adjacent to the eastern rampart of the lake margin. In the first test Seger cones were inserted in the end of the pipe nearest the lake and confined with a screw plug, but as this pipe was lost, the temperature in depth was not determined by this means. The extremity of the pipe remote from the lake was attached by a rope to a block and tackle and nine men volunteered to assist the writer in carrying the pipe end on, so as to immerse it in the lake at a high angle, try for the bottom, and withdraw the apparatus with the aid of the rope.

In the first test the pipe was thrust out over the bank at the east point in a southwest direction toward the center of the lake, the bank here being 15 feet (4 meters) high (fig. 10). The terminal was thrust downward striking the lake surface some 20 feet (6 meters) horizontally out from the shore, at a glowing liquid zone free from crust, and for from 30 to 40 feet (9 to 12 meters) of depth the pipe descended freely at an angle of about 45°, but sagging to the vertical as the length increased. Beyond this depth an increasing resistance was gradually encountered, and finally caused the pipe to arch upward and fail to penetrate farther. Sixty feet (18 meters) of piping was submerged, corresponding to a vertical depth of approximately 50 feet (15 meters). At this place, then, the lake was 50 feet deep some 30 feet (9 meters) from the shoreline, (the pipe beneath the surface extending beyond the point of immersion). Subsidence during the following month indicated that this shoreline beneath the liquid was precipitous. Therefore there was no error due to shelving shore.

On withdrawing the pipe some 30 feet (9 meters) of the submerged portion was recovered quite uninjured by any sign of oxidation or fusion, but the remaining three 20-foot lengths became imprisoned against the bank, owing to the pressing in and piling up of crusts around the pipe, so that it was quite impossible to recover the terminal length which contained Seger cones.

In order to prove that the shallowness of the lake and viscosity of the bottom layers, seemingly indicated by this first test, is general and not local, a second trial was made on the same day at a point 40 yards (37 meters) farther north, and about where the temperature tests had been made. This place was only a few feet from the northeast grotto domes, towards which there was a strong current. The pipe was thrust over the bank more rapidly than in the first test, and catching the current tended to arch downward steeply and to bow somewhat toward the north. The results were quite the same as in the first test. In both cases the writer stood at the lake margin manipulating the pipe as it descended and the increasing resistance was very marked during the last 10 feet (3 meters) of its descent. In this second test 61 feet (18 meters) of piping was submerged before the impenetrable pudding was reached.

The pipe was withdrawn completely this time but only through the most strenuous hauling by nine men in line. Twice it stuck owing to accumulations of lava which caught against the bank. It must be remembered that in such withdrawal the pipe cannot be pulled up hand over hand, because it emerges from the lava red-hot. The only way to pull it out is by walking away from the rampart and leaving the hot portion to trail over the bank. The end of the steel pipe emerged clean and showed no fusion or especial oxidation, nothing to indicate that the depths of the lake were comparable in temperature with the flaming cones. This second sounding apparatus was not equipped with Seger cones.

Confirmation of Soundings by subsequent Subsidence.

The second sounding test, like the first one, but at a different place, indicated a depth of liquid lava, in the lake opposite the northeast rampart, of 50 feet (15 meters), with the lower few feet more viscous than the fluid above, and consequently of presumably lower temperature. This place, like the east point which was the scene of the first test, became during the following month, February 1917, a vertical cliff over the subsided lake. The sounding was made January 23, and on January 19 the lake had been 68 feet (21 meters) below the rim and was rising approximately two feet (61^{cm}) per day, so that on January 23, the depression was 60 feet (18 meters). On February 22 the depression of the lake was 106 feet (32 meters) or 46 feet (14 meters) lower, and the day before, February 21, a cascade developed from the lake *over the submerged ledge of the lake bottom* into a cavernous recess northeast, nearly under the locality where the second sounding test was made.

In other words, the revelation of a month of subsidence was the actual outcropping through the lake at its margin of a portion of its bottom 46 feet below the lake level of the previous month. And the soundings in two places at this margin in the previous month revealed about 50 feet (15 meters) of depth. Here we have close accordance between the results of experiment and the evidence afforded by changes in time.

Incidentally this development of a cascade, at a marginal sinkhole after about 50 feet of subsidence, is nothing new, but has happened repeatedly before as one of the characteristics of subsidence. The evidence of the existence of a ledge over which such a cataract could fall (fig. 2, see section of sinkhole) has in the past been puzzling, but this is fully explained when we realize that the bottom builds up with the rising pool, that the latter is habitually shallow and that when subsidence sets in, the lake magma becomes even shallower, by sinking more rapidly than the semi-solid bench magma. The lake at such a time assumes the appearance of a rapidly streaming river.

These preliminary experiments provide a method and open the way to interesting further work relative to gas composition, viscosity and temperature in depth, direction of the subsurface currents, depth and temperature of the sinkholes themselves, differences between conduits and sinkholes, and variations in depth in the lake under different conditions and in different places. It is hoped that work along these lines will be continued as opportunity offers.

Summary of Depth and Consistency.

Apparently our two queries are tentatively answered, and the answer accords with the conception of lake magma and bench magma outlined in this paper. The liquid lake in January, 1917, had a depth of about 50 feet (15 meters), with sinkholes as downflow shafts, and conduits as inlets, distributed under it and around its margins to the number of at least eight. Secondly the lake magma, judging by its resistance to a sounding rod, was of uniform viscous consistency beneath the crust layer for approximately 40 feet (12 meters) of depth and increasingly stiff to semi-solid for the remaining 10 feet (3 meters).

CONCLUSION.

The main contributions of this paper to volcanologic science as elucidated at Kilauea volcano are as follows:

(1.) The lava column in Halemaumau pit at times of characteristic activity is duplex. It consists, first, of a main semi-solid incandescent body (bench magma), filling the whole true crater from side to side for an unknown depth, perforated vertically from below by several small shafts leading to a saucer in its summit. Saucer and shafts are filled with the minor liquid lava body (lake magma), which exhibits a more rapid convectional circulation than the main body. The lake magma contributes substance to the bench magma by overflow and accretion during a rise of the lava column. A slow circulation, which resembles isostatic adjustment in its mechanism, is discernible in the bench magma. During subsidence the lake magma sinks more rapidly than the bench magma, uncovering portions of the saucer.

(2.) Magmatic gases, circulating by convection in the lava column, are in the upper crater brought into contact with atmospheric oxygen mechanically by the circulation, which acquires a superficial acceleration presumably shallow, and the heat effect is sufficient to produce most, if not all, of the distinctive phenomena of the lake magma.

Two antithetical conditions are realized in the crater by these generalizations. The bench magma is a product seemingly of solidification *above normal viscosity*, and the lake magma a product of liquefaction *below normal viscosity*.

The normal lava column would then seem to be of a substance not commonly revealed at the surface on Kilauea volcano.* An exceedingly fascinating field of speculation is here brought into view, containing the possibility that the great *aa*, or block-lava, flows of Mauna Loa, emergent under high gas pressure and sudden release, are of the normal magma. The intense and distributive oxidation of the gases through such a flow, when released to atmospheric attack, and the ill adjusted solidification and expansion-cooling effects from within outward, added to the fact of acquisition of pahoehoe, or fluent lava, characters near the vent, when furnace conditions are established there, lend color to this view, which, however, cannot be advanced as anything more than a suggestion in the present stage of inquiry.†

The application of the principles developed by this study of Kilauea to the mechanism of other volcanoes, and the terminology of less local limitation to be adopted when stiff bench magma and reheated fluent magma are recognized elsewhere, form topics too far-reaching to be discussed in this paper. The writer has in preparation a contribution on these subjects.

The question of viscosity vs. gas reaction has been the keynote of volcanology since the eruption of Pelée in 1902, and the classification of volcanoes in genetic series is dependent on discovering, in this relation, the meaning of volcano distribution.

The crags of bench magma described in this paper are much like the steep peaks rising from the floor of many lunar craters, and the selenologists can surely help to solve the volcano problem. I am convinced from what I have seen of Kilauea that the problem will never be solved by expeditions or closet theorizings. The record of volcano process, as I have tried to show all too briefly, involves the registration of change and measurement of dimension in relation to passage of time. The only sound mode of attack is through permanent laboratories in the actual volcano field. Such laboratories, adequately equipped, have not yet been established.

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* Since this was written an extraordinary confirmation of the hypothesis here stated was afforded by the east island (fig. 8*b*), the base of which proved to be typical block-lava of the Mauna Loa variety. This prior to Feb. 17, 1917, had been *the Kilauea lake-bottom.* See Jour. Wash. Acad., 1917.

† This Journal, xliii, pp. 255–288, April, 1917.

Hawaiian Volcano Observatory, March 7, 1917.

ART. XVII.—*On the Qualitative Separation and Detection of Gallium*; by PHILIP E. BROWNING and LYMAN E. PORTER.

[Contribution from the Kent Chemical Laboratory of Yale Univ.—ccxci.]

GALLIUM, discovered in 1875 by Lecoq de Boisbaudran,[*] is found in nature most closely associated with the elements aluminium, iron, manganese, zinc, lead, and indium.[†]

Analytically it falls into the aluminium group. It may be separated from the bases giving sulphides in acid solution by hydrogen sulphide; from nickel, cobalt, zinc, manganese, the alkali earths, and the alkalies by ammonium hydroxide in the presence of ammonium chloride; and from iron, titanium, thallic thallium, uranium, indium, and the rare earths by sodium hydroxide in excess, in which reagent the hydroxide of gallium is soluble. In the ordinary course of analysis it appears in the group containing aluminium, beryllium, chromium, and vanadium. From the last mentioned two elements it may be separated by ammonium hydroxide after their oxidation to the acidic condition.

This narrows the problem of separation down to the separation from aluminium and beryllium; and the practical absence of beryllium from products containing gallium leaves the most important separation, that from aluminium.

Lecoq de Boisbaudran, in a series of articles published soon after the announcement of his discovery,[‡] suggested many methods of separation from the other elements, and recommended especially for the separation from aluminium the use as a precipitant[§] of potassium ferrocyanide in the presence of strong hydrochloric acid to about one-third of the volume of the solution.

In previous papers[‖] one of us has shown that silver, lead, zinc, copper, and indium have been successfully separated from gallium by various applications and modifications of known methods. The object of this paper is to give the results of some work upon the application of potassium ferrocyanide to the separation of gallium from aluminium and beryllium, and to describe the outcome of experiments upon the delicacy of the test for gallium by the ferrocyanide method, upon the

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[*] Compt. rend. (Paris), lxxxi, 493.

[†] Boulanger and Bardet, Compt. rend. (Paris), clvii, 718; Hartley & Ramage, Jour. London Chem. Soc., 1897. 533, 547; Hillebrand and Schnerrer, Ind. Eng. Chem., viii, 225.

[‡] Comp. rend. (Paris), xciv, 1154, 1228, 1439, 1628; xcv, 157, 410, 503, 1192, 1332; xcvi, 152, 1696, 1838; xcvii, 142, 295, 522, 623, 730, 1463.

[§] Comp. rend. (Paris), xcix, 526.

[‖] Browning and Uhler, this Journal, xli, 351, Apr. 1916; Uhler and Browning, ibid., xlii, 389, Nov. 1916.

decomposition of the ferrocyanide when formed and upon the application of strong hydrochloric acid to the separation of gallium and aluminium.

It was found that when solutions containing about 0·1 grm. of aluminium or beryllium were strongly acidified with hydrochloric acid and treated with potassium ferrocyanide no precipitation took place, while 0·001 grm. of gallium in the presence of 0·1 grm. of aluminium was easily precipitated and detected at once. Amounts of gallium as small as 0·0001 grm. could be detected after the solution had been allowed to stand an hour or so. These tests were generally made in a volume of liquid from about 5^{cm^3} to 10^{cm^3}, of which from one-quarter to one-third was strong hydrochloric acid.

With traces of zinc present, the use of potassium ferrocyanide as the precipitant may lead to erroneous conclusions, because zinc ferrocyanide is almost as readily precipitated as the gallium. The presence of zinc may be avoided by the careful application of the ammonium chloride and ammonium hydroxide process. Should, however, traces of zinc remain, we have found that they may be satisfactorily detected and removed by treating a sodium hydroxide solution with hydrogen sulphide, which removes the zinc without precipitating the gallium. The filtrate, which must still be alkaline, is acidified, and free hydrogen sulphide removed by boiling. The sulphur is oxidized by hydrogen dioxide in sodium hydroxide solution, and the boiling is continued to remove the excess of hydrogen dioxide. This solution is then acidified with hydrochloric acid and the usual ferrocyanide test may be made for gallium. Solutions were prepared containing gallium and zinc and were analyzed by the experimenter without knowledge of the content. The results follow :

Issued	Found
(1) 0·001 grm. Ga	Zn absent, Ga present
(2) 0·001 grm. Zn + 0·001 grm. Ga	Zn present, Ga present
(3) 0·001 grm. Zn	Zn present, Ga absent
(4) Distilled water	Zn absent, Ga absent
(5) 0·002 grm. Zn	Zn present, Ga absent
(6) 0·050 grm. Zn	Zn present, Ga very faint indication
(7) 0·050 grm. Zn + 0·001 grm. Ga	Zn present, Ga present
(8) 0·050 grm. Zn + 0·0002 grm. Ga	Zn present, Ga present

The faint indication of the presence of Ga in experiment (6) seemed to indicate a trace of that element in the zinc. It is of interest to note that this indication was not obtained until the solution had stood twenty minutes, while in experiment (8) the test for the gallium was unmistakable and practically immediate.

A number of reactions were investigated leading to the decomposition of the gallium ferrocyanide and the recovery of the gallium as the hydroxide, such as treatment with bromine and with nitric acid, and fusion with sodium peroxide and with ammonium nitrate. The most satisfactory proved to be fusion with ammonium nitrate, which destroyed the ferrocyanide radical, and subsequent treatment with sodium hydroxide, which precipitated the ferric hydroxide and left the gallium in solution, from which the hydroxide could be readily precipitated by adding ammonium chloride in excess and boiling.

Gooch and Havens* have shown that iron may be separated from aluminium by saturating solutions containing these elements with hydrochloric acid gas, adding ether and again saturating. The chloride of aluminium is completely precipitated by this method, and the iron remains in solution. This process was applied successfully to the separation of aluminium from gallium. The presence or absence of gallium may be determined by evaporating the filtrate to dryness on a steam bath and dissolving the residue in dilute hydrochloric acid. This solution, which is free from aluminium, may be tested for gallium by means of potassium ferrocyanide. The following series of unknown solutions was tested by this method, the aluminium chloride used having been purified by the hydrochloric acid precipitation :

Issued	Found
(1) 0·0005 grm. Ga	Al absent, Ga present
(2) 0·1 grm. Al	Al present, Ga absent
(3) 0·1 grm. Al + 0·0005 grm. Ga	Al present, Ga present
(4) Distilled water	Al absent, Ga absent
(5) 0·02 grm. Al + 0·001 grm. Ga	Al present, Ga present
(6) 0·0001 grm. Ga	Al absent, Ga present

During the first trial of this method aluminium nitrate was used in hydrochloric acid solution, and it was found that no precipitation took place with potassium ferrocyanide. After treatment with the hydrogen chloride gas and evaporation, however, an indication of gallium was found. This led to an investigation which showed that there was some gallium present in the aluminium nitrate, but that the nitric acid formed by dissolving it in hydrochloric acid was sufficient to prevent the precipitation of the gallium as the ferrocyanide. In the evaporation process the nitric acid is destroyed and the test becomes very delicate.

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* This Journal, ii, 416, 1896.

An investigation was then made of the effect of nitrates in general on ferrocyanides. It was found that when one drop of potassium ferrocyanide is treated with 0·4 grm. of ammonium nitrate in the presence of 6^{cm^3} of 1 : 2 hydrochloric acid it is oxidized completely to the ferricyanide within two minutes, as may be shown by the use of a ferric salt and a ferrous salt. If 0·2 grm. of ammonium nitrate is used under the same conditions, the ferrocyanide is broken up in less than an hour, while if only 0·1 grm. of ammonium nitrate is used a longer time is required, but complete oxidation finally takes place. Other experiments showed that 0·0001 grm. of gallium cannot be precipitated as the ferrocyanide in 5^{cm^3} of dilute hydrochloric acid in the presence of 3 drops of dilute nitric acid, whereas it is readily precipitated in the absence of it. It was further found that if 0·0001 grm. of gallium is precipitated and 1^{cm^3} of dilute nitric acid is added, the precipitate is decomposed and dissolved within forty-five minutes. It is thus seen that in detecting gallium by the ferrocyanide method care must be taken to have no nitrates or nitric acid present, and that these may be successfully removed by evaporation with hydrochloric acid.

June, 1917.

Art. XVIII.—*On the Calibration and the Constants of Emanation Electroscopes;* by O. C. Lester.

In the summer of 1914 the author began a fairly exhaustive investigation of the radioactivity of the numerous mineral springs found chiefly in the mountainous region of Colorado. Most of the work was done in the field with instruments of the usual types constructed in our laboratory. However, owing to certain peculiar conditions encountered in Colorado, it was found necessary to make a careful study of the behavior of the apparatus employed and to determine the significance of certain calibration constants. Further emphasis was given to this study when it was found often practically impossible to compare the work of different observers not only in different countries but even in the same country. This is particularly true of the work of observers who express their results in terms of the mache unit. Such a state of affairs ought not to exist in any branch of science and an attempt is here made to point out the reasons for the discrepancies, the remedy for which is suggested by a study of the calibration constants and the corrections which should be applied in the use of emanation electroscopes.

The emanation electroscopes used consisted of several ionization chambers of different sizes, to each of which could be attached the same electroscope head, including microscope, leaf, and electrode. In general the apparatus is similar to that described by S. C. Lind* except that there is only one insulation plug instead of two. Its essential features are shown in fig. 1. I is an air-tight cylindrical brass ionization chamber having stop cocks V near the top and bottom. Altogether four such chambers were used, all of them taking the same electroscope head but each having its own electrode E. The inside dimensions of the chambers and the outside dimensions of their electrodes are given in the following table. The electrodes are made of light brass tubing capped at each end.

Table I.

I	Length, cm.	Diam., cm.	Electrodes	
			Length, cm.	Diam., cm.
No. 2	24·8	11·1	19	1·6
No. 3	25·1	15·6	19·6	1·6
Nos. 6 & 7	21·2	13·6	13·1	1·6

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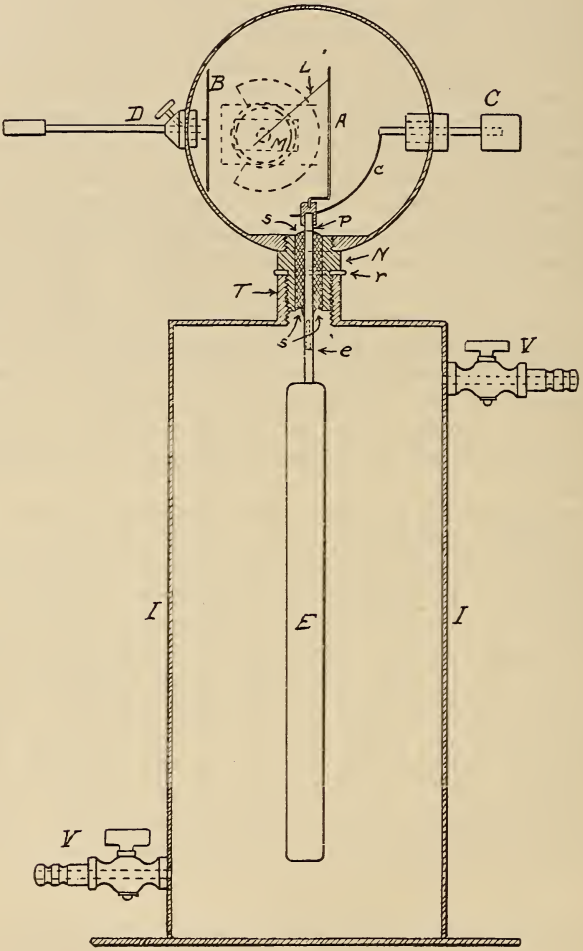
* U. S. Bureau of Mines, Tech. Paper 88, Mineral Tech. 6, p. 17, 1915.

Fig. 1.



Most of the work was done with vessels No. 2 and No. 3, the latter being the most sensitive of the four. Nos. 6 and 7 were constructed after the experience of the first summer, and are, on the whole, the most satisfactory. They were designed to have approximately a volume of 3 liters and a distance of 6^{cm} between the electrode and the outer wall.

Each electroscope consisting of the common head and an ionization chamber with its appropriate electrode was carefully standardized a number of times by means of known quantities of radium emanation obtained from pitchblende as suggested by Boltwood.* For this purpose some finely-ground pitchblende giving $2{\cdot}10 \times 10^{-10}$ curie of radium emanation per mg. on direct solution was kindly furnished by Richard B. Moore of the United States Bureau of Mines, Denver. The emanation from several milligrams of pitchblende was introduced into the electroscope and the activity observed every few minutes until it reached its maximum. In each case a complete and typical activity-time curve was platted. Then from the known amount of emanation present and the observed maximum activity, that fraction of a curie which will produce a movement of the leaf of 1 div. per min. at maximum activity can be calculated. This fraction of a curie is called the *constant of the electroscope.*

Numerous trials show that readings must always be taken between the same points on the scale or symmetrically about the middle point of the portion used in calibration. Thus if the electroscope is standardized for the portion of the scale lying between 70 and 30, the same maximum activity will be found and hence the same constant will hold for readings taken between 60 and 40 but not, for example, if they are taken between 70 and 40 or between 60 and 30. The shorter distance is sometimes convenient when dealing with weak activity.

The constants of each ionization chamber as determined at Boulder at a pressure of $62{\cdot}5^{cm}$ and at a temperature of about 22°C are $2{\cdot}34 \times 10^{-10}$ curie for No. 2, $1{\cdot}89 \times 10^{-10}$ curie for No. 3, and $2{\cdot}07 \times 10^{-10}$ curie for Nos. 6 and 7. These values are the means of six or more concordant determinations for each chamber. Strictly speaking these constants hold only for a given pressure and temperature in the case of chambers whose volume or air density is not large. As the springs examined are at elevations varying approximately from 5,000 ft. to 10,000 ft. which causes changes in pressure from about 64^{cm} to 53^{cm} the constants given above were of little value in the field work. This made necessary an investigation of the way in which the "constants" varied with the pressure. Previous investigations on the variation of ionization with pressure such as those of

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* This Journal (4), vol. xviii, p. 378, 1904.

Rutherford* and Owens† do not fit the conditions of the present work as they used radiations from layers of solid substances in vessels of wholly different shape. The investigations of W. Wilson‡ C. T. R. Wilson§, McLennan and Burton‖ and Patterson¶ deal with the general question, but again under different conditions. Furthermore they are not all in agreement.

In order therefore to find how the activity at its maximum varied with the pressure when emanation was mixed with air in cylindrical vessels and incidentally also to see how nearly the maxima were proportional to the amount of emanation present, a series of tests were run in each chamber. The procedure followed was similar to that described by Madam Curie.** However, what was here sought was a relation which would give the "constant" corresponding to any barometric pressure and thus permit the reduction of the results of observation immediately to curies, rather than a correction term to be applied to the observed ionization current as in Madame Curie's procedure.

After the pressure in the chamber had been reduced to a few centimeters a known amount of emanation was introduced. During this operation the pressure increased to 10^{cm} or 20^{cm}. After the electroscope had stood charged for a little more than three hours the activity was measured at various pressures determined by a mercury monometer. The relations between pressure and activity in vessel No. 2 may serve as a typical example. These relations for varying amounts of emanation are shown in Table II and by curves in fig. 2. The figures in the body of the table are maximum activities in divisions per minute taken from the curves. In fig. 2 the actual experimental data are represented by the continuous lines.

TABLE II.

Mgs. Pitchblende	400	500	600	700	800	Pressure in mm.
5·06	3·14	3·82	4·40	4·86	5·21	
10·55 ?	6·42	7·73	8·78	9·42	9·71	
15·35	9·61	11·49	13·01	14·02	14·58	
20·57	13·10	16·00	17·90	19·18	19·95	
25·20	15·84	19·31	22·19	23·93	24·93	

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* Phil. Mag., vol. xlviii, p 109, 1899.
† Ibid., p. 360.
‡ Ibid., (6), vol. xvii, p. 216, 1909.
§ Proc. Roy. Soc., vol. lxix, p. 277, 1901.
‖ Phys. Rev., vol. xvi, p. 184, 1903.
¶ Phil. Mag., (6), p. 231, 1903.
** Traité de Radioactivité, vol. i, p. 286.

FIG. 2.

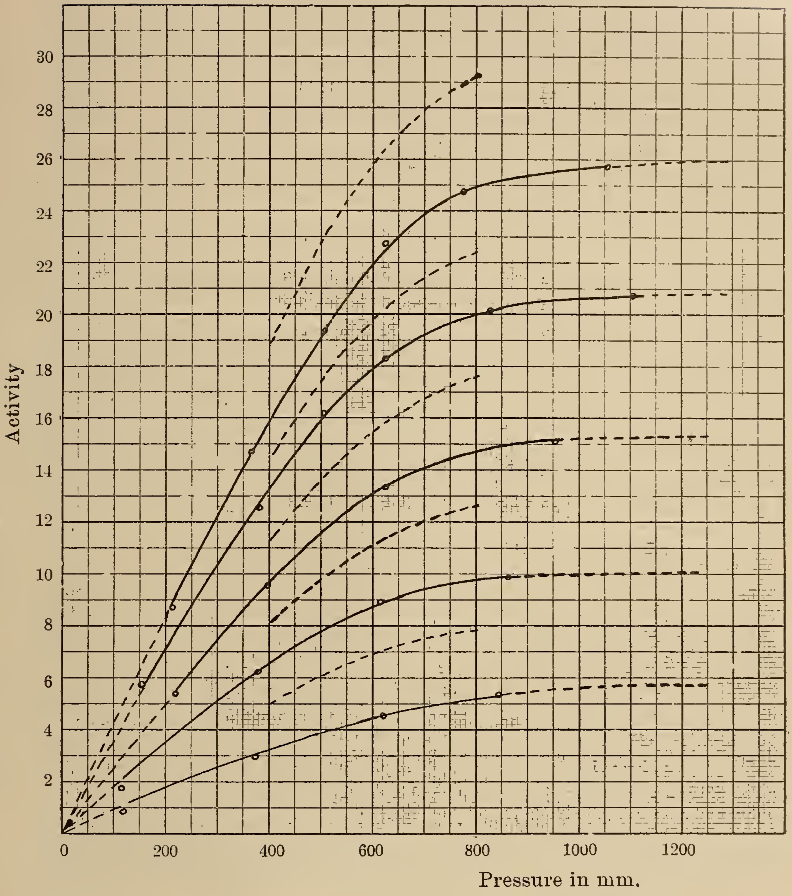

TABLE III.

Pressure in mm. . . .	400	500	600	700	800
	0·620	0·755	0·869	0·960	1·03
	0·608	0·732	0·832	0·892	0·920
	0·626	0·748	0·848	0·913	0·950
	0·637	0·776	0·871	0·934	0·971
	0·628	0·766	0·880	0·950	0·990
Mean	0·624	0·756	0·860	0·930	0·972

Table III shows that the ratio of the activity to the amount of emanation is approximately constant at a given pressure, at least for the range of activity here examined. There is good reason to suspect an error in the weight for the second sample.

The maximum activity multiplied by the "constant" of the electroscope and divided by the volume of water or gas taken gives the number of curies per unit volume which is a fixed quantity. However, since the maximum varies with the pressure the "constant" must vary also, but we should always have activity × constant = curies or

$$mk = \mathrm{C} \qquad (1)$$

which is the familiar equilateral hyperbola or Boyle's Law equation.

Now the constants of each chamber are known accurately for a temperature of 22° C and a pressure of $62{\cdot}5^{\mathrm{cm}}$. From the curves of fig. 2 we find the corresponding mean maximum activities per milligram of pitchblende to be 0·881 divisions per minute for chamber No. 2 and 1·077 division per minute for chamber No. 3. Hence the constant $\mathrm{K_p}$ for any pressure p is found from

$$\begin{aligned} &\mathrm{K_pM_p} = 2{\cdot}053 \times 10^{-10} \text{ for chamber No. 2.} \\ \text{and } &\mathrm{K_pM_p} = 2{\cdot}036 \times 10^{-10} \text{ `` `` `` 3.} \end{aligned} \qquad (2)$$

Where $\mathrm{M_p}$ denotes the mean maximum activity per milligram at the given pressure.

The constant-pressure curve for chamber No. 2, shown in fig. 3, is obtained from the above equation. The values of M are the mean values from Table III. It is evident that even the daily variation in barometric pressure is often sufficient to make a decided difference in the value of the "Constant."

Strictly speaking the curve of fig. 3 gives the constant at various pressures for a temperature of 22° C. Changes in temperature will effect the constant also in so far as they affect the density of the gas in the ionization chamber. But since a change of about one per cent only is produced by a change of 3° C in temperature this source of error may usually be neglected.

In the actual work of testing waters and gases a common practice is to run the observations for a short time and then calculate the maximum activity. Tests on such vessels as those used in our work fully justify this procedure. From the curves of a number of calibration tests run for three and a half hours the activities were read at ten minute intervals from 10 min. to 90 min. These values expressed as percentages of the maximum formed always a closely agreeing scale, for a given chamber, over a wide range of activity. For example, the mean of seven such percentage scales was obtained for chamber No. 2. The largest variation of a single percentage from the mean was 1·6 per cent and most of them agreed more closely than 1 per cent. Actual trial showed that after 40 min. or 50 min. the maximum could be calculated with practically the same exactness that it could be observed. Such a scale is therefore among the most useful constants of the electroscope.

FIG. 3.

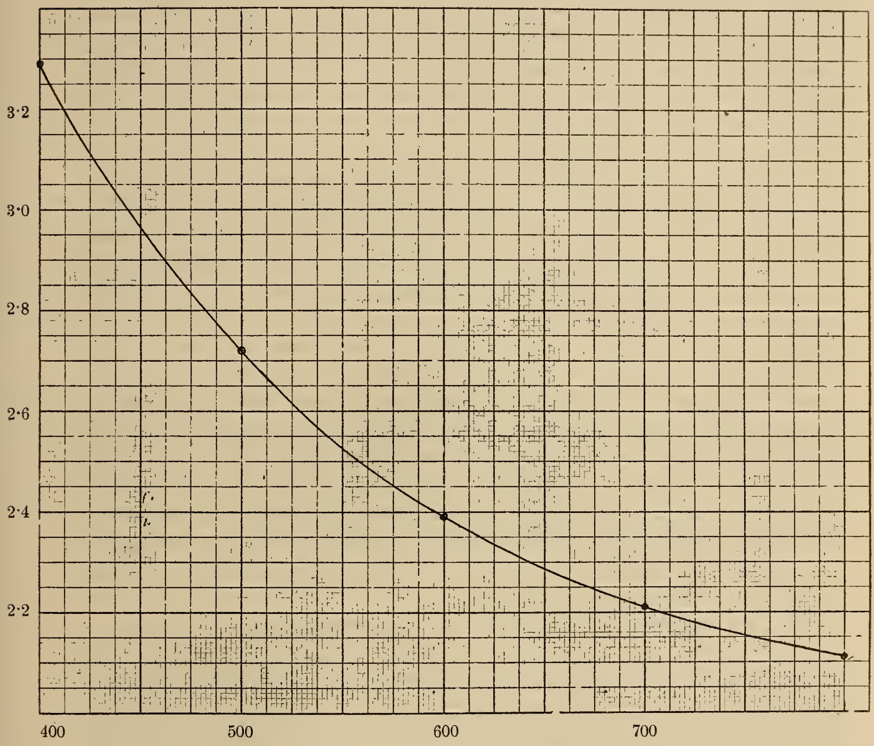

FIG. 3. Constant-pressure curve.

When activities are expressed in terms of the ionization current or in terms of units based upon the ionization current, such as the Mache unit, more constants of the electroscope must be determined. These constants include the electrical capacity, the drop in potential per division of the eyepiece scale, the percentage of the maximum activity due to the active deposit, and the amount of ionization absorbed by the walls of the chamber.

The capacities of the electroscope were measured by the divided charge method. A condenser made of two coaxial cylinders, having cylindrical guard rings and a calculated capacity of 25^{cm} was used as a standard. The mean results are $8{\cdot}4^{cm}$ for chamber No. 2, $7{\cdot}8^{cm}$ for No. 3, and $8{\cdot}0^{cm}$ for Nos. 6 and 7. During a visit in the summer of 1915 Professor J. C. Hubbard very kindly checked some of these measurements by a different method.

The calibration of the eyepiece scale in volts gave quite accurately straight lines for each chamber. The number of volts per division varied from 1·22 to 1·35. The average potential used on the leaf system, over the working part of the scale, was about 340 volts.

The per cent of activity due to the active deposit at maximum activity was determined for each ionization chamber in several different ways; by projecting backward the activity-time curves to the axis of zero time; by projecting backward the curves representing the decay of the active deposit when maximum activity had been reached; by determining graphically and by calculation the maximum activity due to Ra. C. alone and from this estimating the total activity due to the deposit; by calculation from the formula of Curie and Duane* and by tables.† The various methods gave fairly concordant results for each chamber. Four different methods gave for chamber No. 2 the percentages 42·5, 41·9, 42·7 and 43·2. While each of these numbers is the mean of several determinations so close an agreement was scarcely to be expected and is no doubt accidental. The values adopted were 42 per cent for chamber No. 2, 46 per cent for chamber No. 3 and 44·3 per cent for chambers No. 6 and 7.

Among persons interested in the physiological effects of radioactivity and especially among those interested in the therapeutic properties of mineral waters, the mache unit is widely used as a unit of radio-activity. In spite of the fact that this unit is difficult of definition and comparison, and, in the author's opinion, is needless, its extensive use gives it an importance that can not be ignored.

The *mache unit* is defined as 1000 times the saturation ionization current due to one curie of emanation without disintegration products when all the radiation is absorbed in the air of the ionization chamber.‡ In the case of the chambers under discussion it is evident from their dimensions, the density of

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* C. R., vol. cxxxvi, p. 304, 1903.

† Duane, Jour. de Phys. (4), vol. iv, p. 605, 1905. Duane & Laborde, Le Radium, vol. vii, p. 162, 1910. Mme. Curie, Traité de Radioactivité. vol. ii, p. 338.

‡ H. Mache and St. Meyer, Rad. in Biol. und Heilk., vol. i, p. 350, 1912. Gockel, Radioactivität von Boden und Quellen, p. 82.

the air in them, and the difference of potential between the electrodes and walls that there was neither opportunity for the production of all the ions possible nor a sufficiently strong electric field to remove all those that were produced. This makes no difference for measurements in curies* if the chambers have been properly calibrated. However, it is possible from the work of Duane† and of Duane and Laborde‡ to calculate for such chambers as were used the relation between the maximum ionization current actually observed and the number of curies which would produce it if the radiations had been completely absorbed and saturation had obtained.§ In this way it was found that the loss, due to lack of range and saturation, in the ionization current upon which the mache unit is based, amounted to 48 per cent in chamber No. 2, to 46·7 per cent in chamber No. 3, and to 44 per cent in chambers No. 6 and 7. Hence in all the chambers used except No. 2 it happens that the loss in activity due to the above-mentioned causes is almost exactly counterbalanced by that added by the active deposit.

The ionization current in electrostatic units is given by

$$i = \frac{q\,cm}{300\,t} \qquad (3)$$

where q is the drop in potential in volts per scale division, m is the number of scale divisions passed over by the leaf in t seconds, and c is the electrical capacity of the instrument. In the case of chamber No. 2, $q = 1·22$, $C = 8·4$, and if m is the number of divisions per minute passed over by the leaf at maximum activity due to emanation from v liters of water or gas (3) becomes

$$i = \frac{(1·22)(8·4)}{(300)(60)} \cdot \frac{m}{v} = 0·5693\ 10^{-3}\ \frac{m}{v}\ \frac{\text{E.S.U.}}{\text{liter}} \qquad (4)$$

When corrected by Duane's factor for the absorption due to the walls of the vessel and for the activity due to the decay products according to the percentages given above (4) becomes

$$\text{I} = 0·635\ 10^{-3}\ \frac{m}{v} \qquad (5)$$

where I denotes the total ionization current which could be produced by the emanation alone if all its radiation was absorbed in air.

Equation (5) holds for a barometric pressure of $62·5^{\text{cm}}$ only and the observed values of m must be corrected by a factor b

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* W. R. Barss, this Journal, vol. xxxiii, p. 546, 1912.

† Loc. cit. ‡ Loc. cit.

§ G. Berndt, Ann. der Phys. (4), vol. xxxviii, p. 958, 1912. See also Gockel, loc. cit., Chap. VIII, and H. Mache and St. Meyer Phys. Zeitschr., vol. xiii, p. 320, 1912.

which varies with the pressure in exactly the same way as the "constant" expressed in curies. The values of b for various pressures may be taken from a curve easily derived from the activity-pressure curves (fig. 2) or better from the constant-pressure curve (fig. 3). The latter curve and the b-curve have exactly the same form since the value of b is directly proportional to the value of the "constant" at a given pressure. For chamber No. 2 the values of b at pressures of 40, 50, 60, 70 and 80 cm., are respectively 1·41, 1·166, 1·025, 0·949, and 0·905. On putting in the pressure factor equation (5) becomes

$$I = 0{\cdot}635 \times 10^{-3}\, b\, \frac{m}{v}. \qquad (6)$$

This again must be multiplied by 1000 in calculating mache units. Hence from the ionization current

$$\text{Mache units} = 0{\cdot}635\, b\, \frac{m}{v}. \qquad (7)$$

But from the generally accepted relation between the mache unit and the curie and from the calibration of the chamber directly in curies we have

$$\text{Mache units} = (2{\cdot}7 \times 10^9) \times (\text{curies}) = 2{\cdot}7 \times 10^9\, k\, \frac{m}{v} \qquad (8)$$

Where k is the constant of the electroscope defined by equation (2).

In Table IV are given a few results of the calculations in mache units by both methods for chamber No. 2. The data given are based upon observations taken in the field.

TABLE IV.

				Mache units	
Bar. Pr., cm.	$\frac{m}{v}$	$K \times 10^{-10}$	b	From eq. (7)	From eq. (8)
64	7·965	2·307	0·989	5·0	4·97
60	40·60	2·39	1·025	26·40	26·20
"	5·58	"	"	3·63	3·60
57·3	5·245	2·462	1·0575	3·64	3·60
54·35	51·60	2·557	1·099	36·0	35·61
53·6	267·70	2·583	1·110	188·7	186·7

It will be noted that the values computed from equation (7) run slightly higher than those from equation (8). If we equate the two expressions for mache units writing x in place of $2{\cdot}7 \times 10^9$ we get

$$x = \frac{0{\cdot}635\, b}{k} \qquad (9)$$

If we now substitute corresponding values of b and k from the above table and compute the several values of x we find that they agree closely and give as a mean value

$$x = 2{\cdot}726 \times 10^9 \qquad (10)$$

which is the relation between the mache unit and the curie necessary for exact agreement between the results by the two methods if we assume that the saturation ionization current is accurately determined by the constants found and the corrections applied. This value is about half way between the theoretical value $2{\cdot}75 \times 10^9$ sometimes used and the value $2{\cdot}7 \times 10^9$ usually taken.

To be exact, $2{\cdot}75 \times 10^9$ gives the theoretical relation between the mache unit and the curie on the Rutherford-Boltwood standard. According to Rutherford* it is $2{\cdot}89 \times 10^9$ on the International Standard and Mache and St. Meyer† give it as $2{\cdot}67 \times 10^9$ on the Vienna Standard. Of course this relation is nothing but the saturation ionization current due to one curie of emanation without disintegration products, multiplied by a thousand.

Among investigations in the radioactivity of mineral springs, and in particular among those on European mineral springs, there can be found often the results of several observers on the same water or gas. It is rarely that these results agree closely and those of one observer may range anywhere from many times to a fraction of those given by another. With precautions field work can be made practically as accurate as that done in the laboratory. Hence discrepancies in the work of equally careful observers have often been attributed to variations in the activity of the source. On the other hand, there are springs which have shown no appreciable variation in activity when examined systematically at different times of the year by the same observer using the same apparatus. Undoubtedly some springs do vary in activity but the question of their variability and even the amount of their activity can scarcely be determined from the work of different observers so long as there is no uniformity in standards, in methods, and in the nature and the number of the corrections to be applied to the observations. This is particularly true of results expressed in mache units based upon ionization currents. In many cases mache units are apparently calculated from the observed ionization current and not from the saturation ionization current when all radiation is absorbed in the air of the chamber. In the first case the mache unit is dependent upon the dimensions of the particular apparatus used and upon the potential applied

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* Phil. Mag. (6), vol. xxviii, p. 320, 1914.

† Phys. Zeitschr, loc. cit.

to the insulated system which is clearly not intended by its definition.

For the reasons just mentioned the work of European observers in general presents an almost hopeless confusion when accurate comparisons are attempted. It is true that much work had been done before suitable units and methods were devised, and we find therefore many results expressed in terms of the fall of the leaf in volts per unit time or in units even more arbitrary. Such results can not be compared with other work. Still other units used are the Milligram-Second, Milligram-Minute, Gram-Second, etc., meaning the amount of emanation produced by a given amount of radio-active substance in the specified time. The substance is usually the element radium or a radium salt, and when this is specified, as well as its degree of purity, measurements based upon such units can be reduced to curies.

Most European observers, outside of France and England, express their results in terms of the mache unit. Generally the corrections which have been made are clearly stated, but not always. Furthermore the correction for absorption by the walls of the chamber (Duane's factor) has usually been omitted in work where most of the other corrections have been applied. This has been pointed out by Berndt* in an elaborate series of calculations undertaken with the aim of making possible the comparison of the results of different observers. He shows that, depending upon the size of the ionization chamber, the correction for absorption alone may amount to from 10 per cent to 155 per cent.

A given instrument can be calibrated simply and accurately in terms of a known quantity of radium emanation. If the mache unit is to be retained it would seem easier and more accurate to reduce results measured in curies to this unit by means of the theoretical relation between them, than to calculate mache units from the ionization current which involves the determination of several more constants and the application of troublesome corrections. As has been shown above, the two methods, when all corrections are applied, give identical results within the limits of experimental error.

For the drawings which accompany this article and for efficient aid in securing the data upon which it is based the author wishes to express his indebtedness to Mr. J. H. V. Finney, instructor in Physics in the University.

Hale Physical Laboratory.
University of Colorado,
Boulder, Colo.

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* Loc. cit.

ART. XIX.—*Measurements of the Radioactivity of Meteorites;* by TERENCE T. QUIRKE and LEO FINKELSTEIN.

ALTHOUGH the determinations of the radioactivity of various rocks are now numerous, the radioactivity of meteorites is known for only two varieties of meteorites and for only three meteorites. The meteorites examined were tested by Strutt* His results are :—

Locality	Material	Variety	Quantity Taken	Ra per gm. material
Dhurmsala	Stony Met.	Intermed. Chondrite	50 gm	$1{\cdot}12 \times 10^{-12}$ gm
Thunda	Iron Met.	Medium Octahedrite	60	0
Staunton Augusta Co. Va.	" "	"	32	0
Santa Catarina, Brazil	Iron		50	0
Disco Island,	Native Iron		200	$0{\cdot}424 \times 10^{-12}$ gm

Of these materials Santa Catarina is generally accepted to be terrestrial iron and not a meteorite. Our information in regard to the radioactivity of meteorites could be summarized as follows; one intermediate chondrite, a stony meteorite, has a radium content of $1{\cdot}12 \times 10^{-12}$ gm. Ra. per gm. meteorite, and two medium octahedrites, iron meteorites, are free of radioactivity.

Through the generosity of Dr. Oliver C. Farrington of the Field Museum of Natural History, the authors had the following varieties of meteorites placed at their disposal :—fifteen aërolites, or stony meteorites, one chladnite, two eukrites, two white chondrites, one carbonaceous chondrite, one black chondrite, three spherulitic chondrites, three spherulitic crystalline chondrites, one crystalline chondrite, two siderolites or stony-iron meteorites, five iron meteorites, one finest octahedrite, two medium octahedrites, one coarse octahedrite, and one normal hexahedrite.

Chemical Preparation of the Materials

The iron meteorites were dissolved in hot conc. HCl and HNO_3 in a platinum dish. All the stony and stony-iron meteorites were treated consistently. Stony meteorites differ from igneous rocks in that most of them contain a considerable amount of metallic iron and nickel. Each sample was ground

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*Strutt, Proc. Roy. Soc, A, lxxvii, p. 480, Mar. 1916.

to sizes between 100 and 200 mesh, and boiled with conc. HCl and HNO_3. The acid solution was filtered, and set aside, and later added to the residue. The residue was fused with 20 gm K_2CO_3, 20 gm Na_2CO_3, 2 gm $Na_2B_4O_7$, and 0·5 gm $Ba(OH)_2$.* The fused mass was broken up, and dissolved in 200^{cc} water. The solution was filtered, and the residue added to the acid solution in which the metal portion of the meteorite had been dissolved, and boiled until solution was complete. Sulphuric acid was added to the boiling solution, and the barium sulphate filtered off. The barium was separated from the aqueous solution in the same way. The barium sulphate precipitates were combined, and fused with 10 gm $KHSO_4$ in a hard glass test tube. The tube was provided with a rubber stopper fitted with two glass tubes. One of the tubes reached nearly to the bottom of the test tube, and the other just penetrated the stopper. Each tube was bent at right angles to the fusion tube, and the exposed ends which were drawn out to fragile points were sealed.

The granite and diorite samples were treated in the same way, except that the preliminary treatment with acids was left out. In the treatment of the granite it was found necessary to use hydrofluoric acid to get rid of the silica in the residue.

Purification of Reagents

One of the principal sources of error apt to be introduced is the use of reagents which might contain appreciable amounts of radium. This is especially true of the barium salts. Blank tests were made on the reagents used to determine their radium content. Only the barium salts were found to contain enough radium to make the radioactivity of the charge appreciable. It was therefore essential that the barium salts be completely freed from radium. This was done by fractional crystallization as hydroxides according to the method of McCoy†. The barium chloride was dissolved in a special flask, and a 50 per cent sol. KOH which had been previously freed from carbonates by addition of barium was added. The solution was cooled in ice and allowed to crystallize. The mother liquor was filtered off, and discarded. After six crystallizations the barium hydroxide was found to be completely freed from radium.

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* In some preliminary experiments, each of the stony meteorites received from Ward's Natural Science Establishment, and the rock samples, laboratory numbers 105, 108, 109, and 110, were fused with 0·5 gm of $BaCO_3$ instead of 0·5 gm $Ba(OH)_2$. It was found that this brought the radioactivity of the charge up to $0{\cdot}34 \times 10^{-12}$ grams of radium element. However, with the use of radium-free $Ba(OH)_2$ the radioactivity of the charge was found to be imperceptible.

† U. S. Patent No. 1,103,600 (1914).

Estimation of Radium

The estimation of radium is usually carried out in one of two ways:

1. By the gamma ray method.
2. By the emanation method.

The gamma ray method is entirely unsuited for measuring minute quantities of radium. The emanation method, however, can be used to measure extremely small amounts of radium with a fair degree of accuracy. When radium decomposes, the first disintegration product is radium emanation. If the radium-containing substance is kept in a sealed tube, the emanation reaches its equilibrium amount in about thirty days. The amount of emanation N present at any time t is:

$$N = N' (1 - e^{-\lambda t})$$

where N' is the maximum amount of emanation, and λ a constant.

The emanation can be separated completely from the solution or fused material by bubbling air through the liquid. The air may be introduced into a suitable electroscope, and the ionization due to the included emanation measured.*

Standardization of the Electroscope

The electroscope has been in use for a number of years, and has a very slow natural leak. It consists of a brass cylinder 13^{cm} high, and 9^{cm} in diameter. The gold leaf is supported by an ∟ shaped brass strip which is insulated by an amber pillar. The leaf is charged by a battery of small dry cells giving 400 to 500 volts. The movement of the gold leaf is observed with a low power microscope, with a scale in the eyepiece.

The electroscope was standardized by means of standard radium solutions furnished by Dr. H. N. McCoy. Three different solutions were used:

No. 1—$3{\cdot}78 \times 10^{-11}$ gm Ra element
No. 2—$3{\cdot}78 \times 10^{-11}$ " " "
No. 3—$3{\cdot}78 \times 10^{-12}$ " " "

The standards were made by diluting a standard radium solution, and adding a few cc. of dil. HCl.

The electroscope was first evacuated, and dry air from outdoors admitted. The natural leak was then determined by timing the rate of discharge over five divisions of the scale. The electroscope was then evacuated, and the standard which had been sealed for over a period of thirty days was inserted in the air line. The ends of the sealed tubes which had been

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* Cf. Herman Schlundt, 26th meeting, Am. Electrochem. Soc., 1914. H. M. Plum, Jour. Am. Chem. Soc., vol. xxxvii, p. 1811, 1915.

drawn out to fragile tips were broken, and air allowed to bubble through the solution, and pass into the electroscope. The activity rapidly increases and reaches a maximum after three hours. This is due to the accumulation of RaA, RaB, and RaC.

The rate of discharge was measured when the maximum had been reached, that is after an interval of three hours. During this time the leaf was kept charged. The leak was measured in exactly the same way as in the case of the natural leak.

Estimation of Radium in the Sample

The natural leak was determined before each measurement. The tube containing the fused material which had been sealed for a period of thirty days was inserted in the air line. The tips at the ends of the tube were broken off, and the tube heated. When the material had liquefied, air was allowed to bubble through into the electroscope.

After the electroscope was filled, the time of discharge after an interval of three hours was measured in the same manner as the standard. The amount of radium in the sample was evaluated from:

$$\text{Amt. of Ra} = \frac{t_s\,(A_f\text{-}t_f)}{t_f\,(A_s\text{-}t_s)} \times S.$$

where : t_s = time of discharge of standard. (Equilib. amt. Ra)
t_f = " " " " unknown. (" " ")
A_s = natural leak of standard.
A_f = " " " unknown.
S = amount of radium in standard.

The results show that the radioactivity of stony meteorites varies considerably. The meteorite, Juvinas, contains $2{\cdot}17 \times 10^{-12}$ gm of radium element to a gram of meteorite, and the meteorite, Farmington, contains only $7{\cdot}34 \times 10^{-14}$ gm of radium element to a gram of meteorite. Including the determination for the radioactivity of Dhurmsala made by Strutt, seventeen stony meteorites have an average radioactivity of $7{\cdot}61 \times 10^{-13}$ gm of radium to a gram of meteorite. Excluding Dhurmsala, sixteen meteorites have an average radioactivity of $7{\cdot}39 \times 10^{-13}$ gm of radium to a gram of meteorite. Two iron-stone meteorites, Estherville and Llana del Inca, have an average radioactivity equivalent to $6{\cdot}88 \times 10^{-13}$ gm of radium to a gram of meteoritic material. Five of the seven iron meteorites examined are non-radioactive, so far as can be determined, i.e., they do not exceed 10^{-14} grams of radium per gram of meteorite. The other two iron meteorites, Toluca, and Coahuila, seem to be radioactive; Toluca decidedly so, and Coahuila so feebly radioactive

RADIUM CONTENT OF SPECIMENS.

Lab. No.	Name and Locality	Date of Discovery	Class	Variety	Donor	Wgt. of sample	Gms. of Ra el, per gm sample
220	Bishopville, Sumter Co., S. C.	fell Mar. 15, 1843.	Stone	Chladnite	F *	8·66 gm	$5{\cdot}01 \times 10^{-13}$
205	Juvinas, Ardiche, France.	fell June 15, 1821.	Stone	Eukrite	F	12·52	$2{\cdot}17 \times 10^{-12}$
208	Stannern, Moravia, Austria.	fell May 22, 1808.	Stone	Eukrite	F	10·71	$2{\cdot}41 \times 10^{-13}$
204	Mauerkirchen, Upper Austria.	fell Nov. 20, 1768.	Stone	White Chondrite	F	14·62	$1{\cdot}45 \times 10^{-12}$
209	Möcs, Transylvania, Austria.	fell Feb. 3, 1882.	Stone	White Chondrite	F	6·00	$3{\cdot}12 \times 10^{-13}$
206	Mocs, † Transylvania, Austria.	fell Feb. 3, 1882.	Stone	White Chondrite	F	4·40	$5{\cdot}67 \times 10^{-13}$
203	Pultusk, Poland, Russia.	fell Jan. 30, 1868.	Stone	Gray Chondrite	F	11·33	$1{\cdot}28 \times 10^{-12}$
214	Farmington, Washington Co., Kans.	fell June 25, 1890.	Stone	Black Chondrite	F	11·31	$7{\cdot}34 \times 10^{-14}$
217	Mighei, Elizabethgrad, S. Russia.	fell June 9, 1889.	Stone	Carbonaceous Chondrite	F	12·32	$8{\cdot}21 \times 10^{-13}$
201	Hessle, Upsala, Sweden.	fell Jan. 1, 1869.	Stone	Spherulitic Chondrite	F	8·77	$1{\cdot}06 \times 10^{-12}$
202	Forest City, Winnebago Co., Iowa.	fell May 2, 1890.	Stone	Spherulitic Chondrite	F	10·62	$8{\cdot}36 \times 10^{-13}$
207	Tabory, Ochansk, Perm. Russia.	fell Aug. 30, 1887.	Stone	Spherulitic Chondrite	F	11·56	$1{\cdot}8 \times 10^{-13}$
216	Beaver Creek, W. Kootenai Dist. B. C.	fell May 26, 1893.	Stone	Crystalline Spherulitic	F	9·98	$3{\cdot}12 \times 10^{-13}$
219	Holbrook, Navajo Co., Arizona.	fell July 19, 1912.	Stone	Crystalline Spherulitic	F	14·08	$5{\cdot}12 \times 10^{-13}$
200	Saline, Sheridan Co., Kans.	fell Nov. 15, 1898.	Stone	Crystalline Spherulitic	F	9·68	$1{\cdot}33 \times 10^{-12}$
215	Long Island, Phillips Co., Kans.	found 1894.	Stone	Crystalline Chondrite	F	12·02	$3{\cdot}20 \times 10^{-13}$
218	Estherville, Emmet Co., Iowa.	fell May 10, 1879.	Iron-Stone	Mesosiderite	F	16·36	$3{\cdot}97 \times 10^{-13}$
108	Llana del Inca, Atacama, Chile.	found 1888.	Iron-Stone	Mesosiderite	W	2·66	$9{\cdot}80 \times 10^{-13}$
213	Mukerop, Gibeon, Gt. Namaqualand, S. A.	found 1899.	Iron	Finest Octahedrite	F	10·24	0
210	Tonganoxie, Leavenworth, Co., Kans.	found 1886.	Iron	Octahedrite	F	14·95	0
212	Toluca, Xiquepelco, Toluca, Mexico.	found 1890.	Iron	Medium Octahedrite	F	9·01	$2{\cdot}13 \times 10^{-13}$
107	Canon Diablo, Coconino Co., Ariz.	found 1891.	Iron	Coarse Octahedrite	W	10.42	0
211	Coahuila, State of Coahuila, Mexico.	found 1837.	Iron	Normal Hexahedrite	F	10·06	$7{\cdot}69 \times 10^{-12}$
110	Whiskey Lake, Ontario, Canada.		Granite of Precambrian age.			10·00	$3{\cdot}20 \times 10^{-12}$
105	Espanola, Ontario, Canada.		Diorite of Keweenawan age.			10·00	$1{\cdot}22 \times 10^{-12}$

* F stands for Field Museum of Natural History.
W stands for Ward's Natural Science Establishment.

† The two determinations of the radioactivity of Möcs do not agree. However, the two samples were obtained from different specimens, and were not ground or mixed together. The difference in radioactivity may be due to a lack of uniformity in the distribution of radium throughout the meteorite.

that its activity may be due to local siliceous inclusions. However, Strutt found much greater activity in the native iron of Greenland, and it may be that radioactivity is not foreign to many of the so-called iron meteorites. It is clear, nevertheless, that most of the iron meteorites are free of radioactivity, and the siliceous meteorites are all radioactive, so far as known.

Summary

1. A method for the estimation of radium in rocks and meteorites has been described.
2. The radium content of twenty-two meteorites not heretofore analyzed has been determined.
3. From the data it appears that the average stony meteorite is considerably less radioactive than the average igneous rock, probably less than one-fourth as radioactive as an average granite, and that the metallic meteorites are almost free of radioactivity.

The authors are indebted to Professor Herbert N. McCoy, under whose direction this work was carried out, and to Dr. Farrington and the Field Museum authorities for the use of authentic meteoritic material.

Kent Chemical Laboratory, University of Chicago.

Art. XX.—*Occurrence of Euxenite in South Sherbrooke Township, Ontario;* by Willet G. Miller and Cyril W. Knight.

In June, 1917, the writers paid a visit to a feldspar quarry, in which euxenite occurs, three miles from the village of Maberley, Ontario. The quarry is near the center of lot 13, concession V, of the township of South Sherbrooke, Lanark county. The mineral was noted some months ago, during the working of the quarry, by Mr. J. A. Morrow, on whose land it occurs. Mr. Morrow sent samples to the Ontario Bureau of Mines for identification. Through the kindness of Dr. Dunstan, Director of the Imperial Institute, London, England, the mineral was analyzed there and identified as euxenite.

The euxenite occurs in a granite pegmatite dike which has a width of about 75 feet, and cuts banded gneiss of pre-Cambrian age. The dike contains mainly feldspar, which has been worked as a source of potash and for pottery, and quartz; in addition to these minerals there are found considerable black tourmaline, three varieties of mica, black, white and green, and pyrite.

The euxenite occurs in masses from the size of a pea to about two inches in diameter, and is embedded in pink feldspar and in black scaly mica. Pyrite is closely associated with the mineral. Owing to their brittleness, crystals of the mineral were not obtained, but occur occasionally embedded in the pink feldspar. The mineral occurs here and there in the dike, but was found in largest quantity near the center of the dike in a zone about two feet wide. The zone consists of pink feldspar, more or less stained by decomposition of pyrite, in which are nearly parallel seams of black scaly mica from an eighth to a half an inch thick.

The results of the analysis of the South Sherbrooke mineral are given in column I. The analysis in column II is quoted from Dana.*

	South Sherbrooke, Ontario	Alve, Norway
	I	II
	Per cent	Per cent
Ta_2O_5	13·89	35·09 (Nb_2O_5)
Nb_2O_5	12·73	
TiO_2	27·70	21·16
ThO_2	1·34	
Ce_2O_3 La_2O_3 etc.	0·62	3·17 (Ce_2O_3)

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* Descriptive Mineralogy, 6th ed., p. 744.

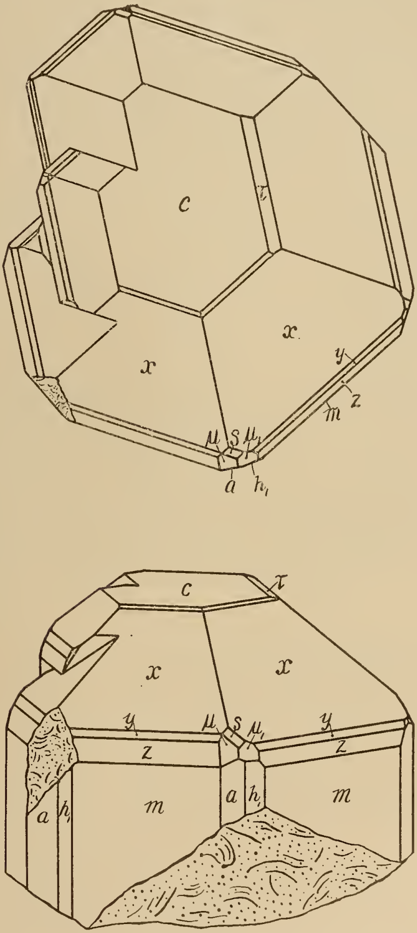
	South Sherbrooke, Ontario I Per cent	Alve, Norway II Per cent
Y_2O_3 etc.	25·64	27·48 (Y_2O_3) 3·40 (Er_2O_3)
Fe_2O_3	2·63	
FeO	0·51	1·38
MnO	trace	
PbO	0·20	
U_3O_8	10·50	4·78 (UO_2)
CaO	0·09	
MgO	0·12	
SiO_2	0·74	
H_2O etc.	3·00	2·63 (H_2O)
	99·71	99·09
Specific gravity	4·99	5·00

Provincial Geologist's Office,
Toronto, June, 1917.

Art. XXI.—*A Remarkable Crystal of Apatite from Mt. Apatite, Auburn, Maine*; by W. E. Ford.

Recently the writer, through the courtesy of Mr. A. H. Petereit of New York City, has been privileged to examine an extraordinary crystal of apatite from the well-known locality near Auburn, Me. It was such an unusual crystal in respect to its size, color and crystal development that it seemed worthy of the following brief descriptive note.

Fig. 1.



The crystal measures 3·8^{cm} by 4·3^{cm} in the horizontal directions and 3^{cm} in the vertical direction and weighs slightly over 100 g. Its color is the wonderful deep amethyst characteristic of apatite from this locality. The crystal contains cracks and flaws and is cloudy in portions, but also in many small areas it is perfectly clear and of a gem quality. The crystal forms observed include the following: $c\,(0001)$, $m\,(10\bar{1}0)$, $a\,(11\bar{2}0)$, $h_1\,(3\bar{1}\bar{2}0)$, $\tau\,(10\bar{1}6)$?, $x\,(10\bar{1}1)$, $y\,(20\bar{2}1)$, $z\,(30\bar{3}1)$, $s\,(11\bar{2}1)$, $\mu\,(21\bar{3}1)$ and $\mu_1\,(3\bar{1}\bar{2}1)$. The accompanying figure represents the crystal as nearly as possible in its true proportions and about 1½ times its natural size. On one side of the crystal there are several oscillations between the faces with consequent parallel growth between different portions of the crystal. Three of the edges between the base and the pyramid x are replaced by narrow faces of a very low pyramid. These faces are curved and do not yield a definite reflection on the goniometer. The only known form that they might be, however, is the pyramid $\tau\,(10\bar{1}6)$. The faces of the pyramid z, as is usual on crystals from this locality, show marked horizontal striations and the prisms a and h_1 commonly show faint vertical striations. All of the other faces are plane with no distinctive markings. Both the right and left forms of the third order pyramid, μ and μ_1, are present, with no apparent distinction to be made between them in regard to their luster, etc. While the figure shows the majority of the faces occurring upon the crystal, several very small and narrow faces of the second and third order pyramids had to be omitted from the drawing.

A small crystal showing the same forms is attached at one side to the lower part of the large crystal but is not represented in the figure. A small amount of cookeite is attached to the crystal.

Mineralogical Laboratory of the
Sheffield Scientific School of Yale University,
New Haven, Conn., June 15, 1917.

WILLIAM BULLOCK CLARK.

Dr. William Bullock Clark, professor of geology in the Johns Hopkins University and State Geologist of Maryland, died suddenly of heart failure on July 27 at his summer home at North Haven, Maine. He was born at Brattleboro, Vermont, on December 15, 1860. Entering Amherst College in 1880 he received his A.B. degree in 1884 and immediately went abroad, spending the next three years in von Zittel's laboratory at Munich where he received his doctorate in 1887. After spending several months in London and Berlin he returned to America as instructor in the newly founded Department of geology at the Johns Hopkins University. With the death of George H. Williams in 1894 Clark became a full professor and head of the department. He was connected with the U. S. Geological Survey in various capacities from 1888 until his death.

Although coming from an old New England stock—the Bullocks having settled in Salem in 1643 and the Clarks at Plymouth in 1623—Professor Clark was for thirty years a citizen of Baltimore, and it is doubtful if there has been anyone who has performed a greater service than he to the commonwealth of Maryland. It needs but an enumeration of his many positions of responsibility to appreciate this unique service. He organized a State Weather Service in 1892 and was its director for 25 years. He organized the State Geological Survey in 1896 and was its director for 21 years. He organized the State Bureau of Forestry in 1906 and was its executive officer for 11 years. In 1898 as State Geologist he was instrumental in starting the good roads movement in Maryland and successfully steered through the shoals of possible political waste in the expenditure of about $2,000,000 in the making of state highways. In 1910 a State Roads Commission was organized to take over the rapidly expanding work of the Highway Division of the Geological Survey, and for four years more he was a very active member of this commission. He represented the state in the resurvey of the Mason and Dixon line, was a member of the State Conservation Commission, was instrumental in forming the state exhibits at the Buffalo, Charleston, St. Louis, Jamestown and San Francisco expositions, and in arranging the state mineral exhibit in the State House at Annapolis. He took an official part in the White House conference on conservation in 1908.

In civic affairs he served as a member of the emergency committee appointed by the mayor at the time of the great Baltimore fire in 1904, and aided in the rehabilitation and improvement of the burnt district. In 1905 he was appointed by the mayor a member of the committee to devise a sewerage system for the city. In 1909 a like appointment resulted in the plans for the development of a civic center for Baltimore. For 16 years he was president of the Henry Watson Children's Aid Society. He was also a member of the executive committee of the State Tuberculosis Association and an officer of the Federated Charities.

Professor Clark was a member of the National Academy of Sciences and chairman of its Geological Section, a fellow of the American Academy of Arts and Sciences, a member of the Philadelphia Academy of Natural Sciences, Washington Academy of Science, American Philosophical Society, Deutsche Geologische Gesellschaft, Paleontologische Gesellschaft, and American Association for the Advancement of Science. He was a councillor and treasurer of the Geological Society of America, of which he was a charter member, and a foreign correspondent of the Geological Society of London. He was, for several years, president of the Association of American State Geologists. Amherst conferred its LL.D. on him in 1908. In 1897 Professor Clark was an official delegate to the International Geological Congress and spent several months in an extended trip through Russia. He was abroad several summers and attended the centenary of the Geological Society of London. He spent the summer of 1906 in Alaska, and traveled extensively in Mexico and throughout the United States. He was married October 12, 1892, to Ellen Clark Strong of Boston, and had four children, all of whom survive him.

Professor Clark was eminently social and had the gift of inspiring affection in men of all walks of life. His influence on the progress of geology was unique. Starting as a paleontologist he soon became an authority on the Echinoidea. He was early diverted to more strictly stratigraphical work and prepared a correlation paper on the Eocene for the U. S. Geological Survey on the occasion of the Washington meeting of the International Geological Congress in 1891. After studying the Upper Cretaceous of New Jersey for the U. S. Geological Survey he attacked the Coastal plain formations of Maryland and Virginia with characteristic energy, and the results of this work were eventually embodied in the systematic reports on the Lower Cretaceous, the Upper Cretaceous, the Eocene, the Miocene and the Pleistocene, published by the Maryland Geological Survey. With the multiplication of administrative duties as head of the Geological Department and member of the Academic Council of the University, as well as the increasing widening of the work of the Maryland Geological Survey, the Weather Bureau, the Highway Commission and the Forestry Bureau, most of his time was engrossed in organization rather than in research, and undoubtedly his greatest monuments are the reports of the Survey he organized and the contributions to Science by a host of younger men who came under his influence—drawing material aid as well as inspiration from his example and ideals.

With the outbreak of the war Professor Clark became actively interested in problems of defence and economic preparedness. He was appointed a member of the National Research Council, was chairman of the subcommittee on road materials, and a member of the committee on camp sites and water supplies. He was also chairman of the committee on highways and natural resources of the Maryland Council of Defense. E. W. BERRY.

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AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XXII.—*Block Mountains in New Zealand*; by C. A. Cotton, Victoria University College, Wellington, New Zealand.*

Contents.

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* References are listed in full at the end of the article.

INTRODUCTION.

THE geologic structure of New Zealand has been described by the writer in a recent article (1916 *a*, pp. 319, 320) as "a concourse of earth blocks of varying size and shape, in places compressed; the highest blocks lying in the northeast and southwest axis of the land masses, so that the whole structure may be termed a geanticline; the blocks initially consisting of an older mass of generally complex structure much denuded and largely planed, and concealed over the greater part of the area by covering strata which had not been disturbed before the 'blocking' took place; the whole since these movements considerably modified by erosion somewhat complicated by the effects of later movements of uplift and subsidence."

In another article (1916 *b*), the block mountains and associated features in a small area in northern Nelson have been described. This paper deals with Central Otago, where the "block" features are unusually well preserved.

As an aid in presentation, the description and interpretation of selected types of New Zealand mountains is preceded by a discussion of the physiographic development of block mountains in general based on the established principles of geomorphology.

PART I. BLOCK MOUNTAINS AND RELATED FORMS.

1. *Structure.*

The structure is postulated as an undermass of rocks with varied structures which before being covered were denuded enormously and reduced to small relief. Though the final planing was accomplished in some parts of New Zealand by the sea, subaërial agencies probably prepared the large planed areas for the final marine planation.

Remnants prove the presence of a former widespread overmass or cover upon the eroded surface of the undermass. It is not necessary to assume that this overmass was laid down as a continuous sheet over the region or that it is entirely of marine origin. It may be postulated, indeed, that the covering beds are in part fluviatile, resting upon a peneplain,* and that other parts of such a surface may never have been covered.

Perhaps the most important factors to be considered in the processes of uplift and denudation are: (1) the nature of the

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* It is not to be inferred from the above statements concerning covering strata in New Zealand that the writer believes submergence and the initiation of sedimentation to have been everywhere simultaneous. It is probable that overlap in the covering strata resulted from submergence of successive "blocks" of the undermass. Further, the statement of Speight (1915), based on the results of prolonged study, that in North Canterbury islands rose through the Upper Cretaceous and Tertiary sea, must not be overlooked.

FIG. 1.

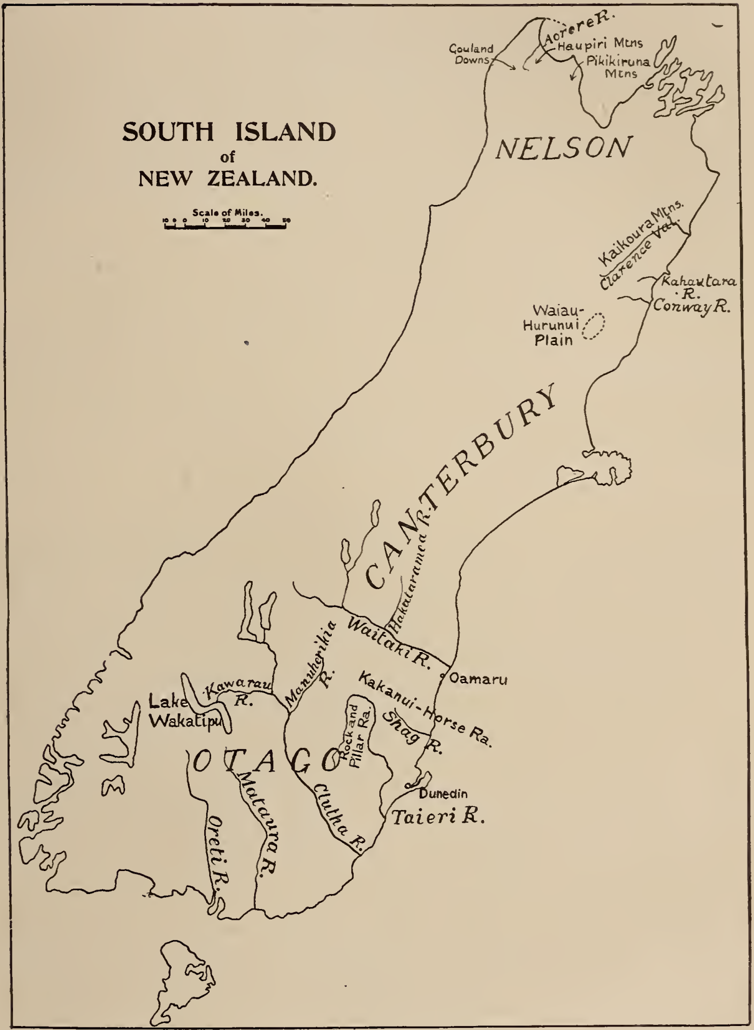

FIG. 1. Locality map of the South Island of New Zealand.
Scale 1 inch = 100 miles.

uplift, (2) the relative strength of, or resistance offered to, erosion by the undermass and the cover, and (3) the nature of the structures in the undermass where the overmass is relatively weak.

The covering strata in New Zealand are relatively weak, consisting in great part of mudstones and incompletely indurated sandstones, also of thin limestones, relatively resistant but soluble, interbedded with weak clastics. A few thick masses of indurated conglomerate which occur in places at the base of the cover offer great resistance to erosion. In some districts thin lava flows occur; but these like the limestones are weakened by interbedding with clastics.

In contrast with the overmass, the rocks of the undermass are generally highly resistant. In northern Nelson these are indurated argillite, quartzite, quartz schist, crystalline limestone, and intrusive granite. In western Otago, gneissic and plutonic rocks occur, and in Central Otago, the undermass consists entirely of schist—relatively a very resistant rock compared with the unconsolidated sands and clays largely developed in the overmass of that district.

2. *The Initial Surface.*

The form of the initial surface depends upon the nature of the uplift. Two types of uplift may be distinguished: (*a*) The blocks are differentially elevated, depressed, or tilted—the displacement being solely by faulting or by faulting replaced to a minor extent by monoclinal flexures. The initial surface must be a mosaic of plane areas at various attitudes, some perhaps horizontal and many inclined, separated by initial fault scarps facing in different directions. (*b*) Strong warping—perhaps better termed folding—attains considerable development; faults though present pass into or replace the limbs of folds, the uplifted blocks being in part anticlinal and the fault angles and trough depressions being in part synclinal. The surfaces of the structural units, which here as well as in (*a*) may be termed "blocks," will be in part warped or flexed, though there may still be notable plane areas, and the fault-scarp boundaries between adjacent blocks will be replaced in part by monoclinal slopes. This is the type of deformation concerned in producing many of the New Zealand block mountains, and, according to Gilbert (1874), a somewhat similar type is not unknown in the North American Great Basin.

The types of initial and sequential forms for regions of uplifted and tilted blocks without cover have been deduced by Davis (1903, 1905, 1912) and matched with examples from the Basin Ranges and elsewhere. Louderback (1904) has described faulted blocks with a cover of resistant lava. In the present paper, attention will be directed principally to forms developed in a region in which the predeformational surface is a plain of deposition, being the surface of a weak overmass lying on a planed undermass.

3. *Possible Types of Drainage.*

The early stages of the drainage of a region in which the initial forms have been produced by the faulting and folding of a weak overmass on a planed undermass must be entirely consequent if the overmass is continuous and if its surface is a plain of marine deposition. Parts, however, of the Otago district were probably emergent prior to the deformation, and some of the streams may have persisted during and after the deformation as antecedents. Such a preëxisting drainage system would be present also in any part of the area where the upper layers of the covering strata were of subaërial origin, or in any part where regional elevation antedating the deformation had brought the upper layers of marine strata above sea level. Few streams are powerful enough to persist through strong deformation, and though a few large streams may be antecedent, the greater part of the drainage, including most if not all of the minor and tributary streams, will be consequent. As movements of deformation occupy some time, erosion can accomplish much while uplift is in progress. A drainage system will be established as soon as any portion of the region is exposed as land, and this early consequent drainage tends to be perpetuated during the continuance of the movements. As movements probably will not go on continuously in all parts of the region, if the consequent drainage resulting from the deformation be alone considered, the early drainage pattern is not necessarily the same as that which would have come into existence had the final structure been instantaneously assumed. In a deformed region may be found, therefore, true antecedent streams, true consequent streams, and streams that were consequent upon the form of the surface assumed as the result of early movements but are antecedent to later movements of the same series. Such streams might perhaps be appropriately termed antecedent consequents or *antecconsequents.* Spill-over courses resulting from the overtopping of divides by alluvial accumulations are also possible.

After cutting down through the covering strata, streams of any or all of these types will be superposed in places upon the structures of the undermass. Besides, all may be expected to develop insequent tributaries, and as the cycle progresses subsequent streams will form upon weaker structures in the undermass and such portions of the covering strata as have escaped complete destruction.

It is necessary to consider criteria for distinguishing the types of drainage. Subsequent streams guided by weaker strata in an inclined series are readily recognized, but when they are guided by shear-zones, ancient fault-planes, or master joints they are generally included with the insequents. Leaving these aside, we may consider the important types of drainage in the early stages of the cycle of erosion introduced by the deformation, namely, true consequents, true antecedents, and anteconsequents, all possibly superposed.

True Consequents.—On the highly improbable assumption that deformation is simultaneous and instantaneous and without contemporary erosion, it follows that consequent streams will make their way down the tilted and warped surfaces and that some consequent lakes will be formed. Under normal conditions of humidity, these lakes will spill over at the lowest gaps along consequent courses, which will be superposed later on the structure of the older mass, gorges will be cut through the higher blocks, and systems of consequent streams will be established. Exactly similar drainage patterns are to be expected if the deforming movements are simultaneous though not instantaneous. If the movements are sufficiently slow no lakes may result, as early-formed consequent courses across the lowest sags in the crest lines of the rising blocks will be continuously deepened by corrasion. Consequent lakes considerably above base-level are short-lived, so they are not likely to leave permanent records of their existence.

Anteconsequent Drainage. There is as little justification for the postulate that movements have been simultaneous throughout a period of deformation as there is for that of instantaneous deformation. Movement may be well-advanced in some parts of a region while other parts are as yet unaffected. There may even be a rhythmic passage of waves across the land surface. (In regional movements such oscillation is well attested; but the present discussion is concerned with strongly differential as distinguished from regional movements.)

In the case of a low-lying block surrounded by differentially rising blocks, the movement of which is not necessarily simultaneous, the lowest gap in the basin rim (erosion being left out of account) may not always be in the same position; and the consequent outlet of a basin established during an early stage of deformation and persisting by rapid corrasion may not at a later stage be situated at the lowest sag in the surrounding blocks.

Antecedent Drainage. Antecedent drainage channels on a surface of the kind postulated must be inherited from a simple centrifugal system of subparallel streams radiating from the old land or that portion of the undermass which escaped burial during the period preceding the deformation. The approximate position of such a nonburied area of the undermass or the source of the material forming the covering strata furnish evidence for the direction of possible antecedent streams. Without such knowledge only streams which cannot be placed with certainty in any other category may be classed as possibly antecedent. The relation of valley directions to the trend of elongated blocks may give information. If, as in Otago, the deformation has produced longitudinal tectonic features—parallel elongated arches and troughs or long tilted blocks separated by fault angles—both true consequent and anteconsequent drainage will follow generally longitudinal courses, though perhaps breaking across here and there from one linear series of depressed areas to another. Antecedent drainage, on the other hand, may cross the longitudinal features diagonally or transversely.

4. *Sequential Forms.*

Davis has recognized two main elements in the form of a simply tilted block mountain, the back slope and the front or scarp. These are the two main elements in the whole initial landscape of a region of tilted blocks.

In a region that has been affected by diverse movements, the elements of the initial landscape are horizontal areas (high or low-lying), back slopes (areas of surface with a more or less uniform and gentle slope), fold surfaces (areas of steeper slope, not necessarily uniform), and fault scarps. There will be transitions from fold surfaces through what may be termed fold scarps to fault scarps. The present problem is to trace the development of topographic features from an initial surface comprising these various elements, upon which a system of consequent drainage becomes established. After postulating an initial relief caused by instantaneous deformation, it is possible to consider the effects of erosion and a continuation of the deformation going on simultaneously.

In the stage of extreme youth, the block fronts (fault and fold scarps) will experience the most rapid changes of form and, as a result of slumping and the formation of consequent gullies, these will supply the largest quantity of waste. Very early, also, the perhaps closely spaced consequent streams of considerable length, which will have come into existence all over the relatively large areas of inclined block surfaces, will be actively engaged in grading their courses (see fig. 2).

From the rapidly deepened consequent valleys, insequent tributaries will be developed, and probably also subsequents. Since the spacing of the consequents alone may be close and the texture of dissection becomes finer when insequents and subsequents have also been developed, and since entrenchment of the whole system beneath the sloping surface of the weak covering strata must rapidly take place, maturity of dissection will be rapidly attained, first in the middle parts of the steepest slopes and later over the whole area of sloping upland. On level upland surfaces, where streams may be widely spaced, on gentle slopes, where stream grade may be attained at no great depth below the initial surface, and also on low-lying blocks, where the surface is at no great height above base-level and where, consequently, deep dissection is impossible, maturity of dissection may be relatively long delayed.

Fig. 2.

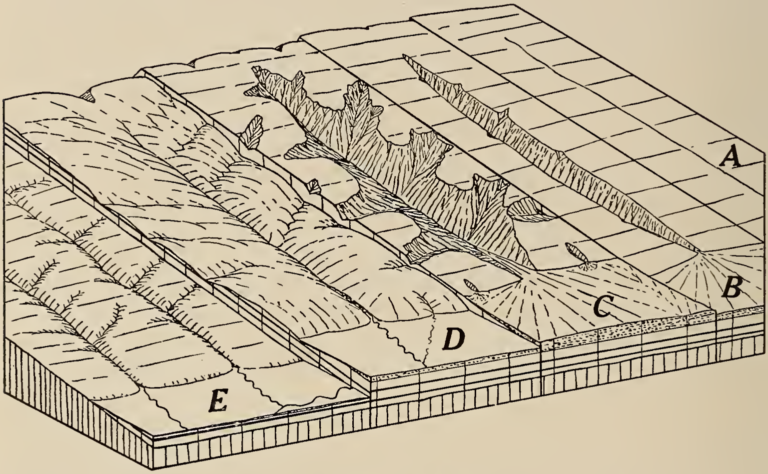

Fig. 2. Diagram of the development of the back slope of a gently tilted block with a relatively resistant undermass and weak overmass from the initial form A through sequential forms B, C, and D to a stripped floor (earlier denudation plain) with shallow dissection, E.

During this stage of the cycle, the troughs will generally be aggraded on account of an enormous quantity of waste from the upland surfaces. During the whole period of deformation, the troughs will be filled as they sink (see fig. 2, B, C, D). The waste may be laid down in part on the floors of lakes, wholly or in part conformable to the deposits of the predeformational period, or it may be deposited wholly subaërially as fans growing outward from the margins of the surrounding blocks, coalescing and forming an aggraded plain, the deposits of which will, in general, accumulate upon a maturely dissected surface developed as a sequel to the deforming movements.

Stripping.—When the consequent and other streams of the sloping uplands cut through the cover and become superposed on the resistant oldermass, the rate of further downward cutting will become comparatively slow. Before this stage the measure of the relief has been increasing progressively with downward cutting and may still increase slightly if maturity of dissection of the surface is still to be attained. After the attainment of maturity, reduction in height of the interfluvial areas of weak covering strata may go on more rapidly than vertical stream corrasion on the resistant underlying rocks. Even if the streams had attained grade without cutting through the cover in the early stages of dissection, after the cover has been largely removed from the higher part of the block they will be forced to cut deeper and will eventually become superposed. With the complete removal of covering strata, all the streams will be incised to some extent. Owing to the resistant nature of the undermass the ravines will long remain narrow, while inclined flat areas on the interfluves will survive. This stage will be attained earliest at the middle parts of the slopes of block surfaces. On lower slopes, undissected interfluvial areas are likely to be larger, and on slightly inclined higher slopes where there is little concentrated wash, remnants of the cover may be expected to survive for some time longer (see fig. 2, E).

Fig. 3.

Fig. 3. A northwestward-sloping stripped plateau surface forming the back slope of the Rough Ridge block in Central Otago, and descending beneath covering strata planed by the Ida Burn.

These sloping plains of denudation, almost entirely stripped of their cover, and crossed by many steep-sided, generally consequent ravines, which increase rapidly in depth as followed upstream, with here and there remnants of the covering strata relieving the otherwise flat interfluvial surfaces, though common in New Zealand, have received scant attention. They have been noted by McKay, Bell (1907), the writer (1916 *b*) in the Aorere district of northern Nelson, and by Thomson (1914) in South Canterbury. The more level portions of similar surfaces in Otago have been termed by Park (1906, 1910) the Barewood Plateau or Central Otago Peneplain; and Speight has recognized a similar surface in the Kaimanawa Mountains in the North Island (1908).

The most perfect examples known to the writer are those forming the back slopes of some of the block mountains of Central Otago, for example, the western slope of Rough Ridge (see fig. 3); a long northeasterly slope from the broken plateaus of Central Otago to the fault-angle depression followed by the Shag River; a similar slope southeastward to the Taieri Plain; a similar slope northeastward from the Kakanui Mountains towards the Oamaru district (see fig. 4); the westward slope of the Hunter's Hills, noted by Thomson, with which are associated similar slopes surrounding the Waihao basin; the surface of the Gouland Downs, Northwest Nelson; and the northwestward slope towards the fault-angle depression followed by the Aorere River, northern Nelson.

Fig. 4.

Fig. 4. Part of stripped plateau surface descending northeastward to Oamaru district, Otago, with a deeply incised gorge, that of the Waianakarua River, on the right, and a large residual mesa of the overmass just to the right of center.

Salients on Stripped Plateaus.—The generally flat surface of a stripped plateau will be broken by a pattern of reëntrant ravines. Salient features may or may not be present. Such may have originated as monadnocks on the eroded surface of the undermass which has been lately reexposed, or as small isolated fault blocks in which the surface of the oldermass has been uplifted above its level in surrounding blocks; or they may be remnants of cover not yet removed, thus closely resembling monadnocks in form. Certain remnants of cover may owe their preservation to local induration or local thickening of a relatively resistant stratum and to the presence of a lava flow of small extent. Mesas or buttes of covering strata may thus be scattered sporadically over a surface. Other salients may owe their preservation to slight inequalities of uplift which have caused unusually wide interfluvial spaces between consequent streams. Salient features developed from monadnocks and from small uplifted blocks may be distinguished with great difficulty even when first laid bare, for monadnocks may have been cliffed by wave action (Noble, 1914, p. 62), and fault-line scarps with a very similar form may be present on one or more sides of a small block. Moreover, salients of both kinds may be dissected by insequent ravines, and thus soon lose their initial form.

In New Zealand remnants of cover are common as salients projecting above stripped plateaus. In northern Nelson these are generally limestone mesas; in eastern Central Otago volcanic rocks cap many small buttes and protect large areas. On the more level plateaus are small salients of indurated quartz conglomerate. The writer has not recognized with certainty any monadnocks.

Mature Dissection of the Undermass.—Stripped plateau surfaces traversed by ravines of moderate depth will persist for a long period if the surface slope is rightly adjusted to the volumes and grade of the streams. In a region of small rainfall an initial slope of a block surface as high as 10° may have small consequent streams and a large number of subequal, graded, shallow ravines occupied by intermittent streams. Though these break up the stripped surface to some extent, unless the stream spacing is very close, the plateau remnants will be relatively stable.

Grading of the ravine sides by soil creep will cause the sharp shoulders bounding the plateau remnants to disappear and the interfluvial areas to be reduced. But still their summits will be accordant with one another and suggest the reconstruction of the tangent surface of the undermass. Such conditions exist in the stripped plateaus of South Canterbury and Otago (see figs. 3 and 4). Later, a surface tends to waste away very slowly unless destroyed by erosion working back from initially steep portions of tbe same block.

Under other conditions plateau remnants are relatively shortlived. If, owing to abundant rainfall, to steepness of initial slope, or to initial irregularities of surface which have resulted in concentration of consequent drainage along a few channels, the graded profile for such streams lies far below the stripped plateau surface, the plateau remnants will be cut up by consequent, insequent, and perhaps subsequent ravines. An early and complete dissection of the surface over the whole block will result, and the block will become an asymmetrical mountain ridge with strong relief throughout (see fig. 5).

Block surfaces in this stage of dissection are common in northern Nelson, examples being the surfaces sloping easterly from the Pikikiruna Mountains to Tasman Bay. Of the same kind are the northwestern slopes of the Kaikoura and Seaward Kaikoura Mountains, in Marlborough.

A special case of large stream volume leading to deep dissection of a plateau surface is that in which the descent from the highest portion of a block to a neighboring trough takes place by a fault or flexure followed by a sloping surface (see fig. 6). Streams of large volume from the higher block will destroy the lower, gently sloping surface with its deep ravines. Such is the dissection of the northwestwardly sloping surface which descends to the Aorere fault-angle depression in northwest Nelson (Cotton, 1916, pp. 66–68).

Fig. 5.

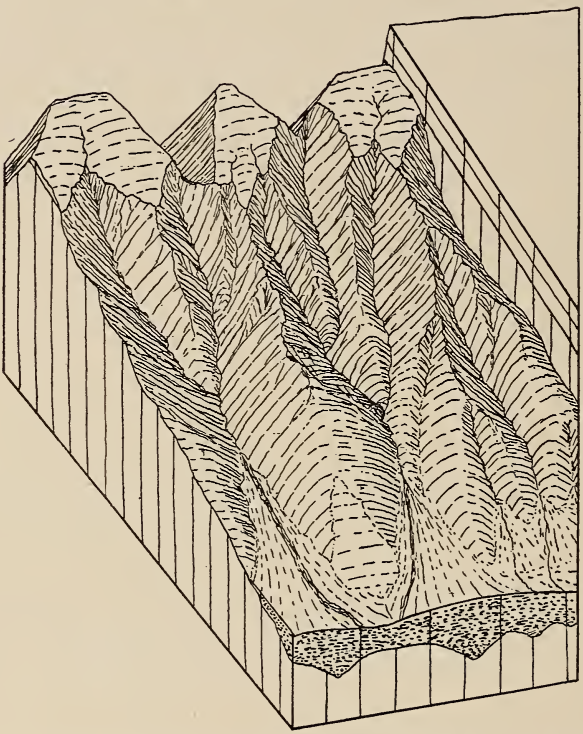

Fig. 5. Dissection of the steeply inclined back slope of a faulted block by consequent and insequent ravines. The initial form is shown on the right.

Fault Scarps and Fold Scarps.—Except for the possible case of antecedent drainage crossing an uplifted block in a direction opposite to that of the general slope of the tilted surface and emerging from gorges on the steeper side of the block, the dissection of the steeper sides of asymmetrical blocks with the structure postulated will be effected entirely by consequent streams. When they have steep fronts the blocks are bounded by faults or steep monoclinal flexures; when the crest line is some distance back, the descent is formed either by a fold surface alone or by a fold surface broken by one or more faults.

To the former class belong the fronts of simply tilted block mountains. They are dissected by consequent ravines which in the stage of early youth divide a scarp into sections and later reduce it to a linear series of triangular facets.

FIG. 6.

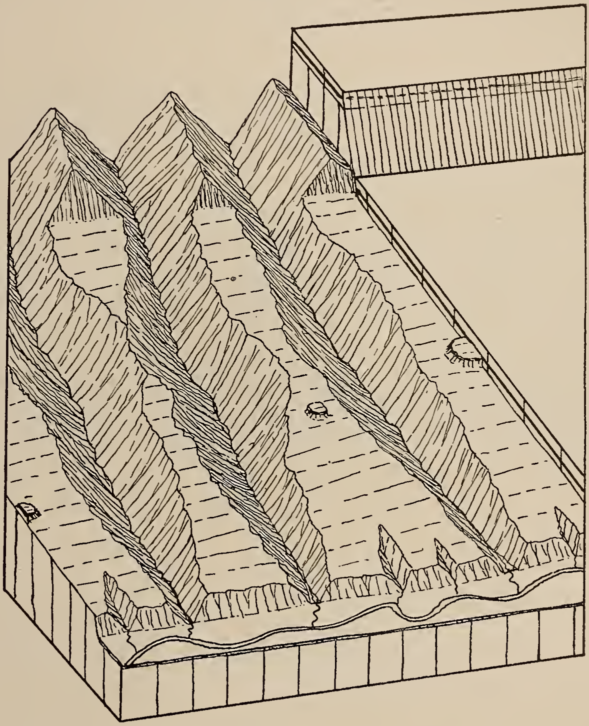

FIG. 6. Dissection of a gently sloping block surface (with a cover overlying a planed undermass) by extended consequent streams from a higher block behind it. The counterpart of this surface is formed in the Aorere fault-angle depression in northern Nelson.

Davis (1912; 1913) has distinguished fault-line scarps of generally similar form to dissected fault scarps, but originating as a result of the removal of weak rocks from one side of a fault which has brought weak and resistant rocks in contact.

Composite Fault Scarps.—In New Zealand many more or less dissected scarps occur, which agree in general form with either fault scarps or fault-line scarps, which may be in their lower parts fault-line scarps, though where the displacement on the faults is considerable, they are true fault scarps in their upper parts.

When faulting occurs in a region where a weak cover overlies a resistant undermass, and the base of the resulting fault scarp is at a considerable height above base-level, removal of the covering strata at the base of the scarp may be going on while movement is in progress. If such removal is prevented by an abundant supply of waste spread out on the covering strata in the form of fans or a piedmont alluvial plain, after movement ceases degradation will soon take place. Thus a fault-line scarp will be exposed below and continuous with the already dissected fault scarp, the two constituting a single morphological feature which may be called a composite fault scarp.

Fig. 7.

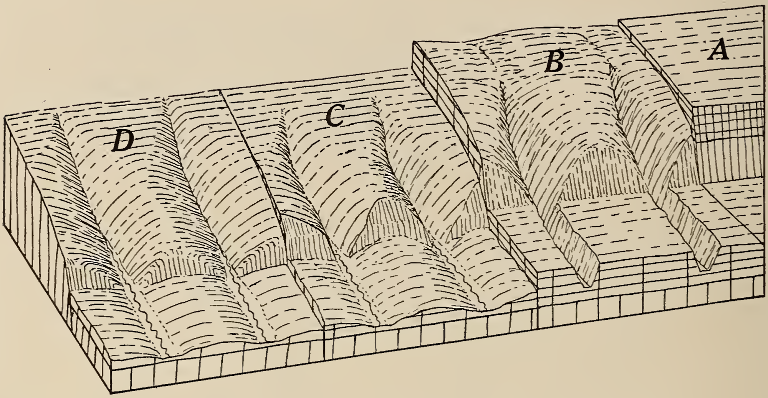

Fig. 7. Diagram of the development of a composite fault scarp, in its upper part a fault scarp and in its lower part a fault-line scarp.

During the early stages of stripping of the fault surface, the ravines by which the upper portion of the composite fault scarp is already dissected may have cut nearly to or perhaps below the surface of the undermass on the down-throw side of the fault. If so, these ravines will divide the fault-line portion of the scarp before it is exposed into sections that will be downward prolongations of the facets of the upper scarp. In some cases these lower fault-line portions of facets may be recognized by their steepness (see fig. 7 C); but the facets will soon dwindle and remnants of the fault-line portion only be left (see fig. 7 D).

Where there is a continuous covering of vegetation, soil creep plays an important part in producing convexly rounded surfaces, as has been pointed out by Davis (1892; 1912) and by Gilbert (1909). In small facets of fault scarps blunting of the edges destroys the flatness of the whole facet, though the dissection of the scarp by ravines may be incomplete. This rounding of facets is particularly well illustrated by a low scarp at Waimate, South Canterbury (see fig. 8), which was first diagnosed as a fault or fault-line scarp by Thomson (1914). Sharp-edged facets seem to occur only in the case of scarps resulting from movements that have been renewed in very recent times.

Fig. 8.

Fig. 8. An eastward-facing composite fault scarp near the southern end of the Hunter's Hills block in South Canterbury.

If the crest line—the divide between consequent drainage of the back slope and of the block front—is some distance back from the base-line, the initial descent from an arched crest to the top of a fault scarp may be gentle. Consequent streams will arise on the upper slope, and the ravines will cut deeply and rapidly into the upper slope and after removing the cover dissect the undermass. Thus, in a comparatively short time, the mountain front will be maturely dissected by steep-graded ravines which will continue to work headward and push the crest line divide down the back slope of the block. On the steep mountain-face spurs will descend between these ravines to end in a line of rapidly dwindling facets at the fault trace, and the stage of maturity will rapidly be attained. The front of the Kakanui-Horse Range facing the Shag Valley in eastern Otago appears to be a scarp of this kind (see fig. 9), also the southeastern front of the Kaikoura Mountains (Cotton, 1913).

Fold Scarps.—Simple fold surfaces and fold surfaces broken by a succession of small faults will give rise to forms very similar to those just described except in their earliest stages. Removal of a weak cover from a fold surface will be rapid and result in the exposure of some portions of the sloping floor beneath; but the graded profile of the streams may be so steep that deep cutting is not favored. Further increase in the depth of ravines will then take place only as a sequel to headward erosion, which may be so slow that flat areas will persist for a comparatively long period, though they may be steep compared with the stripped plateaus of the back slopes. With steeper initial fold surfaces, consequent graded streams may be so deeply incised as to maturely dissect the surface of the oldermass, except, perhaps, for a few facet-shaped remnants. The resulting form is indistinguishable from a maturely dissected fault scarp. Vigorous streams may be expected to push back the crest line divide, which will recede in the stage of maturity down the back slope of the block. A good example of a submaturely dissected fold scarp is the eastern face of the northern end of the Blackstone Hill block (see fig. 10). Of the same nature are the side slopes of a broad saddle of catenary form separating the stripped plateau of the Gouland Downs from the depression of the lower Aorere Valley in northern Nelson (Cotton, 1916 *b*) and probably many other scarps in the same region.

Fig. 9.

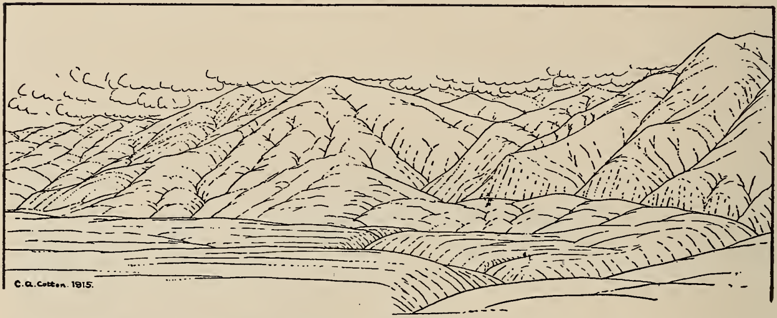

Fig. 9. Maturely dissected scarp of the Kakanui-Horse Range descending southwestward to the Shag Valley fault angle in north Otago. The stripped plateau descending in the opposite direction to meet the fault scarp is seen in the foreground, and, to the right of the center of the foreground, the gorge of the Shag River superposed on the undermass.

5. *Trough-filling.*

An enormous amount of waste results from the stripping of back slopes and dissection of faulted and folded fronts. Exceptionally, such waste may be all removed as it is supplied but in most places deep aggradation of troughs will take place progressively with deformation and with the degradation and dissection of the higher blocks.

Fig. 10.

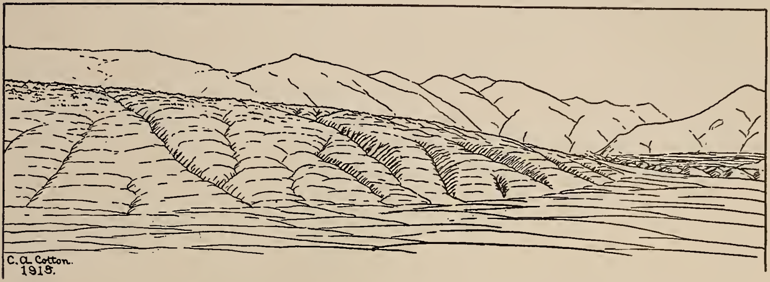

Fig. 10. Submaturely dissected fold surface towards the northern end of the Raggedy-Blackstone block in Central Otago. View looking northward.

Where initial depressions are open towards the sea and portions of low-lying blocks are submerged, or where an area unaffected by movement borders a region of uplifted blocks, the new deposits will overlie the sediments of the predeformational period without stratigraphical break but with abrupt change in the nature of the detritus. Conglomerate may overlie mudstone and pass upward into fanglomerate, as in Marlborough (Cotton, 1914). The passage of fine-grained sediments upward to conglomerate in the upper Tertiary rocks of many parts of the South Island of New Zealand is another example. In marginal areas of shallow water, however, the predeformational cover will be eroded by wave action, while unsubmerged areas will be eroded by subaërial agencies, so that when fans and deltas of waste from neighboring high blocks are built forward these will generally rest unconformably upon a denuded surface.

When the phase of maximum aggradation is reached, intermont basins will be occupied by alluvial plains through which the eroded summits of small, isolated blocks may project. At this stage, portions of the divides between basins may be buried, the waste spilling over from one basin to another in the manner described by Davis in his discussion of the arid cycle

(1905 *b*) and well illustrated in some aggraded depressions in California described by Lawson (1906, p. 455). When such spilling over occurs, the main stream draining a basin may take a spill-over course, become fixed in it during a period of degradation succeeding one of aggradation, and abandon its former outlet.

Upon the surface of the alluvium filling an intermont basin the aggrading streams will flow in braided, ever-changing channels. In the case of a trough opening to the sea the waste will form a delta or a piedmont alluvial plain. Similar forms will also result along initial fault coasts facing the open ocean.

During degradation the filling from some troughs may be removed and the underlying rock exposed. One of the largest intermont basins in New Zealand, the Upper Taieri and Maniototo plain in Central Otago, has reached the stage of dissection at which little alluvial filling remains, and there is little evidence to show whether it has ever experienced extensive aggradation. The planed surface of the covering strata of the low-lying blocks forming the floor of the basin is covered generally by a layer of flood-plain gravel. The planed surfaces form several terraces whose slope indicates that they were formed during intermittent regional uplifts by the same small streams which have since dissected them. In places, portions of the undermass project above the lowland surface. A similar stage of reduction has been reached by most of the Otago intermont basins.

In North Canterbury the large Waiau-Hurunui basin, which Speight describes as having "an origin in deformational movements either of folding or faulting" (1915, p. 348), is floored almost entirely by alluvium. A few "islands" of eroded covering strata project above the basin plain. The alluvial filling has been trenched to some extent as a result of late movements of uplift, but this affords no evidence that the period of maximum waste supply from the mountains to the northwest has been passed. The transverse course of the Waiau and Hurunui rivers across this basin and the adjacent uplifted block indicates an antecedent course (Cotton, 1913). These streams are possibly anteconsequents, for the Hurunui outlet is situated at a sag in the crest of the range. The basin of the Hanmer Plain in North Canterbury, which is enclosed by high blocks, is completely floored with alluvium, and the covering strata that probably exist are completely buried.

With long-continued stillstand, piedmont alluvial plains, like basin plains, must be subject to dissection after the upland blocks have been reduced by erosion. The writer can not point with certainty to any example of it in New Zealand. The dissection of the Canterbury Plains by the Waimakariri, Rakaia, and other rivers is perhaps an example (Speight, 1908).* It is equally probable that this dissection has been the result of a disturbance of the nicely balanced proportion of water to waste brought about by some climatic change.

Dissection may be caused at a much earlier stage of the cycle by coastal retrogradation or by regional uplift. A good example of deep dissection of piedmont plains occurs in an aggraded tectonic depression which extends inland in a southwesterly direction along the base of the Seaward Kaikoura Range and is followed by the coach road from Kaikoura to Waiau. It has been described by Park (1911) as the Waiau "Glacial" Valley. The streams which supplied the alluvium forming the floor of the depression descend from the mountain range, some of them uniting and reaching the sea as the Kahautara River, which leaves the depression at its northeastern end, and others uniting and flowing inland to join the Conway River, Owing to recent uplift the streams are now all deeply entrenched below the aggraded surface which is being rapidly destroyed by the headward erosion of insequent ravines.

PART II. THE BLOCK MOUNTAINS OF CENTRAL OTAGO.

1. *Historical Sketch.*

The origin of the relief of Central Otago has been studied by various writers, and various theories of origin have resulted. Hector (1862, 1869, 1881, 1890) considered the structural features as the result of normal erosion affected by later regional earth movements. One of Hector's publications (1870) includes an indefinite statement assigning a tectonic origin to the major topographic features. Beal (1871) ascribed the smooth ridges and hillsides to the work of ice and the depressions to stream erosion. Hutton (1875) also believed that the rock-bound depressions of Central Otago, "old lake basins," had been excavated by ice. McKay (1884, 1884 *b*) recognized the orogenic movements to which the present relief is due and formulated a hypothesis which agrees in some essentials with the views presented in this paper. In 1897 McKay recognized a number of great faults in this region, and called attention to the importance of these movements in determining relief. He apparently did not recognize the evidence of tectonic origin in the forms of the mountains and described the depressions as "lake basins" and the higher fluviatile gravels as "lake terraces."

Park in 1890 and Gordon in 1893 noted the high inclination of some of the beds of the covering strata and appear to have

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* In a recent publication, Speight (1911) ascribes the building of the Canterbury Plains to a postglacial pluvial period and the deep incision of the rivers below the plains surface to a later period of dry climate.

been convinced that it was evidence of deformation. Gordon mentioned an interstratified leaf bed at St. Bathans "at about the same inclination as the face of the schist rock against which the quartz drift is lying" (p. 119), and appears, however, to have regarded the covering strata as local fluviatile deposits, and the predeformational relief as strong.

Park in 1906, 1908, and 1910 described the ranges as block mountains and recognized that the initial forms roughed out by the deforming movements still determine the general forms of many of the mountains of Otago. He pointed out that the upland surfaces in Central and eastern Otago are portions of a dislocated plain of erosion which he termed a peneplain. This plateau had been recognized by Andrews (1905, p. 192), and mentioned also by Marshall (?1905, p. 103), both of whom regarded it as a peneplain; but neither of these authors appears to have understood the manner in which the surface had been dislocated, both regarding the relief of Central Otago as the work of erosion. With regard to the origin and filling of the so-called lake basins, Park favored an explanation involving contemporaneous deformation along lines of fault. He regarded the whole of the cover that had been affected by the deformation as lacustrine and, therefore, younger than the initiation of deformation.

Though Park (1910) has described the South Island as covered by an ice sheet in the Pleistocene glacial period, he has not specifically appealed to glacial sculpture to account for the erosional features of the Otago block mountains, merely crediting the excavation of the Dunstan gorge to the work of ice (1906), and describing some morainic accumulations in the adjacent portion of the Manuherikia depression. The Dunstan gorge was also described as guided by a fault line (1908).

The writer's hypothesis involves planation, sedimentation, and deformation followed by a period of erosion, during which large areas of the planed undermass have been reëxposed by stripping of the cover.

2. *Structure.*

For a great part of its length, the Otago Central Railway follows a chain of broad tectonic depressions and to these the road system of Central Otago is also mainly confined. It is in connection with this chain of depressions that the salient "block" features occur that present the closest analogy with the block mountains described in other parts of the world (see figs. 11 and 13).

Throughout a great part of the area the undermass consists of metamorphic rocks irregularly but not generally closely folded, and moderately though not highly resistant. To the northeast, folded, unaltered or but little altered, and more resistant sedimentary rocks form the undermass. The transition from typical greywacke to typical schist is in some places quite sharp. Such junctions in Otago are, perhaps without exception, fault junctions. Along the boundary between the main schist area and the main greywacke area the two types of undermass may be distinguished at a distance of several miles by the details of the relief forms developed on them, and the presence is thus indicated of a mosaic of blocks separated by a system or systems of relatively ancient faults to which the present relief is largely or wholly indifferent. Some of the blocks of the mosaic are too small to be shown on the small-scale maps hitherto published.

Fig. 11.

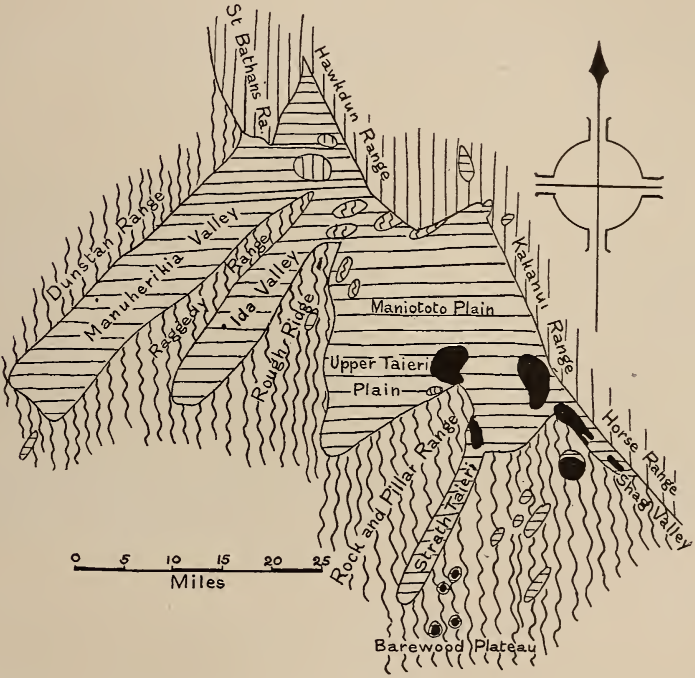

Fig. 11. Geologic sketch map of the block mountains associated with Central Otago chain of depressions. (Boundaries after McKay, with slight modifications.) The areas in which schist undermass rocks reach the surface are marked by waved north-south lines, the areas of greywacke (unaltered or little altered) by straight north-south lines, and those in which the overmass forms the surface, or is thinly covered by alluvium, by straight east-west lines. Volcanic rocks of the overmass are shown in black.

The relief due to movements on these ancient fault lines (together with that resulting from earlier folding) probably had been almost or wholly destroyed prior to the deposition of the overmass or cover. Though the later faulting to which the existing relief is largely due appears to have followed the lines of the older faults in some places, the displacement has generally been reversed.

Upon a planed surface of the undermass rests an overmass of covering strata, which are preserved in the tectonic depressions, but are almost entirely removed from the uplands and highlands. Over a great part of the area the overmass consists of beds of fine quartz, sand, clay, brown coal, and greywacke gravel. These are generally weak and incoherent with the exception of an indurated layer—in places possibly more than one layer—several feet in thickness of quartz grit with a siliceous cement. Basalt, relatively a very resistant rock, occurs towards the east interbedded with the covering strata over a considerable area.

The overmass of Central Otago could not have been continuous unless an emergent land-mass outside this area furnished the detritus. To the northeast, east, south, and west of Central Otago, however, are remnants of a sheet of marine-covering strata, and to the north the undermass is composed almost entirely of greywacke. The lower beds of the cover throughout Otago are accumulations of detritus resulting from denudation of schist similar to that on which they rest. It is quite probable, therefore, that some portion of the eroded surface of the undermass has never been covered and so is a true peneplain (possibly with monadnocks). But the overmass was much more extensive than now. It is significant that this conclusion, at which the writer arrived independently from a study of the geomorphology, had been reached much earlier from a study of the beds themselves by McKay, and clearly stated in his later writings.

McKay writes of the so-called quartz drifts (a term applied in New Zealand to superficial and bedded auriferous deposits of fine conglomerates or grits—not glacial deposits) as follows:

> "These accumulations are so disposed that they are in a large measure—what remains of them—protected from being destroyed by ordinary denuding agents, being either overlain by younger deposits or involved between older and younger strata, so that the same result is effected. That their area in past times was much greater than at present there is abundant evidence in the disjointed scattered patches that are preserved and in the great abundance of cement stones ["sarsen stones" of cemented quartz grit] over surfaces considerably distant from any deposit of loose quartz drift, and the quantities also of this particular kind of rock in the newer drifts and recent gravel deposits in interior Otago." (1897, pp. 88-89.)

To the writer's mind conclusive evidence as to the former wide extension of an overmass is afforded by the occasional preservation of small outliers of the cover on the upland plateaus; by the wide distribution of the "sarsen stones" (fig. 12) derived from the cemented quartz grit; and by the manner in which planed surfaces of the older rocks emerge from under beveled clay and brown coal strata, as well as quartz grits, with the same inclination.

Fig. 12.

Fig. 12. "Sarsen stones" on the back slopes of the Rough Ridge block.

3. *Major Tectonic Features.*

As in most parts of New Zealand, the larger features in Otago with the exception of the volcanic massif of the Dunedin district are undoubtedly of tectonic origin. The positive forms fall under the head of block mountains of simple or moderately complex types, and in the Central and northeastern district more than one of the types of block structure recognized by Gilbert (1874) in the ranges of the Great Basin are distinguishable. These initial forms have been also sculptured in detail by erosion.

The area is characterized by uplifts of relatively simple types—uplifted masses either tilted or bounded on both sides by faults forming a set of elongated blocks with a definite southwest and northeast orientation and enclosing elongated depressions. Blocks bounded on all sides by faults have not been recognized; most of the boundary faults diminish in displacement and are evidently replaced by flexures (fig. 13).

Towards the southwest, owing to diminishing displacement on the faults and flexures bounding them, the depressions are no longer distinguishable. With the mountain blocks they merge into a high, broken plateau, in which detailed investigation doubtless will reveal the presence of a number of distinct blocks.

FIG. 13.

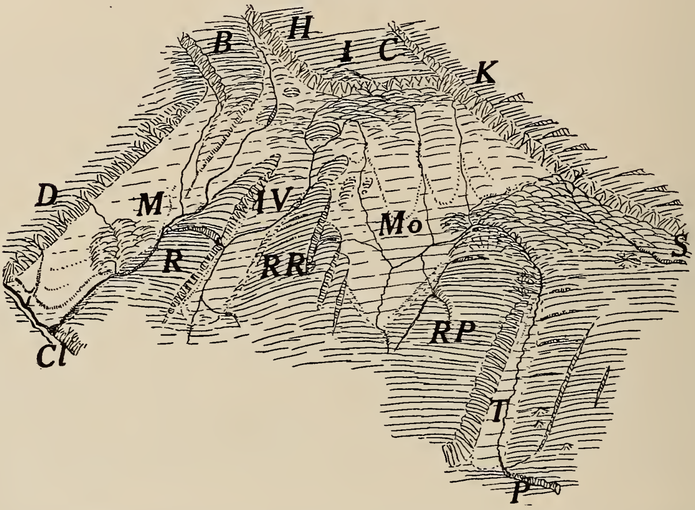

FIG. 13. Generalized diagram of the Central Otago chain of depressions and the associated block mountains. D, Dunstan block; M, Maniototo depression; R, Raggedy-Blackstone block; IV, Ida Valley depression; RR, Rough Ridge block; Mo, Maniototo depression; HP, Rock and Pillar block; T, Strath Taieri depression and Taieri River; P, Barewood Plateau; B, St. Bathans block; H, Hawkdun block; I, Mount Ida; C, Clark's Diggings fault angle; K, Kakanui block; S, Shag Valley fault angle; Cl, Clutha River.

Towards the northeast, on the other hand, the crests of the mountain blocks slope down so as to merge more or less completely in the lowlands and form a chain of nearly continuous depressions, which is a fault angle between the northeasterly slope of the southern block-complex and a great scarp with a general northwesterly trend, or a series of scarps broken by several offsets, which forms the boundary of a northern complex of high blocks.

In the latter fault-block complex, which may be termed the northern highland of Otago, the general trend of the dislocations is northwesterly; but still farther to the northeast the first-mentioned system again makes its appearance with perhaps a more northerly trend. The northeasterly trending system of late uplifts due to dislocations and folds is widespread in New Zealand, while the northwesterly system seems practically confined to Otago, making its appearance again to the southwest of the schist area of Central Otago.* The dislocations of the two systems do not, as a rule, occur together so as to define a regular rectilinear mosaic, but the blocks within the area traversed by the dislocations of each system are elongated like anticlinal and synclinal folds.

It is noticeable that while the block boundaries along the great northwest and southeast scarp that forms the boundary between the depressions and the northern highland coincide more or less exactly with the lines of junction of greywacke and schist areas of the undermass, the metamorphics, which presumably were originally the more deep-seated rocks, occupy the downthrown side. That is to say, the dislocations have followed the lines of more ancient faults of even greater throw, but have displaced the crustal blocks in the reverse direction.

The Central Otago System.—Confining our attention to the blocks somewhat directly connected with the Central Otago chain of depressions, we find that the most westerly of these—the Manuherikia depression—is bounded on the northwest by a highland block, the Dunstan Mountains, with an average height on the crest of 5,000 feet, or 4,000 feet above the floor of the Manuherikia depression. The even crest of the block indicates that its upper surface is flat, and any cover that formerly lay on the planed surface of the undermass has been stripped from it. The southeastward slope from the crest to the depression is a fault scarp, probably not of the simplest type.

The floor of the Manuherikia depression (fig. 14) has an average height of about 1,000 feet above sea-level. It is about 40 miles long and 8 miles wide. It contains a great thickness of the overmass, the beds of which are cut into terraces and dissected into residual hills, a relief that reaches a height of about 600 feet. The overmass is much obscured by a veneer of postdeformational alluvium.

The depression is bounded on the southeastern side by a narrow, elongated upland block 3 or 4 miles wide, which a transverse stream divides into two portions. The southwestern portion is called the Raggedy Range and the northeastern, Blackstone Hill. The whole may be termed the Raggedy-Blackstone block. Its somewhat undulating crest line is generally about 2,000 feet above sea-level, but rises to 3,200 feet in

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* In a recent paper, Speight (1916) ascribes the courses of some of the rivers of Canterbury to dislocations with a northwesterly trend.

Blackstone Hill. The back slope has an inclination of about 10° towards the northwest, where the stripped surface of the undermass passes under the covering strata of the Manuherikia depression. The southeastern face, or front, of the block is a fault scarp (fig. 15) against which are upturned the covering strata in the next depression.

This depression, known as Ida Valley, is traversed by the Ida Burn and Pool Burn. The mean height of its floor above the sea is about 1,500 feet. It is about 25 miles long and 3 or 4 miles wide and has the same northeast and southwest trend as the associated blocks. It is floored largely by postdeformational alluvium, but the covering strata appear at a few points along the margins. At the southwestern end the stripped floor appears and rises to merge with the upland plateau.

Fig. 14.

Fig. 14. View looking westward across the Manuherikia depression from the back slope of the Raggedy-Blackstone block. The southern end of the Dunstan block is seen in the distance and the valley of the Manuherikia River in the foreground.

To the east another upland block forms Rough Ridge. Its crest is very even for many miles with a height of about 3,200 feet above the sea. On its northwestern and northeastern sides this block is similar to the Raggedy-Blackstone block.

Farther south, however, it is complex and relatively wide, two broad splinters descending towards the northeast and forming offsets on the lowland level between the northeast-trending fault-scarp portions of the boundary line between the Rough Ridge block and the next depression to the east.

This depression, about 250 square miles in area, includes the Upper Taieri plain and the Maniototo plain—the whole being termed here the Maniototo depression. The lowest part of its floor is about 1,000 feet above the sea; the mean height of the Upper Taieri plain is about 1,200 feet and of the Maniototo plain about 1,500 feet. Considerable portions of the surface are covered by a layer of postdeformational alluvium, but at many points the beds of the overmass appear, among which on the eastern side are sheets of basalt. At the northwestern side low islands of the undermass emerge through the cover, the largest being almost continuous with the first splinter from the Rough Ridge block. To the south, as in the neighboring Ida Valley depression, the stripped surface of the undermass emerges, and the line of division between the depression and the southern highland plateau is not simple.

Fig. 15.

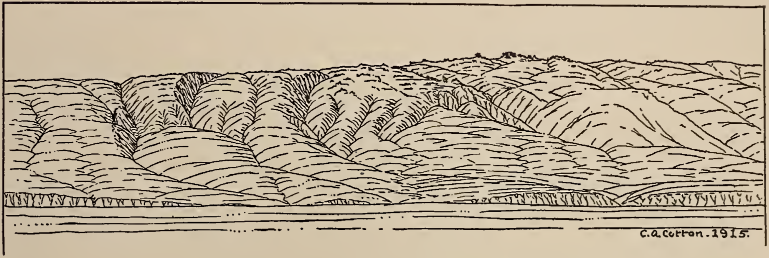

Fig. 15. The scarp or front face of the Raggedy-Blackstone block (Blackstone Hill portion).

A high block southeast of the Maniototo depression forms the Rock and Pillar Range, about 8 miles broad. Its western boundary is in part a fault scarp replaced towards the north by a steeply dipping "fold-surface," which passes under a sheet of cover preserved by basalt. The top of the range, presumably a stripped plateau, is gently inclined towards the northwest. The whole drainage of the highland surface is led away in that direction, and profound gorges are cut in the western scarp. In the highest portion of this block, the southeastern edge is about 4,500 feet above the sea, more than 3,000 feet above the floor of the depression on the western side and nearly 4,000 feet on the eastern side. At its northeastern end the block surface passes beneath the cover. A small portion, like the neighboring cover, is here maturely dissected.

On the southeastern side a very regular and apparently simple fault scarp about 20 miles in length, with an average height of 3,700 feet, descends from the even crest to a long, narrow fault-angle depression named the Strath Taieri, followed longitudinally by the Taieri River. Its planed floor, beneath which is preserved a narrow strip of the overmass, descends from about 1,000 feet above the sea at the northern end to about 600 feet at the southern end.

Fig. 16.

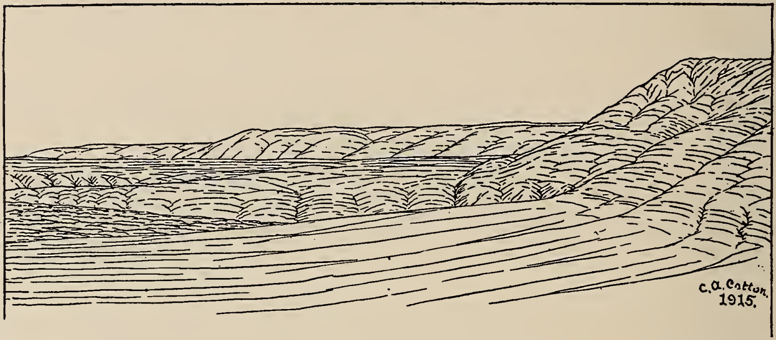

Fig. 16. View looking west across the Barewood Plateau. The Rock and Pillar Range is on the right, and the Lammermoor and Lammerlaw Ranges are seen in the distance, their fronts being the scarp of a high plateau.

On the southeastern side of the Strath Taieri depression the surface of the stripped undermass rises very gently to a plateau (fig. 16) varying in height from about 1,000 feet to 2,000 feet above sea-level. The plateau is traversed by a number of low, southeastward-facing fault scarps (fig. 17). In the fault angles some strips of cover are preserved and there are also lava-capped remnants on the uplands. This area with that to the southwest has been called by Park the Barewood Plateau. Its southwestern continuation is bounded on the western side by the fault-scarp margin of a higher plateau area practically continuous with the top of the Rock and Pillar block, though at a slightly lower level. This is the same broken plateau into which merge all the upland and lowland blocks enumerated. The conspicuous 2,000-feet fault scarps along the boundary between the higher plateau and Barewood plateau have caused portions to be known as the Lammermoor and Lammerlaw ranges.

The Manuherikia, Ida Valley, and Maniototo depressions are practically continuous towards the north, being separated only by gently upwarped areas in which the undermass rises sufficiently high to be stripped of its cover. The Maniototo depression is separated from the Strath Taieri, however, by a considerable area in which the covering strata, now maturely dissected, have survived as uplands owing to the presence of basalt.

The Northern Highland of Otago.—The northern boundary of the chain of depressions described above is formed by a series of scarps with a predominant northwesterly trend. Beginning at the western side, the northeastern end of the Dunstan block is a narrow, northwest-trending fault-angle depression occupied by Dunstan Creek separating the Dunstan block from the St. Bathans Range. The St. Bathans block merges at its southeastern end into the Manuherikia depression. It is elongated in a northwesterly direction and to the northwest merges into the highland region. It presents a fault scarp to Dunstan Creek and is strongly tilted to the northeast, the back slope descending in that direction to a fault-angle depression forming a northern prolongation of the Manuherikia depression, which is bounded on the opposite side by a long, straight, and conspicuous fault scarp, that of the

Fig. 17.

Fig. 17. Bird's-eye view of the slightly dissected stripped surface of a gently tilted, narrow fault block descending northwestward (toward the camera) and meeting a low fault scarp, the crest of which is seen in the foreground. Note that the dissection is entirely consequent and insequent. The point of view is a small lava-capped butte of rounded form, a remnant of a former more continuous cover.

Hawkdun Range (fig. 18). This scarp forms the northern boundary of the Ida depression also.

The straight front and remarkably even crest of the Hawkdun block have been noted by McKay (1897) and by Park (1906). Professor Park informs the writer that the surface of the summit plateau is strikingly flat and horizontal.

The Hawkdun plateau descends southward from an average altitude of 6,000 feet to something over 5,000 feet in a distance of about 12 miles. At its southern end is the dissected dome of Mount Ida, rising 300 or 400 feet above the plateau (fig. 19). It is perhaps a monadnock as suggested by Park (1906, p. 6).

The boundary between the depressions and the northern highland area swings around Mount Ida and extends due east for 10 miles, forming a great reëntrant occupied by a portion of the Maniototo depression, though part of the relatively low-lying area along the base of the scarp is occupied by a number of low-lying, subsidiary blocks, now forming uplands of moderate height in which the undermass is exposed.

Fig. 18.

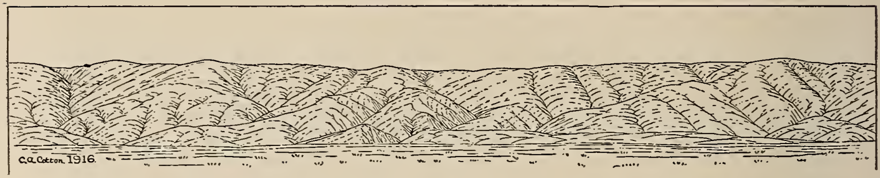

Fig. 18. Maturely dissected fault scarp of the Kakanui block. View looking north across the eastern margin of the Maniototo depression.

The surface of the Hawkdun block slopes gently eastward from the Hawkdun scarp and Mount Ida down to a fault angle over 4,000 feet above sea-level, bounded by the fault scarp of the Kurow and Kakanui Mountains, which faces west-southwest and rises about 2,000 feet higher. Remnants of the overmass are preserved in this fault angle on the highland surface at the locality known as the Mount Buster or Clark's Diggings (McKay, 1884, *c*).

The Kakanui fault scarp continues south-southeastward (fig. 20) and forms for 15 miles the eastern boundary of the Maniototo depression, having in this portion an average height of 5,000 feet above the sea. The great reëntrant in the highland rim occupied by a portion of the Maniototo depression is thus completed and the general southeasterly trend of the great scarp is restored. The scarp continues southeasterly to the sea, a distance of nearly 30 miles. From the crest line of this portion of the Kakanui fault scarp, the back slope of a great tilted block descends gently to the northeast as a somewhat undulating, stripped plateau surface and dips beneath marine strata near the coast. A branch of the Maniototo depression extends towards the coast as a fault angle along the base of the Kakanui fault scarp, forming Shag Valley. Its southwestern side is a gently sloping and slightly undulating stripped plain descending from the Barewood Plateau. In the fault angle some remnants of marine covering strata are preserved.

Fig. 19.

Fig. 19. The scarp of the northern highland with Mount Ida in the center, as seen from subdued hills of covering beds in the Maniototo depression, just east of the northern end of Rough Ridge.

4. *Drainage.*

The Central Otago Chain of Depressions.—The main lines of drainage in the chain of depressions of Central Otago appear to be entirely consequent on the deformation; but this statement does not exclude the possible occurrence of "anteconsequent" streams. The existence of true antecedent streams is not very probable.

The Manuherikia depression is traversed longitudinally by the Manuherikia River, flowing southwestward to join the Clutha (or Molyneux) River. The head of the Manuherikia occupies the fault angle at the base of the Hawkdun fault scarp, and its largest tributary, the Dunstan Creek, coming in from the northwest emerges from the fault angle between the Dunstan and St. Bathans blocks. These streams are fed by a large number of small tributaries which with the exception of the Pool Burn are consequent on the slopes of the neighboring block mountains.

The Pool Burn, which enters the Manuherikia depression from the southeast, cuts transversely across the narrow Raggedy-Blackstone block in a deep gorge. This transverse course has been described by Park as a capture (1906, p. 13), but none of the features generally associated with recently effected captures are to be seen in the valley system. Neither of the longitudinal streams of the Ida depression–the Pool Burn and the Ida Burn–which unite to flow through the gorge, can have been reversed by capture unless the capture took place before the excavation of the covering strata.

FIG. 20.

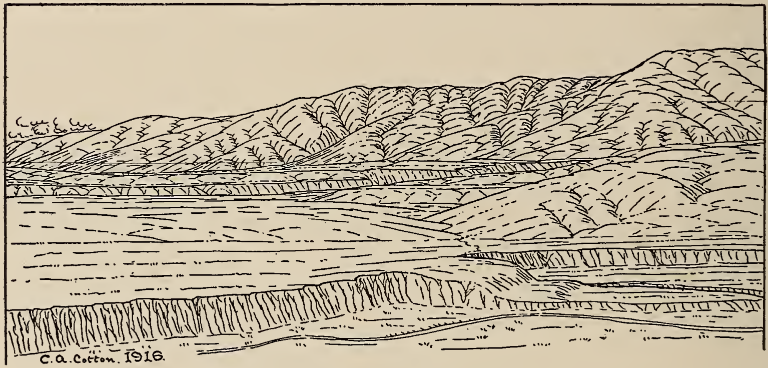

FIG. 20. Maturely dissected fault scarp of the Kakanui block. View looking north across the eastern margin of the Maniototo depression.

Park says, "The Ida Valley basin, as shown by the river terraces and surface contours, at one time drained into the Maniototo Basin." He describes the Ida Burn for a distance of over 12 miles as a reversed stream; but in that distance it has a fall of 500 feet, and it flows the whole distance in a flat-floored valley opened to the full width of the Ida tectonic depression. Such terraces as survive descend in the same direction, giving no indication of reversal. There is, moreover, no stream nor abandoned valley of erosion that can be interpreted as the beheaded former course of the Pool Burn. Furthermore, it is difficult to explain why a tributary of the Manuherikia should breach the Raggedy block. The climate is arid; other consequent streams on the back slope of the block are intermittent and feeble; and have not even begun to cut gorges through the range.

As the Pool Burn gorge (fig. 21) crosses the Raggedy-Blackstone block at a low sag in the crest line, there can be little doubt that it is consequent on the deformation. Whether the present transverse stream marks the point at which a consequent lake in the Ida Valley depression spilled over or whether the excavation of the gorge kept pace with the deformation cannot now be determined.

Fig. 21.

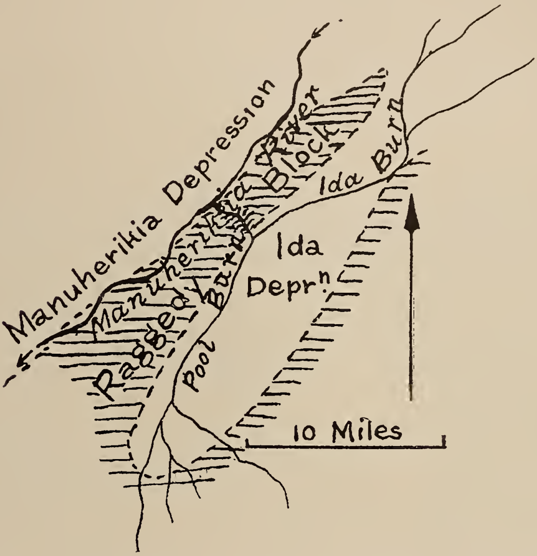

Fig. 21. The course of the Pool Burn.

The centripetal consequent streams of the Ida Burn and Pool Burn systems are of insignificant size and in dry seasons practically disappear. Both the Ida Burn and the Pool Burn are fed by numerous wet-weather consequents which run down the front of the Raggedy-Blackstone block and the back slope of the Rough Ridge block; but the main volume of the Ida Burn comes from the greywacke highland to the north and of the Pool Burn from the schist plateau to the south. Their courses are thoroughly graded on the weak material of the overmass in the depression, broad valley plains have been developed, and the streams are bordering on senility. However, the gradient of the valley floor of the Ida Burn is considerably steeper than that of the Pool Burn. This difference is due to the much greater load of waste which the northern stream has to transport, and which comes from the great fault scarp of the greywacke highland. The little dissected schist plateau from which the Pool Burn flows supplies a relatively small quantity of waste.

The numerous parallel, southward-flowing, consequent streams in the northern or Maniototo Plains portion of the Maniototo depression are exactly similar in their gradients and their arrangement to the streams of the northern end of the Ida Valley depression. The Ida Burn and the Wether Burn are separated by a narrow interfluve consisting of the outcropping undermass of a northerly continuation of the Rough Ridge block. The Wether Burn and the other similar streams form the northern members of a centripetal consequent system in the Maniototo depression and are tributaries to the Taieri River.

Those streams also consequent on the deformation, which enter the depression from the schist upland plateau to the south, like the Pool Burn, flow with very gentle gradients across the wide valley plain which there forms the floor of the depression. The chief of these, the Upper Taieri, wanders freely, and oxbow lakes abound upon its flood plain. As a result of the steeper gradient of the northern streams owing to larger supply of waste, the east-and-west axis of the lowland in the Maniototo depression has been pushed far to the south.

The drainage of this depression finds an outlet by way of the Taieri River into the Strath Taieri depression, crossing the area of mature dissection around the northern end of the Rock and Pillar block in the fault angle between that block and the Kakanui fault scarp to the north. This portion of the course of the Taieri is probably consequent on the deformation, being determined either by the spilling over of a consequent lake in the Maniototo depression or cut down during slow deformation. The floor of the depression was obviously much higher in an early stage of the cycle before part of the overmass had been removed. It is unnecessary, therefore, to suppose that the present rather young gorge was cut contemporaneously with the deformation. Its cutting must, however, have gone on while the floor of the Maniototo depression was being excavated to its present depth.

The southwesterly course of the Taieri River through the Strath Taieri depression is obviously consequent on the deformation, as also are most if not all the larger tributaries this river receives in its course across the Barewood plateau. The course of the Taieri River itself in a southeasterly direction across the plateau appears to be consequent, as it follows the lowest sag in the surface. It is graded, or almost so, with a gradient of about 20 feet per mile, but it is still in the narrow-floored, rock-walled Taieri Gorge (fig. 22), which is incised at one place to a depth of about 1,000 feet below the plateau surface.

The Shag Valley fault angle is drained by the Shag River, which rises in the maturely dissected uplands overlooking the Maniototo Plain and follows the line of the depression in a northeasterly consequent course to the sea.

Most of the tributaries of the streams in the Central Otago depressions flowing over the rocks of the undermass might be considered superposed consequents instead of normal consequents, if it can be shown that their directions were determined by the slope of a former cover. They are indifferent to both the dip and the strike of the underlying rocks, but as they follow the slope of the surface of the undermass they may be classed as simply consequent, whether they were initially guided by the slope of the planed and tilted surface now visible or by the slope of an overmass for which that surface formed a floor.

Fig. 22.

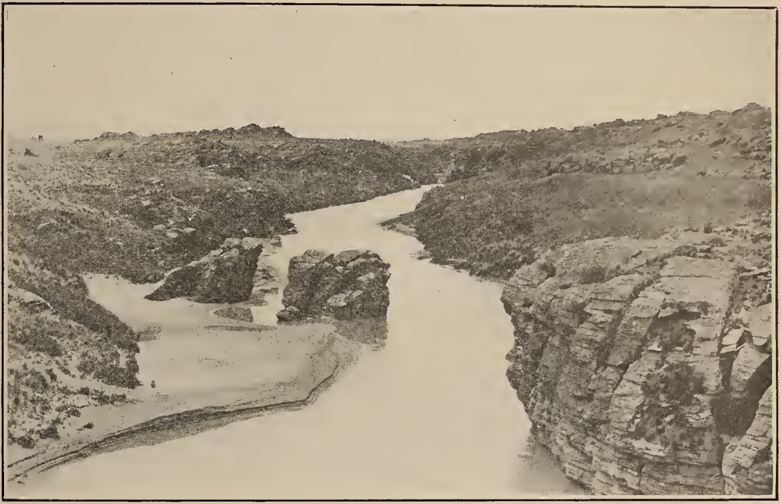

Fig. 22. View looking down the Taieri River at the upper end of the great gorge in which it traverses the Barewood Plateau.

A distinctly different kind of superposition is shown by the Manuherikia River and the Ida Burn, flowing parallel with the tilted Raggedy-Blackstone and Rough Ridge blocks, and also by the Shag River. Portions of these streams are now superposed on the undermass of the sloping plateau as a result of shifting far over to the side of the guiding depression and failing later to slip off the gently inclined surface while cutting vigorously downward in response to rejuvenation. Each such portion is now imprisoned in a narrow rock-walled gorge, while reduction of the general level of the adjacent portions of the depressions is being carried on by minor streams. The case is closely analogous, though not strictly homologous with that of the horseshoe bend of Hoxie Creek, described by Gilbert as an exception to the general rule of monoclinal shifting (Henry Mountains, 1877, pp. 137–138).

For some portions of the course of the Manuherikia thus imprisoned in schist gorges Park has given a different explanation (1906, p. 12). He says, "The river leaves its old course and plunges suddenly into a deep, narrow rift" which is formed by "a number of intersecting faultlike fractures, along which the river runs, passing from one to the other."

Similar superposition has been described in the Clarence Valley fault-angle depression in Marlborough (Cotton, 1913, pp. 233–234). The Aorere Valley fault-angle depression in northern Nelson apparently affords another example, for which, however, Bell (1907, p. 27) has proposed a theory of capture similar to that advanced by Park for the Manuherikia.

The Clutha River System.—Beyond the area with which we are immediately concerned are the largest rivers of the region—the Waitaki to the north and the Clutha (Molyneux) to the south. The latter crosses the Manuherikia depression at its southern end, where the Clutha is joined by the Manuherikia River. The upper course of the Clutha is guided by a smaller similar chain of depressions which may be termed the Upper Clutha chain. A large tributary, the Kawarau, also receives the drainage from a number of narrow fault angles. Intermediate portions of its course may be in great part consequent on the deformation, being guided by the lower sags or fault angles in the highland plateau, considerable areas of which, as Park has shown (1908), still survive in the various flat topped ranges. The Kawarau is now the outlet for Lake Wakatipu, which formerly overflowed at its southern end by way of the air gap leading to the upper Mataura. The upper Kawarau, now deepened into a gorge throughout its length, is thus probably of recent origin and perhaps subsequent.

The combined waters of the Kawarau and the Clutha form a river of great volume and enormous energy. The portion of this stream which cut the deep Dunstan Gorge (fig. 23), leading from the tectonic depression of the Upper Clutha to the Manuherikia, seems to have been guided by a sag in the highland plateau between the Dunstan block and the Old Man Range to the southwest. It may, therefore, be classed provisionally as consequent. The same origin may be assigned to the gorge in which the Clutha leaves the Manuherikia depression in a southerly direction. Farther downstream the river traverses a succession of narrow tectonic depressions. The Clutha river system may, therefore, be regarded as almost entirely consequent.

The Mataura and Oreti also flow generally in broad tectonic depressions and must be classed as generally consequent.

Fig. 23.

Fig. 23. View looking southeastward down the Dunstan Gorge, by way of which the Clutha River breaks into the Central Otago chain of depressions after leaving the Upper Clutha chain.

The Waitaki River System.—The great Waitaki River occupies in its upper course a broad tectonic depression, the details though not the general form of which have been modified by glacial action.* In its middle and lower course the Waitaki is guided by a linear tectonic depression irregularly bounded by the fault scarps and back slopes of a complex of blocks in the bottom of which some low-lying remnants of covering strata are preserved (Marshall, 1915).

The Waitaki River is thus probably wholly consequent on the deformation. It follows a complex graben along the north-

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* Kitson and Thiele (1910) describe the Waitaki Basin as "due to preglacial erosion, faulting, with probably some warping, modified by glacial action" (p. 551).

ern boundary of the block-complex with predominating northwesterly trend which forms the northern highland of Otago. In the Middle Waitaki graben there are a number of small blocks in various attitudes. On the northern or Canterbury side of the graben the dislocations seem to belong to the northeasterly system, though trending somewhat irregularly, while farther north the highest blocks are elongated generally in a north-and-south direction.

One great depression, occupied by the consequent course of the Hakataramea River, a tributary of the Waitaki, is of great length and has a width on the floor of about five miles. It is bounded on the west by an imposing fault scarp of the block forming the Kirkliston Range, 6,000 feet high; but its chief peculiarity is a bar of the undermass about half a mile wide and rising about 400 feet above the level of the river, which forms a kind of sill across the outlet, cutting off the excavated lowland within from the Waitaki depression and river. The sill is traversed by a narrow, rock-walled gorge cut by the outflowing Hakataramea River. A layer of bedded fluviatile gravel on the top of the sill proves that the great lowland of the Hakataramea Valley upstream from the sill has been eroded by the river during the time occupied in cutting the outlet gorge through the sill. A number of terraces in the depression mark stages in the excavation of the lowland. In the earliest postdeformational cycle, the undermass of the sill of the Hakataramea depression had probably not been revealed by erosion.

5. *The Surfaces of Uplifted Blocks.*

Stripped Plateau Surfaces.—With the exception of the lava-protected areas, the cover has been stripped from the uplifted block surfaces. The only indication of its former existence is the occurrence of "sarsen stones." The planed surface of the undermass is thus revealed, and in a few places submaturely or maturely dissected.

The stripped plateau surface survives over large areas, even on slopes exceeding 10°. The precipitation is small and the slopes are drained by systems of numerous, intermittent, parallel consequent streams and a few unimportant insequents; but no distinctly subsequent streams or positive relief forms on the surface of the undermass have been observed. The edges of the interfluves are almost invariably rounded by soil creep.

The type of stripped sloping-plateau surface with very shallow dissection is of general occurrence in Central Otago and the neighboring area to the northeast. (See figs. 2, 3, 17.) This type of surface appears to have a close analogue in that found on the flanks of the resequent or stripped anticlinal ridges of Table Mountain sandstone in southeastern Cape Colony (Davis, 1906, fig. 6).

Details of the Surface on Schist Blocks.—The same general type of relief is found on the schist and on the greywacke blocks. The surfaces of the latter are smooth and soil-covered (fig. 24); on the former are many residual tors—great castle-like, joint-bounded masses of bare schist (fig. 25). Tors are characteristic of a Central Otago landscape, and they have suggested the names given to many of the schist mountains—as, Rough Ridge and Raggedy Range. In the humid area towards the coast, tors are not found; they are largest and most abundant in the most arid districts, a gradual transition being traceable from the humid to the arid area. The development of the schist tors is, therefore, controlled by climate. They are found on both horizontal and sloping block surfaces, and their form is most characteristic and regular where the schist lies nearly horizontally.

FIG. 24.

FIG. 24. Youthfully dissected stripped surface of a small greywacke block in the larger fault angle between the northern end of the Raggedy-Blackstone block and the scarp of the northern highland.

The uneven resistance of the schist to erosion is probably not due to differences in composition, as suggested by Rickard (1893, p. 419). Finlayson (1908, p. 73) and Park (1908, p. 12) have noted that the tors are bounded by joint planes. It would appear, therefore, that the schist is more susceptible to weathering in the interior areas on account of some peculiarity in the jointing, and it may be that the surface was deeply and irregularly weathered prior to the deposition of the covering strata. The occurrence of scattered logs of timber on the block surfaces (Park, 1908, p. 23; Speight, 1911) where the climate now borders on aridity, proves the existence of forest established in an earlier, moister period. If the forest covering was continuous, deep and irregular weathering may have taken place even in the current cycle.

Fig. 25.

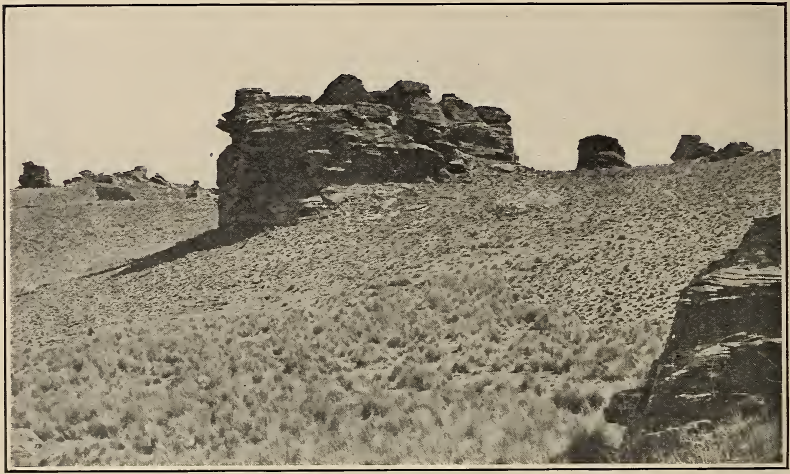

Fig. 25. Schist tors on Rough Ridge.

Whether differential weathering is or is not still going on, weathered material is being rapidly removed from the surface of poorly protected soil, and it is thus that the tor pattern has been etched out.

As greywacke does not occur in the most arid area, the contrast between greywacke and schist surfaces may be seen only in the vicinity of the scarp of the northern highland where the climate is semiarid. It may be that tors would form on a greywacke surface in the arid district. But as the greywacke is always thoroughly jointed, possibly no portions of the rock are sufficiently free from joints to survive as tors.

It is to be noted that the presence of tors on the plateaus and sloping uplands indicates a general lowering of the surface. Tors 20 and 30 feet high are very common, and on the higher plateaus some reach a height of 70 to 80 feet (Park, 1908, p. 12). This reduction of the block surfaces is not the result of channeling. The convexity of the edges of the interfluvial areas indicates that soil creep plays a part; but on the more nearly level interfluves, erosion is more probably of the sheet-flood kind.

Salients on Block Surfaces.—Preëxisting salients on a plain that has been strongly and in places irregularly deformed can not always be recognized with certainty even in an early stage of the postdeformational cycle (p. 257), and some may have been overlooked by the writer. On such of the Central Otago blocks as have been evenly uplifted, however, salients are absent. Mount Ida, on the edge of the northern highland, is perhaps a monadnock. Park suggests that Mount St. Bathans also is a monadnock rising above the level surface of the Dunstan Range (Park, 1906, pp. 6 and 8), but this is a distinct block (p. 278).

On the northern end of the Rock and Pillar block and on the gently tilted blocks of the eastern or Barewood Plateau are small prominent salients which are probably without exception lava-capped remnants of the overmass.

Scarps of the Schist Blocks.—The majority of the scarps following lines of dislocation in Otago are at the present stage of denudation in part fault-line scarps revealed by the removal of the covering strata. Since the fault scarps on the same lines had not been destroyed by erosion prior to the development of fault-line scarps, there is no danger of misinterpreting the geologic history in considering them entirely as simple fault scarps. Fault scarps form the boundaries of a number of blocks in Central Otago, and sufficient evidence of faulting is furnished by the attitude of the covering strata at the bases of the scarps. Along the front of the Dunstan block these beds are shown by Park (1890 *c*) and McKay (1897, figs. 20, 21, 26, 27) to be steeply inclined, vertical, and even overturned. The dip of the schist-foliation has been shown also by Park (1906) to become steep in the vicinity of the fault line, showing that the scarp is at least at its southwestern end a composite fold and reverse-fault scarp similar to that forming the southeastern slope of the Kaikoura Mountains in Marlborough (Cotton, 1913). This block boundary is the line of the Manuherikia fault of McKay (1897). The evidence of compression found here is in accord with what is known of the dislocations farther west.

Along the front of the Raggedy-Blackstone block the strata are upturned, as shown by Park (1890 *a*, p. 21), along a fault termed by McKay (1897) the Blackstone Hill fault. McKay writes: "This line runs nearly parallel to that along the southeast base of the Dunstan Mountains, and both lines have on the opposite side of the valley an outcrop of quartz drifts dipping at a lower angle in a northwest direction, or away from the range that bounds the valley on the southeast side" (p. 112). There is no definite evidence that the fault is reversed.

In other cases the beds of the cover lie practically horizontally close to the bases of the scarps, as in the eastern scarp of the Rock and Pillar block, and in the scarp of the Hawkdun block (McKay, 1897, fig. 16), indicating probably normal faulting.

Fold scarps of small extent and not yet maturely dissected occur near the northeastern ends of the tapering Raggedy-Blackstone, Rough Ridge, and Rock and Pillar blocks on their eastward-facing fronts (fig. 10), and on the northwestward-facing portion of the last.

Fig. 26.

Fig. 26. The eastern portion of the Maniototo Plains and the scarp of the Kakanui Range.

The fault scarps of the schist blocks, especially where the schist is weak, have crumbled to very gentle slopes. The great scarp, nearly 4,000 feet high, forming the long, straight southeastern face of the Rock and Pillar block, has an average slope of 20°.

The Scarps of Greywacke Blocks.—The scarps of the greywacke blocks along the margin of the northern highland of Otago are little-dissected fault scarps forming the fronts of tilted blocks, as are also the scarps of the block complex in and beyond the Waitaki Valley depression.

Among the well-preserved scarps which form the fronts of simple tilted blocks there is a decided family resemblance, and they contrast strongly with the scarps of schist blocks. The average slope of greywacke fault scarps is nearly twice as steep as that of schist scarps. Like the schist fault scarps, though generally not deeply dissected, these may be described as submature or mature with graded slopes. The difference in steepness between the schist and greywacke scarps is to be ascribed, therefore, to the much steeper gradient which in the greywacke blocks represents a condition of equilibrium after the first rush of scarp destruction by crumbling and slumping initiated by the deformation.

In low scarps (up to about 1,000 feet) the average slope of the salients (scarcely to be dignified by the term spurs) is about 40°, and that of the intervening reëntrants somewhat less. Definite sharp-edged facets are not found, the salients being generally of even slope and broadly convex as a result of grading of the slopes by soil creep. Instead of ravines the reëntrants are usually funnel-shaped shoots that merely scallop the edge of the upland surface. They are occupied by streams not of water but of angular fragments of rock. Such a scarp is found in the front of the southern end of the Hunter's Hills block in Southern Canterbury (fig. 8), and a much higher one forms the western slope of the St. Bathans block, the shallowness of the dissection of the front of which is due to the strong backward tilt of the block.

In high scarps which do not conform to this extreme type, mature dissection has been effected by steep-grade permanent streams whose heads penetrate only a short distance back into the highland plateau. Of this nature are the Hawkdun and Kakanui fault scarps (figs. 18, 20, and 26).

6. *The Floors of the Central Otago Depressions.*

In general the depressions contain no great accumulations of alluvium as a result of postdeformational aggradation. The vast quantity of waste resulting from the stripping of the overmass from the uplands and its erosion in the lowlands, as well as that derived from the erosion of portions of the undermass, has been removed in the course of ages by streams, many of which seem puny and almost powerless. In those large areas in which the covering strata extend below local base-levels and have thus escaped complete removal, planation of their surface is far advanced. This is particularly true of the southern parts of the Ida Valley and Maniototo depressions, floored by the level valley plains of the Pool Burn and the Upper Taieri River.

The northern portions of the Ida Valley and Maniototo depressions and of the Manuherikia depression, which are practically continuous, may be described as a local peneplain, the erosion of which has been lately revived several times. The upper courses of the streams of the northern part of the Maniototo depression are at present confined to shallow valleys, the flood-plain floors of which, though of no great width, open out downstream and become continuous. They form a plain which slopes towards the confluences of the streams with the Taieri and is accordant with the valley plain of the Upper Taieri. The recent revival of erosion along the base of the northern fault scarp is perhaps due to climatic changes affecting the supply of waste to the headwaters of the streams. The valley plains and the terraces are covered by a layer of greywacke gravel.

In the southern part of the Manuherikia depression the relief is considerable. There are broad areas of high terrace owing to the recent deepening of the valley of the Clutha, of which the Manuherikia is a tributary. The effect of this may extend into the upper Manuherikia; but it has not yet appeared to affect the streams of the Ida Valley depression; while those of the Maniototo depression do not belong to the Clutha system.

There has been a small rejuvenation in the Taieri River where it flows through the Strath Taieri depression; but the floor of this narrow fault angle is for the most part a valley plain.

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Art. XXIII.—*Dinosaur Tracks in the Glen Rose Limestone near Glen Rose, Texas;* by Ellis W. Shuler.

The finding of dinosaur tracks is sufficiently rare that it is worth while to record all new localities, and especially formations carrying such tracks; the unique occurrence of these tracks in limestone rock seems to merit a somewhat detailed description. Thanks for calling the attention of the writer to the locality and for helpful discussion is due to Prof. J. D. Boon of the Texas Woman's College of Fort Worth, Texas.

The dinosaur tracks figured in illustrations 1 and 2 are exposed in the flat bottom of a ravine near Glen Rose, Texas, where they are locally known as the "bird tracks." The tracks are found in a hard white limestone which forms the bed of the stream. The layers immediately over the limestone are less resistant to stream erosion and the stream has stripped back to steep banks a flat bottom more than fifty feet wide, one side of which is covered by stream gravel and sand.

Eight tracks were found, five in the uncovered portion and three covered by stream gravel. The tracks show a uniform step of 4 feet and 2 inches. The dinosaur was moving N.E. and the tracks are directly in line, each step following consecutively and not alternately from side to side. The tracks show three toes with a measurement of 16 inches from the anterior end of the middle toe to the heel and a width of ten inches. Imprints of claws occur at the end of each toe. There is no evidence of a fourth toe or dew-claw. All tracks are surprisingly alike, there being small evidence of right and left foot.

The beds in which the tracks are found are placed in the middle third of the Glen Rose Formation, which belongs to the Trinity division of the Comanchian. According to R. T. Hill* the Glen Rose Formation has in this locality a thickness of 315 feet. The middle third of the formation is composed of thick and massive indurated limestone.

Figure 3 shows in detail the section immediately above and below the layer carrying the tracks. The measured section is as follows:

Section of Glen Rose Limestone where dinosaur tracks are found near Glen Rose, Texas.

a)	Shell breccia, indurated. 89% calcium carbonate	1½ inches
b)	Shale, calcareous; greenish yellow. Limy at the top	8 inches
c)	Shale, greenish yellow. Weathers into a fine-grained clay. 33% calcium carbonate	5 inches

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*21st Ann. Rept. U. S. G. S., pt. VII, p. 153.

d) Limestone, white, indurated. Contains dinosaur tracks. 75% calcium carbonate	$2\frac{1}{2}$ inches
e) Limestone, shaly, hard	4 inches
f) Limestone, gray, impure	1 inch
g) Limestone, shaly, yellowish gray	5 inches

FIG. 1.

FIG. 1. Dinosaur tracks in the Glen Rose Limestone, near Glen Rose, Texas.

As given in the table above a chemical analysis of the limestone layer (*d*) shows that it contains 75 per cent of calcium carbonate, while the shaly layer immediately above contains 33 per cent of calcium carbonate. The layer below will probably show more than 50 per cent calcium carbonate.

A microscopic examination shows that both the indurated layer with the tracks and the shale layer above it contain finely comminuted angular fragments of quartz, which in the shale measure up to 1/10 mm., while in the limestone only up to 1/50 mm. In thin section the limestone layer shows an occasional minute bivalve shell in a groundmass of fine granular calcite with fragments of quartz and clay material.

The common association of dinosaur tracks has been with sandstones and shales, rocks which bear visible evidence of littoral conditions. But the dinosaur tracks near Glen Rose, Texas, are found in a hard white limestone, which at the time of the passing of the dinosaur must have been in the form of a stiff, tenacious lime mud forming a surface layer of about three inches into which the foot pressed to depths of two to two and a half inches. Had no dinosaur tracks been found the section would probably have been interpreted as having been laid down in deep marine water and at a distance from shore, since no part of the section shows a calcium carbonate content less than 33 per cent.

FIG. 2.

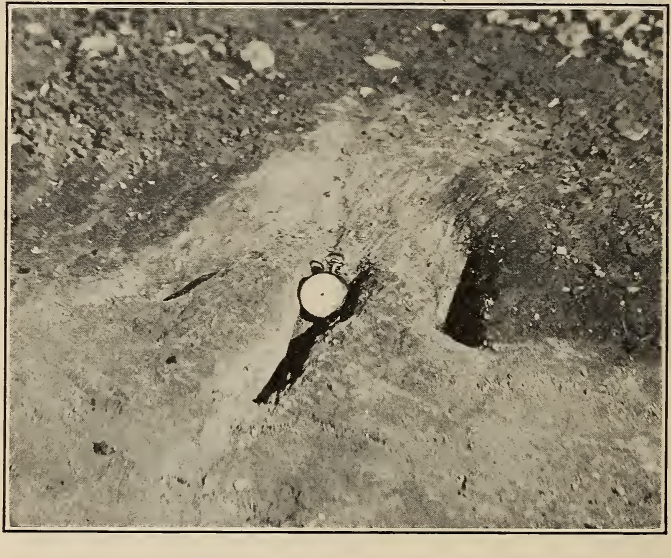

FIG. 2. Near view of Dinosaur track in limestone.

What then were the conditions under which the tracks were made? First of all, the dinosaur was walking on a mud surface, lime mud to be sure, but mud. The foot was pressed down into the lime mud sliding forward somewhat, as is seen in the imprint of the heel, figure 2, until the ends of the toes were buried beneath the surface of the mud. The mud was sufficiently plastic to hold the form when the foot was withdrawn.

The tracks were probably made while the mud was underneath the water. There are neither sun-cracks as evidence of desiccation or emergence of the muds; nor ripple marks or other evidence of current action. The limy clays immediately above the limestone, which were deposited after the passing of the dinosaur, show little stratification and were evidently laid down by very gentle currents.

Fig. 3.

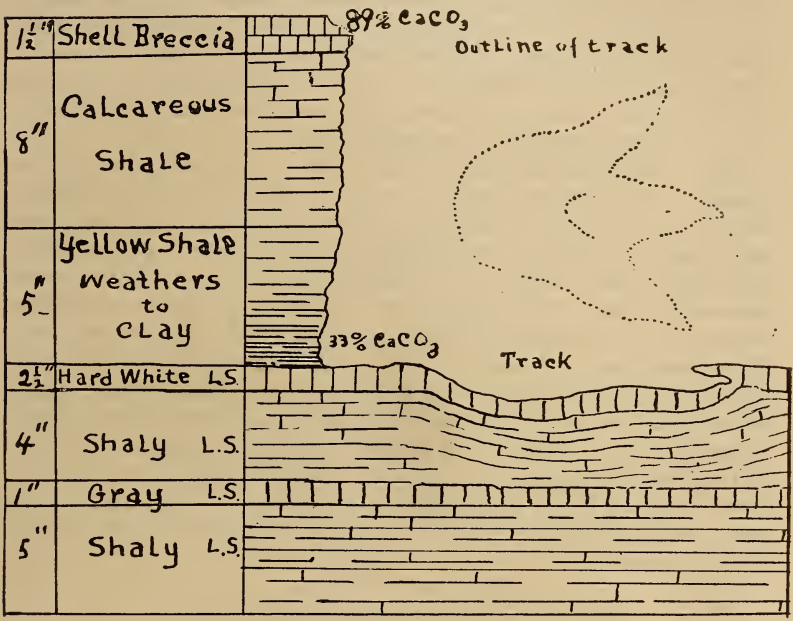

Fig. 3. Cross section of beds in which the dinosaur tracks are found. Outline of track one-twelfth natural size.

That the dinosaur was a land animal seems highly probable from the character of the foot. That it was wading also seems probable. A range of depth of water five to ten feet does not seem unreasonable but a further important question is the distance away from shore. The Glen Rose formation was laid down in a transgressing sea, which if the surrounding area were near to base level, would sweep over wide areas with shallow depth in a brief period of time. If the waves were cutting against limestone rocks, lime muds would be deposited near the shore. On the other hand it is true that the muds in question might have been chemically precipitated. There is at present no critical test to distinguish detrital lime muds from those chemically precipitated unless triturated quartz grains be valuable for that purpose.

If the dinosaur was wading near shore then, since the dip of the beds is very gentle it would be necessary to think of the seas of Glen Rose time as very shallow, extending over many square miles but only a few feet deep, perhaps not more than five to ten feet deep. Current action except under stress of storm was probably slight; yet the brecciated zone at the top of the section does show current action. Shell fragments up to an inch in cross section were transported.

There is still a further problem to be solved and that is the position of the Trinity sands during the deposition of the Glen Rose limestone. R. T. Hill's position that the Glen Rose limestone passes laterally into Trinity sands seems to be substantiated by many facts. It is noteworthy that in the vertical transition from Trinity sands into Glen Rose limestone there are abrupt alternations of limestone and sand without intermediate shale beds. It seems quite probable that the lateral transition was equally abrupt and that while Trinity Sands were being laid down along shore Glen Rose limestones were forming near shore, so near in fact that only the transition beach of Trinity sands and marls intervened. If such were the conditions then it would have been easily possible for a land animal to have waded out far enough in a shallow sea to have left tracks in lime muds.

Eubrontes (?) *titanopelopatidus* sp. nov.

For this lower Comanchian dinosaur track the following name is offered: *Eubrontes* (?) *titanopelopatidus* sp. nov., which being interpreted is "the lime mud strider."

Southern Methodist University, Dallas, Texas.

ART. XXIV.—*Outline of the Geological History of Venetia during the Neogene*;[*] by GIUSEPPE STEFANINI.

AT this time, when a fierce struggle is in progress and most of the European nations are fighting to return to the geographic and natural limits of their frontiers, it is perhaps not without interest to cast a glance at the geological history of one of the most important battle-fields, one, where, perhaps, the struggle is fought most fiercely from the point of view of natural difficulties, namely the region of Venetia.

The ideas which I am going to set forth rapidly are a résumé, or rather the conclusions of a somewhat exhaustive memoir, which was published more than a year ago, and which is the fruit of studies which have taken many years of work.[†]

If, then, from the following pages, based entirely upon objective studies, made without any foreign prejudice regarding the purely geological subject which I treated, the reader will be led to draw the conclusion that the Trentino and Valsugana, from the geological point of view (as well as from the ethnological point of view), are inseparably attached to the Venetian region, having been a part, since the most remote time, of the same maritime basin, one cannot accuse me of having been guilty of unscientific prejudices or of having wished to bring forward proofs in support of a national issue, which, moreover, has no need of such arguments for its support.

Nature and Extent of the Neogene Deposits in Venetia.

The Neogene series is represented in the Venetian region by its two series—the Miocene and the Pliocene—in very different proportions. The Miocene sediments occupy, all told, an extent of approximately 360 square kilometers; the Pliocene, on the contrary, is represented by only a very small remnant of an almost inappreciable extent in the province of Treviso, to which can be added two others, likewise very restricted, in the province of Brescia. The *maximum* thickness of Miocene beds in central Venetia—where the complete series is represented—totals perhaps 3000 to 3500 meters, while the Pliocene is only a hundred meters in thickness.

All of these deposits, from the lithologic point of view, present a very monotonous *facies;* they are clastic deposits, marly or molassic,[‡] originating evidently from the denudation of a

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[*] Communicated by Prof. Edward W. Berry; translated by George E. Dorsey.

[†] Memorie dell' Instituto Geologico della R. Universita di Padova, vol. iii, 1915.

[‡] The term molasse is applied to marine, brackish and freshwater littoral, either calcareous or argillaceous rocks, easily worked, with interbedded conglomeratic lenses, characteristic of the Alpine region during periods of oscillation of the strand.

continent which was rising. In the Lower Miocene are found sands and "calcaires grossiers" with glauconite, passing into "molassic" deposits, or into marly limestones which are sometimes employed in the manufacture of hydraulic lime. A fauna rather rich in pectens and echinoids, with some corals and barnacles characterises the stages of this period, fairly easily recognizable,—the Aquitanian and the Langhian (Burdigalian).

The Aquitanian rests on the upper Oligocene in Vicenza, Treviso, and Belluno; to the west of this central region (Verona, Trentino) the Aquitanian is transgressive on terrains of different ages, more or less ancient; to the east (Friuli) it is absent, and it is the Langhian that is the immediately succeeding stage resting directly on the Eocene Flysch or on the Cretaceous limestones. And yet in western Venetia there are spots where the Langhian is transgressive, for example, in the immediate vicinity of Verona.

The middle Miocene presents a facies entirely marly at the base (Helvetian); a marly sand at the top (Tortonian); glauconite appears to be absent even in the clastic condition. In the Tortonian the "molasses" alternate with layers of pebbles, more and more thick and frequent. The fauna is especially rich in molluscs of a tropical or subtropical type. The middle Miocene is largely developed in eastern and central Venetia; to the west deposits of this age are known only in Valsugana and in the neighborhood of Bassano; from all the remainder of Vicenza, Verona, and the region around the Lago di Garda it has been removed by erosion.

The upper Miocene is represented by an alternation of conglomerates, marls, and "molasses," many times repeated, rich in impressions of leaves and in terrestrial and fresh water shells. Occasionally teeth of Dinotherium and of mastodons are found in lignite beds, which form a very characteristic horizon at the base of the series. The upper Miocene formations cover large areas in Friuli, Treviso, and in the Trentino; they have not yet been recognized farther to the West.

Finally, the Pliocene, reduced by erosion to extremely restricted remnants, has its usually marly fossils, and presents a curious mixture of echinoids and stenobolic marine, almost bathyal molluscs, together with leaves of continental trees.

Because of the often displaced position of the beds, and of the nature of the rocks,—all more or less easily eroded,—the Neogene deposits as well as the Paleogene generally do not form outcrops of great extent in the Venetian region. On the contrary they are separated into numerous remnants, spread in part at the edge of the prealpine chain, facing the plain (extra-alpine remnants), and in part in the interior of the mountain region (intra-alpine remnants).

Concerning the structure, one can say, in general terms, that the Miocene by its mere presence marks synclinal zones; for, indeed, it is in the synclines protected by the older and more resistant rocks, that the Miocene beds, always more or less marly or "molassic," have been preserved from complete destruction. Four synclines can be recognized affecting the Miocene terrains of the intra-alpine remnants,—from Friuli (or the province of Udine, or eastern Venetia) through Belluno (province of Belluno) and Valsugana, to the Lago di Garda.

A band of Neogene deposits of varying width, in general elevated or overturned, borders almost without interruption the prealpine chain, forming chains of hills, elevated some hundreds of meters, "en échelon" in many lines, from Udine to Bassano and beyond; further to the west this band divides into many small fragments, composed of horizontal or nearly horizontal beds, surmounting the Paleogene formation of Vicenza, of Verona, and of the province of Brescia. The extra-alpine remnants can in general be considered as the southern wing of the prealpine anticline, although the latter may sometimes be complicated by secondary folds.

The Preadriatic Gulf.

Contrary to accepted opinions, I have been led to think that he intra-alpine remnants, enclosed in general in the bottoms of the valleys, are not evidence of little gulfs, or of narrow arms of the sea, which the surrounding mountains must have formed before the deposition of the Miocene beds. The Miocene beds of the intra-alpine remnants have been ruptured, elevated, overturned, at the same time as the Paleogene or Mesozoic beds on which they rest, and which in turn compose the surrounding mountains; they are only the remains, protected from the forces of erosion, of a formation which must have been continuous or almost continuous, at least from the Tagliamento to the Chiese, and extending in the interior of the country to Belluno, Borgo Valsugana, and Riva di Trento; that is to say (fig. 1) over the whole extent of the Venetian region in the broad sense of the word. The fragment at C. Cauiana, elevated to a height of 1065 meters, is a most striking proof of this.

This group of fragments of greater or less extent, is moreover well characterized compared to other Neogene basins. To the east are found only marine deposits in the Balkan Peninsula, in Servia; to the north, the nearest marine Miocene formation is found in the Vienna Basin. Everything causes one to think that the Venetian Neogene basin had an individuality all its own, and that it was bounded by a coast on the east, as well as one on the north and the west, while it opened broadly to the south. The characteristics of the facies of the different remnants, compared with their distance from the supposed edge of this gulf, confirms this hypothesis; for the beds of the same horizon, which a minute study has often permitted me to recognize in the different areas, show in general a facies less littoral in those remnants farthest removed from the shores, and vice-versa.

In conclusion, the Preadriatic Gulf was only an arm of the sea, which during the Neogene occupied the valley of the Po, and in which were deposited the now classic beds of the Colline de Turin, and of Langhe, Sarravalle, Tortona, Plaisance, and Asti; beds with which the formations of Venetia are very closely allied paleontologically and geologically.

HISTORY OF THE PREADRIATIC GULF.

Form and extent of the Gulf.

What has been the history of this gulf during the Neogene period? And, first, how did it originate?

Presumably during the lower Oligocene the Venetian region was almost entirely submerged by the sea, which deposited the beds of Montecchio Maggiore. Perhaps, connected with the basic eruptions of Vicenza, a regression occurred at the end of the lower Oligocene since the deposits with lignite and impressions of leaves, so frequent among the beds of this period in Vicenza, indicate close proximity to a continent. Islands or peninsulas then occupied the neighborhood of Verona and the Tessini hills; eastern Venetia had also emerged. The upper Oligocene, or Chattian, marks an incursion of the sea, and is characterized by beds with Nullipores, and Lepidocyclina, accompanied by small nummulites.

The shores of this Chattian gulf, occupying a part of Vicenza, Treviso, and of Belluno, are relatively easy to identify, for they correspond to the boundary between the region where the lower Miocene is conformable on the upper Oligocene, and the region where the Miocene is transgressive.

The Preadriatic Miocene gulf was due to a transgressive movement of the sea and it reproduced in the closest manner, the form of the preceding Oligocene gulf. This Miocene transgression, if my deductions are correct, does not appear to have been produced suddenly. The western borders of the gulf were already more or less completely invaded by the sea at the beginning of the Aquitanian while the eastern border remained dry until the Langhian. Indeed, in the beds in the Province of Verona (as distinguished from those of Verona proper, where it is the Langhian which rests in ravines in the

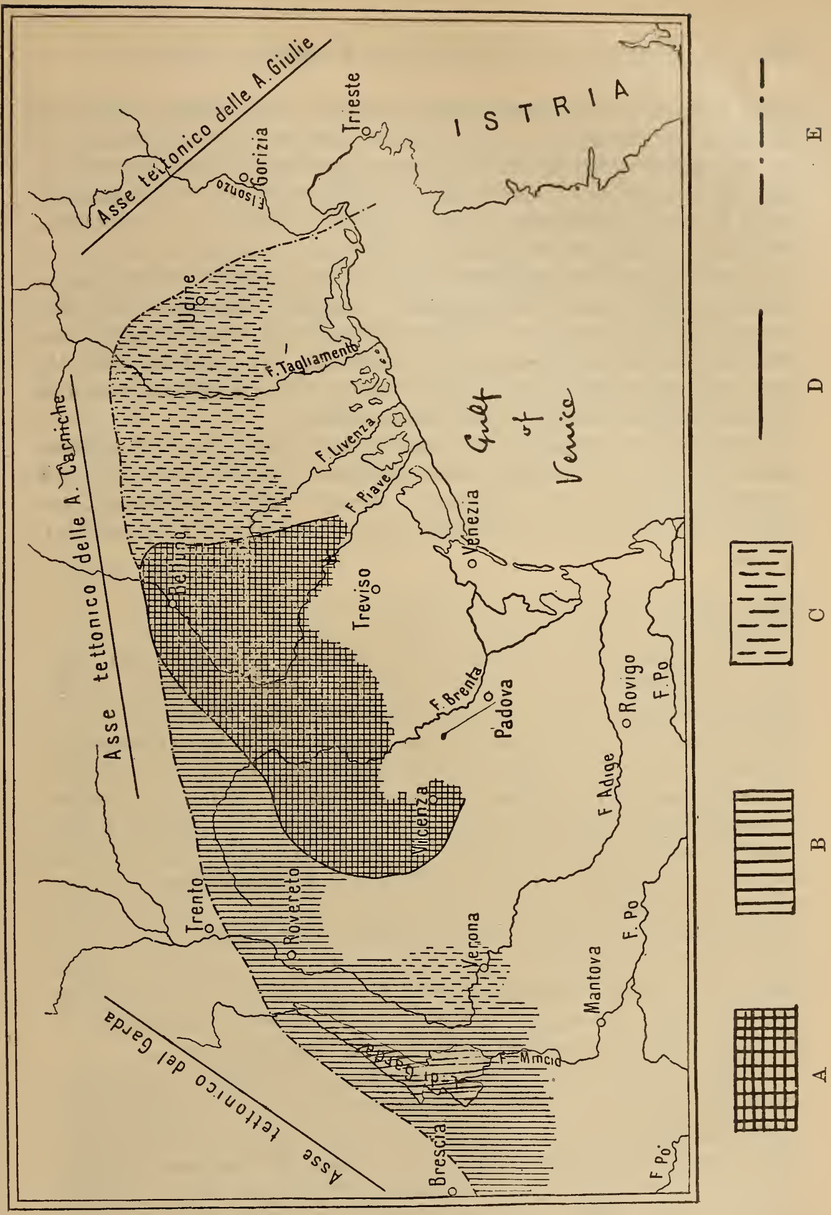

Fig. 1. The Preadriatic Gulf.*

A. Region in which the Aquitanian is conformable on upper Oligocene.
B. Region in which Aquitanian is transgressive.
C. Region in which Langhian is transgressive on Eocene or earlier rocks.
D. Approximate limits of Chattian Gulf (upper Oligocene).
E. Approximate limits of the Preadriatic or lower Miocene Gulf.

* It should be noted that the portrayed outline of the Gulf is truncated by the folding of the beds, which is parallel for the most part with the structural axis of the Carnic Alps (W.S.W.—E.N.E.) and has produced a great shortening in the North and South direction.

upper Eocene) the Aquitanian rests on the lower Oligocene beds, and although the transgression may not always be marked by an angular unconformity, it is in general evident because of the nature of the basal beds—conglomerate or "breccioles" with littoral fossils, and often formed of débris of reworked fossils from the underlying formations.

In Friuli, on the contrary, it is the Langhian whose beds, having at the base a transgressive conglomerate, rest at times unconformably, and at others apparently conformably, on middle Eocene or Cretaceous formations. In western Venetia also the sea invaded the land during the Langhian and the islands around Verona were submerged.

It was thus during the two sub-periods which form the lower Miocene that the transgression became complete and the sea probably attained its maximum extent. This probably coincides with the time of greatest depth—namely the upper Langhian.

The Fauna.

The fauna which invaded the Venetian area with the Miocene trangression is a warm sea fauna. This is evident in the Aquitanian and in the lower Langhian, but especially in the Tortonian,—that is to say in the stages which are represented by the most littoral facies. The molluscan fauna of the Tortonian is a truly tropical fauna, extremely rich in Terebras, Cones, Mitras, Ficules, Cerithiums, Melanias, Turritellas, Carditas, Arcas, Aviculas, etc., which both by their development and by the extraordinary thickness of their shells, indicate a warm climate, and waters rich in carbonate of lime. And, likewise, the remains of plants and terrestrial vertebrates, which the rivers carried into the sea, though rather rare, are an indication of a similar climate; they show that the coasts were then covered with forests of pines and palm-trees,* inhabited by Rhinoceros, Dinotherium, Mastodons, Tragulids, etc.

But to return to the marine fauna: in addition to the ideas which they give us of the conditions of the climate, they prove also that broad and easy communications then existed between the Preadriatic gulf and the rest of the Mediterranean Basin. which in turn had broad connections with the oceans. Indeed, it is in these latter, and particularly along the shore of Senegal and of the Gulf of Mexico, that one finds recent faunas which show the closest affinities to those which lived in the Miocene Mediterranean, compared to which the fauna of the

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*E. g. Sabal, confined to America in the existing flora and reaching its northern limit of range in North Carolina, occurred in Europe in the lower Miocene a distance of at least ten degrees farther north and thrived throughout the whole Alpine area.

Venetian gulf shows insignificant differences due to local races or varieties.

The terrestrial faunas are most striking, at least from a paleogeographic point of view. The relative frequency of species identical to or closely allied with those of the Rhone Valley, of Switzerland and of the Vienna Basin, associated with others of still wider range, proves that the Alpine region at that time formed probably a single biological province. These continental faunas of the Pontian, as well as those strictly littoral ones of the upper Tortonian, by their similarities indicate very close relationships with the faunas living today in the warm countries of the "ancien continent" (Melania, Terebralia), although one could cite as well in Trivia a bond of union with the faunas of North America, due probably to some collateral phylum of slow evolution.

Succession of facies.

Some very interesting conclusions can be drawn from a study of the succession of facies in the Neogene series (see table fig. 2), and from their geographical distribution during each stage of this period.

The Miocene beds of Venetia represent a complete cycle of sedimentation. The series commences in the lower Miocene with "molasses" of shallow water origin in the center of the gulf, by littoral conglomerates or sands along the shores. A difference of facies is evident from a comparative study of the rocks, it is confirmed by certain details of the fauna. I shall cite only one illustration—the near shore barnacles, which with the Nullipores abound in the beds of the Aquitanian and of the lower Langhian in the intra-alpine remnants, but are always replaced in the extra-alpine deposits by species of the same genus, but living on sponges or on shells, and consequently able to live in an environment farther removed from the shore.

But on this rocky foundation, with beating waters, rich in organisms, peopled with sharks, cetaceans, and sirenians, the depth rapidly increased; in the center of the basin the psammophyllic (sandy) faunas with Clypeasters and Scutellas are replaced before the end of the Aquitanian by Spatangids, Pholadomyas, and Pleurotomids.

At the end of the Langhian the depth reached its *maximum*, and in the marly or marly-calcareous beds of this stage abound the simple corals, Pinodonta, and in the extra-alpine region, Cephalopods (Aturia, Nautilus) and bathyal Cirripedia. In the intra-alpine region, on the contrary, in spite of its considerable depth, the shore is still reasonably near: here and there (Belluno) the large and deep estuary of a stream of some importance is recognizable by the nature of the deposits. These are sandy gravels, enclosing organic remains of continental origin, —plants and animals, which attracted a large voracious horde, for sharks teeth and whale bones are found in the sands of Belluno associated with teeth of Rhinoceros, shells of Trionyx and of Emys, pine cones, leaves and trunks of palms (Sabal, Palmacites). But, in general, elsewhere in the extra-alpine deposits the upper Langhian corresponds, as regards depth, to the bathmetric zone with brachiopods and corals. From this time, the evolution of the facies undergoes a sequence the exact opposite of that of the lower Miocene, the beds of the middle and upper Miocene indicating a slow and continual filling of the basin. The Helvetian is represented by marly beds, deposited in a tranquil sea, in the zone of Laminaria or sea-grass, inhabited by bivalves.

The lower Tortonian corresponds to the highest part of the same zone, and the deepest part of the littoral zone in the broad sense; in Friuli one can recognize in this sub-stage two facies only very slightly different—a facies more strictly littoral, richer in pelecypods, and a somewhat deeper facies, whose fauna is almost exclusively of gastropods. The first corresponds to a more northern zone, nearer shore; the second is located farther to the south and farther offshore. And this shore was a coast with an extremely gentle slope with very fine sediments such as that of the present western Adriatic.

In the upper Tortonian the sediments suddenly become very coarse, the sandy or sandy-calcareous beds become of greater and greater thickness and frequency until,—after a horizon with a littoral facies in the strict sense (intertidal zone) characterized by marine, brackish water, or continental faunas intermingled, with Auriculides, gigantic oysters, etc.,—the advance of the deltas continued, and at the end of the Tortonian the whole region had passed into continental conditions. The delta, first sub-marine, had become sub-aerial in the Pontian, the calcareous conglomerates of which it is formed alternating with marls and variegated clays with fossil leaves, with "molasses" with terrestrial fossils and fresh water beds with layers of lignite.

At the close of the Miocene a continental phase returns analogous to that at the beginning of the period; but the lower Miocene possesses all the characteristics of a deposit of a rocky coast, while the Tortonian and Pontian, on the contrary, correspond to delta deposits respectively sub-marine and sub-aerial.

Thus the entire Miocene Preadriatic gulf was filled with sediments, brought to the sea at first by rivers more or less mature, carrying sand and clay, then (after the Helvetian) by young torrential streams bringing pebbles torn from regions recently emerged. Among the various talus slopes which composed the delta, there appeared here and there, in the midst of a tropical vegetation, lakes or ponds, in which lived Melanias, Planorbis, Pisidium; into which fell with the leaves and branches of Cinnamomum and other trees destined to become buried and to form beds of lignite, the shells of Helix and Clausilia; and where herds of Hyomoschus, Dinotherium, and Mastodons came to water.

The early drainage system.

It is in these early rivers, accordingly, that the beginning of the recent drainage system can probably be found, whose origin has not been overlooked by the geologists of the region, particularly Mms. Taramelli, Rossi, Dal Piaz, etc.

The lithologic nature of the pebbles forming the Pontian conglomerates in the extra-alpine region of Venetia varies greatly from place to place, according to the nature of the rocks outcropping in the corresponding river basins. Thus there are conglomerates formed almost entirely of dolomite, and of limestones with flints, oolites, and Hippurites in eastern Venetia. In eastern Treviso they become polygenetic, and mixed with these limestones are Triassic or Permian sands, red limestones and even nummulitic limestones. They enclose mica schists, gneiss, granites and quartz porphyries in western Treviso, evidently connected with streams rising in the Valsugana and Cima d'Asta, where many of these crystalline rocks are only exposed to-day. Definite traces of this early drainage system can elsewhere be recognized in certain patches of a conglomerate with rounded pebbles which one meets here and there in the interior of the region, in the mountain region of Friuli, at an elevation of 1500–1600 meters above sea-level, everywhere on the divide between the valley of upper Tagliamento, and the head of the valleys of the Meduna and the Arzino. The study of the rocks which are found as pebbles in the Pontian conglomerates permits us to make still other deductions. The Mesozoic limestones (particularly the Turonian and Senonian limestones with Rudistes) form, it will be remembered, the periphery of the Alpine chain in this region,—that is to say, the base of the intra alpine zone,—but they never appear farther in the interior, where the Upper Cretaceous (locally called Scaglia) is transgressive on Jurassic or Eocretaceous limestones. The great frequency of pebbles of this Rudistes limestone in the Pontian conglomerate of Friuli is a further proof in support of the hypothesis just enunciated, of the partial emersion of the intra-alpine zone before the end of the Tortonian; for it is only in the Tortonian that these pebbles begin to appear. On the other hand, it must be noted that the marine Tortonian beds, lying conformably on the earlier Miocene, are found forming a part of the intra-alpine deposits, in central and western Venetia. Thus, it is toward the end of the middle Miocene that the peripheral region of the gulf underwent an elevation which carried it well above sea level, while the central part of the gulf was only filled up in the upper Miocene with sediments which the young streams brought into it in large part from the recently emerged region.

Age and nature of the Miocene Displacements.

As to the duration and the nature of the movements which affected the region at the time of the emergence, one must be warned lest he believe that the succession of facies, everywhere not so thick as are observed during the middle and upper Miocene, is an indication of a slow and general elevation of the bottom. On the contrary, the Tortonian alone measures 700 meters in Friuli. Now these lower beds exhibit already a strictly littoral character and could never have been deposited in a depth of several hundred meters. Upon as good grounds this same reasoning could be continued for the complete series of middle and upper Miocene beds, a thickness of 1800 to 2500 meters.

There is no doubt in my mind that the deposition of this enormous quantity of clastic material, corresponding to the emergence and the erosion of the Alpine continent, was accompanied by a slow but general and continuous sinking of the bottom; a subsidence, however, which was not sufficient to prevent the formation of deltas which continued until the complete filling up of this part of the basin.

A gradual sinking of the bottom is, according to the studies of Barrell, an indispensable condition for the formation of delta deposits of enormous thickness, such as the sub-Himalayan formations, which suggest, in many respects, resemblances to the subalpine formations of Venetia.

In conclusion, during the middle and upper Miocene, the Preadriatic gulf was the seat of two opposite movements. While the peripheral region underwent the emergence of which I have spoken above, other areas farther seaward, and especially those which corresponded to the central part of the gulf, the sinking of the bottom, begun throughout the entire region at the beginning of the period, continued, and the materials which the youthful streams tore from the recently emerged country contributed largely to the filling of the basin which persisted in the extra-alpine zone.

The Pliocene transgression.

The geocratic* period just mentioned was not of long duration. At the beginning of the Pliocene the sea returned, bear-

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* Geocratic = uplift, or a negative movement of the strand.

ing a fauna which was the direct forerunner of the recent faunas of the Adriatic and the Mediterranean province in general, although considerably mixed with Senegalian elements. The argillaceous nature of these deposits, and the phenomena of elevation and resulting intense erosion, which immediately followed, easily explains the small extent to-day of the lower Pliocene, now preserved in two extremely limited fragments; at Cornuda (Province of Treviso), and at S. Bartolommeo de Salo (Brescia). At Cornuda they rest conformably on the Pontian conglomerates, dipping at about 10 degrees; at S. Bartolommeo they lie in deep gullies in the Senonian "Scaglia," and are often found raised "en bloc" and almost horizontal to 530 meters above the sea.

In both cases they are fine marls of a quiet and fairly deep sea, rich in Brissopsis, Schizaster, Amussium, Arca, Natica, etc., but deposited probably at no great distance from the coast, as is indicated by the impressions of leaves of Platanus, Ilex, and Rhododendron, which they contain.

The conformity of the Pontian and Plaisancian at Cornuda shows that there were no violent movements in this region, nor any considerable interruption in sedimentation between the Miocene and the Pliocene. The return of the sea was accomplished quietly; the waters simply submerged the deltas of the basin which they had recently built up. This was merely a return of the Preadriatic gulf.

Pliocene uplift, and the rejuvenation of the drainage system.

It was only a short return, however, for this talassocratic* phase did not last long.

At Cornuda as well as at Salo proofs of a phase of intense displacement are evident. At Salo there was elevation without considerable folding, at Cornuda the latter occurred.

The combined study of these two fragments permits us to identify, with a precision very rare in our science, the geological date of these movements. At Cornuda almost horizontal Villafranchian conglomerates (upper Pliocene or lowermost Quaternary) lie in ravines, at times in strongly inclined Plaisancian marls, at times on Pontian conglomerates likewise inclined, at times on older formations. The Astian appears to be absent. At Salo the sub-horizontal Plaisancian, lying in valleys in the Cretaceous deposits, has been elevated more than 500 meters, while a short distance from here at Castenedolo, the sub-horizontal Astian lies only 120 meters above sea-level. One can thus say that the period of displacement, which is manifested in a simple elevation at Salo, and by folds at Cornuda, took place between the Plaisancian and the Astian.

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* Talassocratic = hydrocratic = depression, or a positive movement of the strand.

It is with this moment in the geological history of the region that we can correlate the rejuvenation of the drainage system, whose old valleys are met at from 600–650 meters above sea-level. The high limestone plains of Friuli and the epigenetic gorges which abound in the whole prealpine zone are the most striking examples. Indeed, throughout the upper Miocene and the Plaisancian the drainage system, which we have seen developing since the upper Tortonian, had progressed toward maturity with the partial peneplanation of the country. The high limestone plains of the Karst, which border the Alpine chain in this region, in my opinion, are only remnants of this peneplain, still only partially completed when the elevation of which I am going to speak was produced, carrying these remains to heights varying between 800 and 1,200 meters above the present sea-level.

The erosion of the profound and narrow gorges which open like passage-ways in the Mesozoic limestones at the mouths of most of the valleys in the Venetian plain, date back to the upper Pliocene. Farther in the interior of the region it is not difficult to find similar traces of this old drainage in the very ancient alluvial deposits, lying at 700–800 meters.

Post Pliocene Continental Formations.

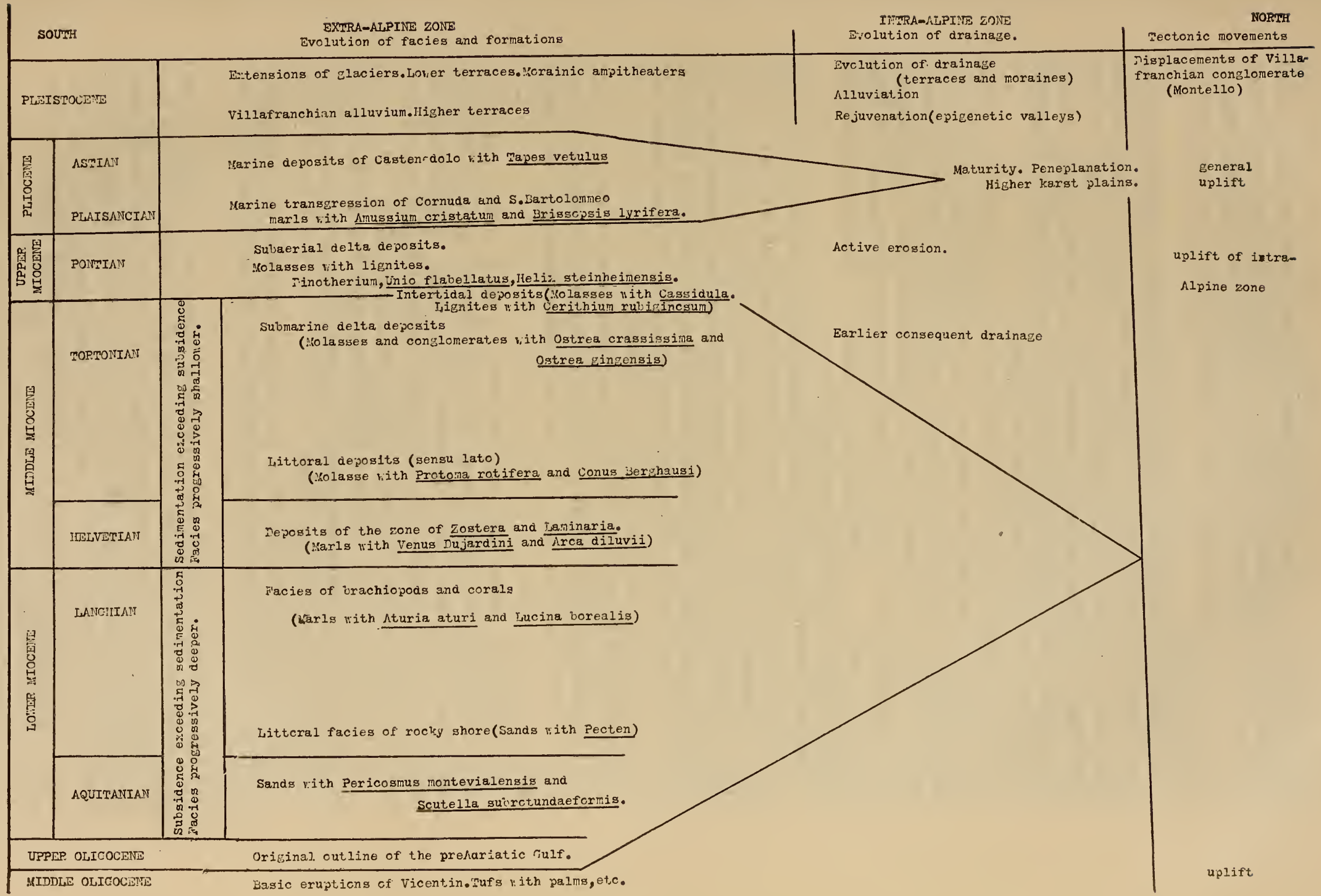
After this phase of active erosion, which in the extra-alpine region is indicated by a well marked angular unconformity and by very evident lithologic differences, another phase of sedimentation ensued at the beginning of the post-Pliocene, and conglomerates were deposited as enormous talus slopes at the mouths of the valleys on the plain. These are the conglomerates which the older Italian authors called "preglacial," but which according to the modern view can be considered as corresponding to a glacial period or a very early interglacial period.

Above these formations were deposited the well known morainic arcs of Tagliamento, Piave, Garda, etc., while in the interior of the valleys, embedded in these old alluvial deposits, other alluvial deposits were laid down, in turn greatly terraced. But tectonic movements did not completely cease in the Quaternary, for the Villefranchian conglomerates, of which I am going to speak, are themselves bent into an anticlinal dome in the hills of Montello and Conegliano.

Character of the Tectonic Movements.

Summarizing—the Venetian region during the whole of the Neogene was a gulf opening into the sea, which then occupied the basin of the Po.

This gulf was already outlined in the upper Oligocene; it became larger during the lower Miocene, reaching its greatest



SOUTH			EXTRA-ALPINE ZONE Evolution of facies and formations	INTRA-ALPINE ZONE Evolution of drainage.	NORTH Tectonic movements
PLEISTOCENE			Extensions of glaciers.Lower terraces.Morainic ampitheaters Villafranchian alluvium.Higher terraces	Evolution of drainage (terraces and moraines) Alluviation Rejuvenation(epigenetic valleys)	Displacements of Villafranchian conglomerate (Montello)
PLIOCENE	ASTIAN		Marine deposits of Castenedolo with Tapes vetulus	Maturity. Peneplanation. Higher karst plains.	general uplift
	PLAISANCIAN		Marine transgression of Cornuda and S.Bartolommeo marls with Amussium cristatum and Brissopsis lyrifera.		
UPPER MIOCENE	PONTIAN		Subaerial delta deposits. Molasses with lignites. Dinotherium,Unio flabellatus,Helix steinheimensis.	Active erosion.	uplift of intra-Alpine zone
MIDDLE MIOCENE	TORTONIAN	Sedimentation exceeding subsidence Facies progressively shallower.	Intertidal deposits(Molasses with Cassidula. Lignites with Cerithium rubiginosum) Submarine delta deposits (Molasses and conglomerates with Ostrea crassissima and Ostrea gingensis) Littoral deposits (sensu lato) (Molasse with Protoma rotifera and Conus Berghausi)	Earlier consequent drainage	
	HELVETIAN		Deposits of the zone of Zostera and Laminaria. (Marls with Venus Dujardini and Arca diluvii)		
LOWER MIOCENE	LANGHIAN	Subsidence exceeding sedimentation Facies progressively deeper.	Facies of brachiopods and corals (Marls with Aturia aturi and Lucina borealis) Littoral facies of rocky shore(Sands with Pecten)		
	AQUITANIAN		Sands with Pericosmus montevialensis and Scutella subrotundaeformis.		
UPPER OLIGOCENE			Original outline of the preAdriatic Gulf.		
MIDDLE OLIGOCENE			Basic eruptions of Vicentin.Tufs with palms,etc.		uplift

FIG. 2. Generalized and diagrammatic summary of the Geologic history of Venetia during the Neogene.

depth toward the end of this substage; it was slowly filled up with sediments in the middle Miocene, assuming at the end of the Miocene a continental phase. Invaded in part once more by the lower Pliocene, bearing a fauna of less tropical aspect, the region emerged again and for the last time before the end of this period.

During this long time tectonic movements caused at least four violent disturbances. The first took place in the middle Oligocene, and was accompanied by the basaltic eruptions of Vicenza. To these ancient movements is due the shape of the Preadriatic gulf, which assumed its shape, we repeat, immediately after,—i. e., in the upper Oligocene.

The successive tectonic movements were produced along the same major lines, at the end of the middle Miocene, at the beginning of the upper Pliocene, and in the middle Quaternary. With the second of these periods of uplift is correlated the beginning, and with the last two a rejuvenation of the drainage system, revealed by the nature of the sediments and by very plain morphologic records.

The existence of continental Quaternary terrains, and of the underlying marine Pliocene buried under alluvium at an elevation considerably below the present sea-level in the plain of the Po, is confirmed by every-day experience in the construction of deep wells, proving that these last Pliocene and post-Pliocene elevations have been probably accompanied or immediately followed by sinking in the adjoining regions.

I have already said that the same phenomenon occurred at the beginning of the upper Tortonian—the intra-alpine zone rose, the extra-alpine zone, that is to say the bottom of the gulf, sank.

In studying these movements from a still wider point of view, I believe the conclusion can be drawn that, in all the instances considered, the elevation of a zone, which may be called a zone of erosion, is coincident with the sinking of the bottom in the corresponding basin of sedimentation.

As to the direction of these different folds, it is evident that they are always produced parallel to the shores as well as in the direction of pre-existing folds.

The Venetian Prealps are a result, then, of the juxtaposition of folds more and more recent, as one passes from north to south.

This phenomenon, pushed to the extreme, particularly in the eastern part of the region, will produce the complete dying out of the alpine folds toward the plain, with the overturning and stretching of the lower flank of some of them, pushed sometimes to the formation of true overthrust faults, which give a very characteristic nature to the structure of the Prealpine chain of Venetia.

Art. XXV.—*On the Qualitative Detection of Germanium and its Separation from Arsenic;* by Philip E. Browning and Sewell E. Scott.

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

Germanium, discovered in 1886 by Clemens Winkler,* is found in nature most closely associated with the elements silver, lead, mercury, cadmium, arsenic, tin, zinc, titanium, and niobium. Analytically it falls into the group with arsenic and tin, since its sulphide is precipitated in strong hydrochloric acid by hydrogen sulphide, and this sulphide dissolves readily in ammonium sulphide. The chief problem of separation, then, appears to be its separation from arsenic and tin. From tin, and antimony also if it is present, the separation is quite readily made by heating the sulphides with ammonium carbonate, which readily dissolves the germanium sulphide and leaves the tin and antimony sulphides practically unattacked.

Buchanan† has quite successfully separated germanium from germaniferous zinc oxide containing lead, cadmium, arsenic, and traces of selenium, by dissolving this oxide in strong hydrochloric acid, distilling about one-half of the volume of the liquid, the distillation taking place in a current of chlorine gas in order to keep the arsenic in the higher condition of oxidation, and precipitating the germanium sulphide from the distillate by hydrogen sulphide.

The object of this paper is to give the results of some work upon the Buchanan method, and a simple modification of it devised for rapid qualitative tests.

Portions of zinc oxide‡ containing germanium, amounting in all to about 425 grm., were distilled according to Buchanan's method, and about 1·45 grm. of germanium sulphide was obtained from the distillate, an amount which would be equivalent to a yield of about ·24 per cent reckoned as the element germanium. This agrees closely with the percentage, ·25 per cent, which the oxide was said to contain.

It was observed that the sulphide from the distillate obtained below the temperature of 108° C. had a slight yellow color, indicating the probable presence of a trace of arsenic. The sulphid from the distillate coming over between 108° C. and 116° C. was in general much freer from arsenic, being practically pure white.

A simple form of apparatus was devised, consisting of a small flask fitted with a stopper through which a bent delivery tube passed into a test-tube, the end being just above about 5

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* Ber. Dtsch. Chem. Ges., xix, 210.

† J. Ind. Eng. Chem., viii, 585.

‡ Furnished through the kindness of the New Jersey Zinc Co.

cm^3 of water. The test tube was then immersed in a beaker containing snow, ice, or cold water. As a substitute for the passing of chlorine gas, a little potassium permanganate, manganese dioxide, or potassium chlorate was placed in the flask with about 10 to 15 cm^3 of strong hydrochloric acid and the germaniferous zinc oxide. The liquid in the flask was slowly brought to the boiling point, and about one-half distilled. By this method 1 grm., in another case 0·5 grm., of the oxide gave a distillate from which a heavy white precipitate was obtained with hydrogen sulphide 0·1 grm. gave a decided precipitate, and ·125 grm. a noticeable trace. From these results it would appear that less than 0·0001 grm. of germanium can be detected by this procedure.

This method was applied successfully to a small sample of the mineral argyrodite previously decomposed by nitric acid, the product having been evaporated to dryness to remove excess of acid. The amount of germanium sulphide obtained from the weighed sample of mineral taken indicated the presence of about 8 per cent of germanium, which is very close to the percentage given for argyrodite. 5 grm. of a leady residue from the purification of zinc, which had given spectroscopic evidence of germanium, gave a noticeable test for that element by this method.

To further confirm these results a solution of germanium sulphid in ammonium hydroxide was prepared, containing 0·001 grm. in a cubic centimeter, reckoned on germanium. Portions of this solution were used to determine the delicacy of the test, and it was found that 0·0001 grm. could always be easily detected, even in the presence of 0·2 grm. of pure ZnO, and 0·00006 grm. gave a satisfactory test when present with 0·025 grm. of ZnO.

A series of tests for germanium was prepared by one of us and given to the other, without the experimenter's knowledge of the substance present; the results are given below :–

(1) 0·2 grm. $SnCl_2$ + 0·0005 grm. Ge....Reported Ge present. Decided white ppt.
(2) 0·2 grm. $SnCl_2$....................Reported no Ge. Very faint cloudiness.
(3) 0·2 grm. As_2O_5 + 0·0005 grm. Ge....Reported Ge present. Same as (1)
(4) 0·2 grm. As_2O_5....................Reported no Ge. Very faint cloudiness.
(5) 0·2 grm. ZnO + 0·001 grm. Ge......Reported Ge present. Decided white ppt.
(6) 0·2 grm. ZnO....................Reported no Ge. Not even cloudy.
(7) 0·001 Ge....................Reported Ge present. Decided test.

(8) Distilled water .... Reported no Ge. No cloudiness.
(9) $0{\cdot}1$ grm. As_2O_3 + $0{\cdot}0001$ Ge .... Reported Ge present. Good test.
(10) $0{\cdot}2$ grm. SnCl .... Reported no Ge. Faintly cloudy. No ppt.
(11) $0{\cdot}0001$ grm. Ge .... Reported Ge present. Good test.
(12) $0{\cdot}2$ grm. As_2O_5 .... Reported possible trace of Ge very faint.

In all of these tests potassium permanganate was added with the hydrochloric acid before distilling, to provide the chlorine necessary to prevent reduction and distillation of $AsCl_3$ in the event of the presence of arsenic. Blanks were made with $KMnO_4$ to determine whether the chlorine evolved would cause a precipitate of sulphur in the distillate when hydrogen sulphide was added. The results of these determinations showed in only a few cases a faint cloudiness, probably due to sulphur, but in no case did a precipitate settle as in experiments where 0·0001 grm. Ge was present. Experiments (2), (4), (6), (8), (10) and (12) also showed that the use of potassium permanganate does not vitiate the germanium test. The distillates in Experiments (2) and (4) were allowed to stand over night after saturation with hydrogen sulphide without any precipitate separating from the very faintly cloudy solution.

Winkler * recommends the following method for the separation of germanium from arsenic. The sulpho salts formed by fusing the mineral containing the elements with sodium carbonate and sulphur are dissolved in water, and the solution is carefully neutralized with sulphuric acid, when the sulphide of arsenic is precipitated leaving the germanium in solution. By treatment of this solution with hydrochloric acid and addition of hydrogen sulphide the germanium sulphide is thrown down.

Two modifications of this method were tried by us to bring about this separation. First, a solution of the sulpho salts was saturated with carbon dioxide. This treatment caused the precipitation of from 60 per cent to 75 per cent of the arsenic, while no germanium was precipitated. Second, a solution of the sulpho salts was treated with ammonium acetate, acidified with acetic acid, and then treated with hydrogen sulphide. Under these conditions the arsenic was completely precipitated, and the germanium remained in solution. This process was tried on solutions containing arsenic only and germanium only, as well as upon mixtures, with equal success. Finally, some solutions of content unknown to the experimenter were prepared by one of us, and the report by the other showed the accuracy of the method.

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* Journ. prakt. Chem., xxxiv, 177; xxxvi, 177, June, 1917.

Art. XXVI.—*A Peculiar Type of Clay*; by H. Ries.

The clay referred to in this paper was received by the writer from western Texas, and is of such unusual character as to be worthy of record. On superficial examination it appeared to be a gritty clay resembling loess. When mixed up with water it developed sufficient plasticity to permit its being molded into bricklets without difficulty, and these when fired at 950° C. baked to a porous body of moderately hard nature, but which on exposure to moisture disintegrated completely, indicating that the clay contained a high percentage of either lime or magnesium carbonates.

It was the microscopic examination of the material that showed its extraordinary character, for it was found to consist almost entirely of small rhombs (fig. 1) of varying size but averaging about $\cdot 008^{mm}$ in diameter. The quantity of very fine undeterminable clay particles was practically negligible. A chemical analysis showed the clay to contain 98½ per cent dolomite and 1½ per cent iron oxide and alumina. From the above it is seen that the clay is made up almost entirely of dolomite rhombs, and so far as the writer is aware is different from any clay that has been described.

While it may appear incorrect to some to call this material a clay, it is nevertheless such in the physical sense, being macroscopically an earthy material possessing distinct plasticity when wet. Mineralogically and chemically it is far from a normal clay in its composition. Most clays on chemical analysis show an appreciable percentage of alumina, which may range from as little as 10 per cent (or even less in a few) in many impure clays, up to 38 or even 40 per cent in high grade fire clays and china clays. The clay here described is therefore most abnormal in respect to its alumina content.

There are of course a great many calcareous clays which may contain a large amount of lime and magnesium carbonates, but none of these approach the type under consideration. Thus in a series of Wisconsin clays, the maximum percentage of carbonates found in one was, 22·48 per cent CaO, and 8·95 per cent MgO.* A more extreme case is represented by a clay from Seguin, Guadeloupe County, Texas, which contained 41·30 per cent CaO, but only ·42 per cent MgO.† None of these clays therefore approach the present case in total carbonates, and fall far below it in magnesium contents.

The extraordinary difference does not end here, but applies to the texture. Most clays when examined under the micro-

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* Ries, Wis. Geol. and Nat. Hist. Surv., Bull. xvi, p. 105.

† Ries, Clays of Texas, Bull. Univ. Tex., No. 102, p. 200, 1908.

scope show a variable number of irregular grains, some of them of siliceous character, as well as a large quantity of very small particles, which may be bunched together, and are in part of colloidal character, so here again the Texas clay shows an exceptional texture.

Finally in addition to the peculiarities already mentioned we may consider the cause of its plasticity.

Various theories have been advanced to explain the plasticity of clay, and a most interesting summary of these has been given by N. B. Davis.* As he points out in the conclusion of his paper, plasticity seems to be due to the existence of gelatinous or colloidal matter, which may be of organic or inorganic nature, but that the effect of these materials may be further modified by absorbed salts, the relative proportions of large and small grains, and perhaps by the size of the grains themselves.

Fig. 1.

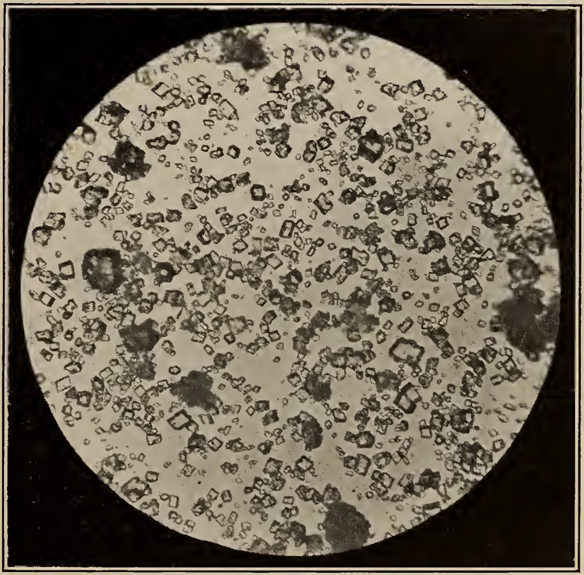

Fig. 1. Photomicrograph of dolomitic clay, showing the rhomb-shaped grains composing it. × 160.

This view no doubt applies to most clays, but the question may be raised as to whether it fits the present case. If so, then it must require an exceedingly small amount of colloidal mate-

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* Amer. Inst. Min. Engrs., Trans., vol. li, p. 451, 1916.

rial to develop the characteristic plasticity of clay, in this case not more than 1½ per cent, if we assume all of the iron oxide and alumina to be in that form.

While this small amount of gelatinous material may serve as a contributory cause in this instance, it may well be questioned whether the shape of the dolomite rhombs does not exert some influence, for it would seem that because of their great number, and small size, the flat faces of many of these must be in contact, or separated by a thin film of water when the clay is wet. The surface tension would tend to hold the surfaces of the grains together, but not prevent them slipping under pressure, thus giving mobility to the mass, and increasing its plasticity.

The case is not entirely similar to the supposed effect of plate structure, thought by some to be present in kaolin, and to explain its plasticity, but it is more like that of finely ground calcite, which Wheeler states developed plasticity after treatment in a ball mill,* with the difference that the small amount of colloidal material may have helped to increase its plasticity somewhat.

Department Geology,
Cornell University.

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* Mo. Geol. Surv., xi, p. 106, 1896.

ART. XXVII.—*Marine Terraces in Southeastern Connecticut;*[*] by LAURA HATCH.

Introduction.

IN mapping the geology of the Stonington quadrangle, Connecticut, the writer has been interested in testing the contrasting hypotheses used in interpreting the accordance of summit levels in Southern New England. The problem is particularly important for the physiographer, because of the attribution of wave erosion to areas believed by many to be type examples of subaërial peneplanation.

Topography of the Stonington Quadrangle.

The topography of the Stonington quadrangle consists of two strongly contrasting types. One is found in the narrow belt of rough land which extends eastward along the coast from Watch Hill, R. I., and which is continued toward the west in Fishers Island. Within this belt rock outcrops are practically absent, and the knob-like hills, irregular ridges and undrained depressions show a well-developed terminal moraine.[†] North of the belt of terminal moraine, the topography is controlled chiefly by rock hills which increase in height toward the northwest. Many of the hills are isolated, but in places merge for five or six miles so as to form an almost continuous upland between drainage lines. Many of the hills are broad, most of them being a mile or more in the longer dimension, and all have noticeably flat tops.

At a distance the sky line made up of many hills shows a remarkably even surface. On closer examination, however, one sees that the upland level is not a general slope toward the sea, nor is it a rolling topography suggestive of subaërial erosion alone, but its parts really constitute a series of broad low steps or terraces which have been greatly dissected by stream action.

To restore a general picture of the upland surface a system of projected profiles was used. For this purpose the quadrangle was divided into strips paralleling the major river valleys and averaging about 2½ miles in width. Profiles of the divides between the north–south valleys, and of the tops of the hills within the same strip, were projected on the same paper. The results are shown in fig. 1. It will be seen at

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[*] Published by permission of the Superintendent of the Connecticut Geological and Natural History Survey.

[†] This moraine is a continuation of the Harbor Hill moraine on the inner side of Long Island.

once that there is considerable level land and accordance of hill tops at elevations which correspond over the whole area.

These elevations are, beginning at the highest:

5. 480–520 feet elevation, which may be called the 500-foot level.
4. 380–420 “ “ “ “ “ “ “ 400 “ “
3. 300–340 “ “ “ “ “ “ “ 300 “ “
2. 180–220 “ “ “ “ “ “ “ 200 “ “
1. 80–120 “ “ “ “ “ “ “ 100 “ “

There is another possible terrace at 40–60 feet above sea level which is fairly well shown around Stonington, but elsewhere is so modified by glacial deposits that it will be disregarded in this discussion.

Distribution of Terrace Levels.

The highest, or 500-foot level, is shown on Chapman Hill (fig. 1B) and is reached by the other high hills of the region (fig. 1 C, D, E). These hills, however, are so few and have such small summit areas that one is forced to examine the country farther north (Moosup quadrangle) to see if the 500-foot level is one of great extent. Such an examination shows that a 500-foot elevation is attained by all the higher hills in the southern part of the quadrangle, and is well developed around an area of higher land near Sterling, Conn. In places in Voluntown Township it remains in summit patches a mile and more in length, and ½ to ¾ mile in width. The development of these flat patches over so broad an area, at the same level as the higher hill tops to the south, does not seem fortuitous, especially when we find that the hills are made of different rocks and in different attitudes. So, although only suggested in the Stonington quadrangle, the 500-foot level will be considered the highest level which must be taken into consideration in the history of the region.

The 400-foot level is the best defined of all in the Stonington quadrangle, and is best preserved on Swantown. Wintechog, Cassadock, and Champlin hills as shown in fig. 1 D, C, A.

The 300-foot level is well-developed in the two westernmost groups of profiles (fig. 1 D, E), but is poorly shown farther east.

The 200-foot level, on the other hand, is best developed on the east (A and B, fig. 1), but also shows in the accordance of levels of most of the hill tops near the coast.

The 100-foot level also is not seen so much in well-developed upland levels as in distinct terraces on the fronts of the hills near the sea. Quarry Hill at Westerly has the broadest summit area at this elevation.

A study of these profiles, combined with a study of the field itself, leads the writer to believe that these levels were probably produced by wave action. The remarkable flatness of the upland patches combined with the development of the same level in adjacent hills shows that some erosive agent must have cut at these elevations. That these levels abut against distinctly higher hills and that the line separating the two levels roughly parallels the shore, and not the river valleys, seems to make wave erosion the most important agency in their formation. When it is also found that these levels correspond over wide areas, and that, therefore, it is possible to draw shore lines to show the extent of these former sea advances, the hypothesis is strengthened to a strong probability.

FIG. 1.

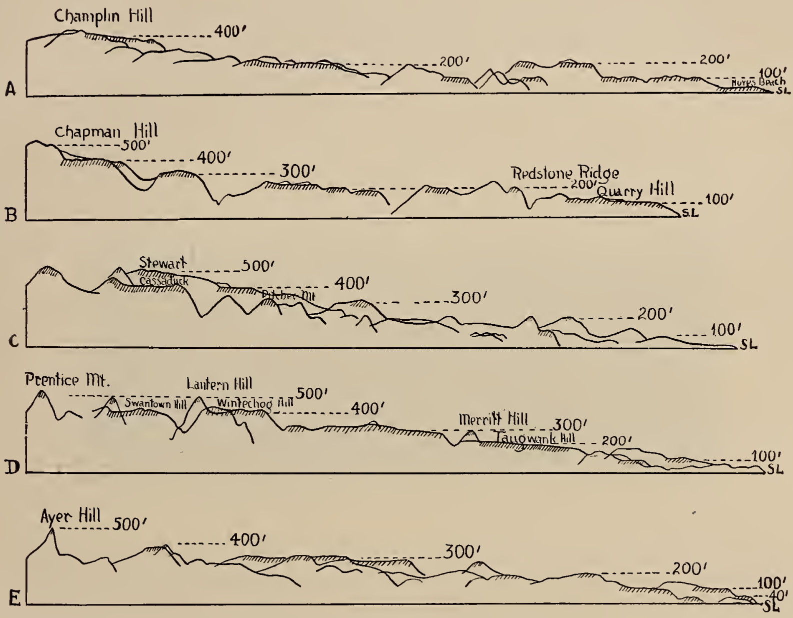

FIG. 1. Profiles of hills and divides in the Stonington Quadrangle.

Assuming then that the terraces were wave-cut, a study of the shore lines developed at the various elevations shows that they were very irregular. They bend in, decidedly, along river valleys, and thus may show (except in the case of the 500-foot level) that the sea advances alternated with periods of subaërial erosion, the marks of which were never quite obliterated during the marine periods. This would have made the waves effective over larger areas, for in attacking long promontories and islands they could chisel off the summits in much less time than would be expended in producing a rock bench over an equally broad zone.

Unfortunately the vertical distance between terraces (about 100 feet) is so small and the scarps so gentle, that the unaided eye generally can not differentiate the various levels in the field at distances of a mile or more. At the southern end of Wintechog hill, for instance, the upland narrows and drops to the 300-foot level within a quarter of a mile. A view taken from the top of Pitcher Mt. 2½ miles east of this point, gives the profile of this drop in the middle of the sky line (fig. 2). It will be noted that the 300-foot level which is shown in the left side of the view is not readily distinguished from the 400-foot level of Wintechog hill on the right. The difference is brought out, however, and the scarp between the two levels readily located, by holding a straight edge parallel to the horizon line in the left part of view.

Fig. 2.

Fig. 2. Drop between the 300-foot and 200-foot levels at the southern end of Wintechog Hill. View taken from Pitcher Mt., showing that at this distance, 2½ miles, adjacent terraces can not be differentiated by the unaided eye. The scarp between the levels occurs at point A, and can be seen by holding a straight edge parallel to sky line in left half of view.

Where the 200-foot level abuts against the 400-foot level the difference is easier to see.

Relation of the Terraces to the Geology of the Region.

There would be little value in a study of this kind, however, unless we might eliminate the hypothesis that such terraces may be due to differences in rock structure or hardness. Fortunately the geology has been worked out* over the larger part of the area so that this hypothesis may be tested. This part includes most of the better-defined terrace levels, and a number of each, which may be compared.

The best profile (showing all the terraces) is undoubtedly that of the long divide extending south from Wintechog Hill, and which may be continued northward to Bay Mountain in the next quadrangle. The geology along this line is shown in fig. 3. Four distinct terraces are seen, and except for the gentle rise between the 200- and 300-foot levels, the terrace levels show no relation whatever to the rock structure. This rise occurs at the contact of normal Sterling granite and an injection gneiss. This position, however, does not seem significant, for the rocks are not notably different in hardness and the contact elsewhere has no topographic expression. The 300-foot level is distinctly shown in fig. 1 E, covering considerable area, and there is probably no error in considering it a separate terrace.

Fig. 3.

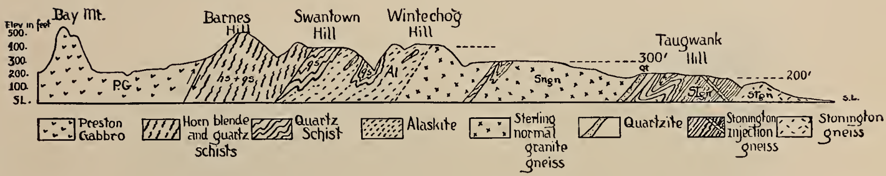

Fig. 3. Geology along divide extending south from Wintechog Hill and continued north to Bay Mt. (Moosup Quad.). Geology by G. F. Loughlin, U. S. Geol. Surv., Bull. 492, 1910, and by writer, Conn. Geol. and Nat. His. Surv., Bulletin in preparation.

The best terraces are found on the hard rock, but are not due to differences in hardness, for the same rock, such as alask-

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*The northwest corner of Stonington quadrangle was mapped by G. F. Loughlin, U. S. Geol. Surv., Bull. 492, 1910. The southeast part was mapped by the writer, Conn. Geol. and Natl. Hist. Survey Bulletin in preparation.

ite or Westerly red granite, holds terraces at lower as well as the higher elevations.

The most resistant rock of the region is the Lantern Hill quartz, and one would look for evidences of wave erosion at more than one level where it occurs, if the hypothesis of successive periods of wave erosion is plausible. Such evidence seems to be present, for the profile of the hill shows the 400-foot level well developed over the middle portion (Long Hill) while there is a perceptible notch at about the 300-foot level on the southern side. At the northern end also a portion of the hill still reaches the 500-foot elevation. This higher knob may be seen in fig. 4, and its position at the northern end of the hill certainly strongly suggests marine (as contrasted with subaërial) erosion for the carving of the 400-foot level above which it rises.

Fig. 4.

Fig. 4. Lantern Hill as seen from the west. The main part of the hill retains the 400-foot terrace, while the higher portion to the north rises to 500 feet.

Possible Errors in Interpreting the Topography.

Glacial Modification. Continental ice modified the preglacial surface somewhat by scraping it and depositing drift in places. But the rock hills were little changed, as they are not *roche moutonnée* forms, but still retain their flat tops. Many show the little knobs on the northern ends (see Swanton, Cassadock and Wintechog hills, as well as Lantern Hill described above), which may be explained as remnants of former wave erosion and which would be the first to disappear under strong glacial carving. As the hills (except in the terminal moraine) are all made of rock, glacial deposition may also be disregarded. On account of the glaciation of the region, however, no light can be thrown on the subject from the presence or absence of marine deposits on these terraces. If marine deposits were laid down in such exposed positions, they have either been stripped off by the glacier or have not yet been differentiated from the fluvio-glacial material of the region.

Possible Inaccuracies of the Map.

Error might creep in because of inaccuracies of the map. In this region, however, the tops of the hills were accessible* at the time the surveys were made, and are probably contoured with approximate accuracy.

Nature of Surface on which Terraces were Made.

It is important, however, to see on what sort of surface the marine terraces were developed, and where the Cretaceous peneplain of neighboring areas is represented in this region.

There is undoubtedly an erosional surface of some sort underlying the Cretaceous sediments wherever found, and it is probably largely subaërial in origin. How much farther this erosion surface or peneplain may be extended over the crystalline rocks of the Appalachian and New England regions is not known, although the general accordance of summit levels in these regions has been considered due to peneplanation in this period. A second partial base level has been noted in the river valleys and attributed to Tertiary erosion.

In the Stonington quadrangle all traces of two such erosion surfaces seem to have been obliterated. It is practically impossible to conceive of a peneplain that would include all the broad flat tops of the hills at the various levels. It would have to be warped along the very sinuous shore lines, and along each line would have to be warped exactly the same amount over the whole area. There would have to be four distinct vertical down folds if the broad areas at the 500-foot, 400-foot, 300-foot, 200-foot and 100-foot levels are considered parts of it. If they are, then why should hills such as Lantern, Ayer Hill and Prentice Mountain, which rise from broad areas

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* The early roads, far from shunning the hill tops, were either the shortest routes between points (as the Providence-New London turnpike), or were laid out on the broad upland areas as far as possible to avoid the swampy or sandy lowlands in the valleys. The very flat, relatively good farm land on these hills also led to their early clearing.

at the 400-foot level, all reach to the elevation of the broad upland patches farther north? It is just as useless to try to work out any one level for the peneplain, for in that case the accordance of levels above and below it must be accounted for. Partial base levels are seen along the river valleys, but are as hard to reduce to any one erosion surface as the tops of the hills.

The Cretaceous peneplain must have crossed the region somewhere, however, if the interpretation of various workers in neighboring fields is correct. The only clue to its position within the quadrangle is found in a well boring on Fishers Island.* Bedrock is found 280 feet below sea level and is overlain immediately by clay similar to the Cretaceous material on Long Island. If this depth may be taken as the position of the peneplain at three miles from shore, it has a slope of 90 feet per mile below the sea. This slope continued across the Stonington quadrangle would take it far above the present surface (fig. 5). The peneplain might, of course, be warped to correspond to the tops of the higher hills, but if so it changes from a slope of 90 feet per mile to one of 14 feet per mile within a distance of eight miles from the coast. It could not, however, be made to include the best flat areas without the complex warping mentioned above. In any case, the peneplain surface is practically unrecognizable in the region, the topography having been entirely recarved by subsequent erosion.

FIG. 5.

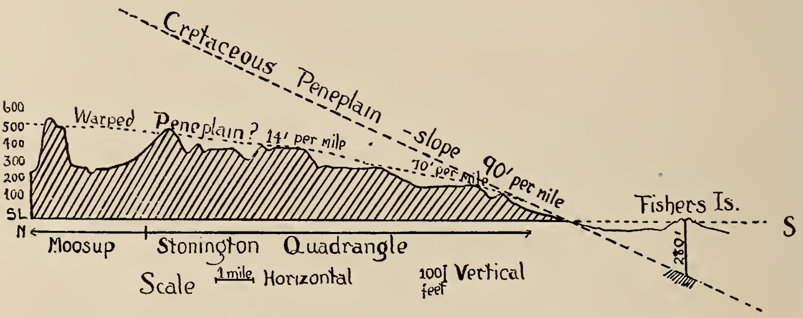

FIG. 5. Possible relations of the Cretaceous peneplain to the topography of the Stonington Quadrangle.

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* Fuller, Myron L., Geology of Fishers Island, N. Y., Bull. Geol. Soc. Amer., vol. xvi, pp. 367–390, 1905.

Although there is no distinct evidence of the Cretaceous peneplain, there is a suggestion that the region was at one time reduced to a plane of no relief and covered with coastal plain material. This is apparent from superposition of some of the streams on very hard rock, such as the Shunock-Pawcatuck river, which probably would not have crossed the Redstone Ridge at Westerly unless let down upon it. But the date of the superposition was long after Cretaceous time, as can be worked out from the larger rivers of Connecticut.

The southeast courses of the rivers in Connecticut are believed to be due to the southeastward tilting of the Cretaceous peneplain. This course is shown in the lower Connecticut and Housatonic rivers, but also in the upper tributaries of the Thames River (four miles west of the Stonington quadrangle). The lower course of the Thames, and practically all the smaller rivers in the shoreward parts of Connecticut, show a decidedly north-south arrangement, as in the Stonington region. This seems to call for another advance of the sea at a later date, with a coating of marine sediments to obliterate the southeast trending valleys near the sea. After this advance the land rose uniformly, causing the streams (except the Connecticut, whose deeper valley was not quite obliterated) to take a southerly, as contrasted to their southeasterly, course to the sea.

The change from a southeasterly to a southerly course is most clearly shown in the lower Housatonic river, while the Thames, the only large river near the Stonington quadrangle, shows the same thing near Norwich. In both cases the higher hills reach the 500-foot level near the places where the rivers change in direction.

It is thus believed that there was an incursion of the sea at the 500-foot level, like that postulated for the Cretaceous, and that the topography of the Stonington quadrangle dates only from this incursion, whatever its date.

Whether the 500-foot level was a peneplain of subaërial erosion which was covered by marine sediments as the sea advanced, or whether it was carved out primarily by the sea, can not be told. The writer believes that at least the finishing touches were probably given to it by the sea, because of its similarity to the terraces at lower elevations which so strongly suggest a marine origin.

The lower terraces, then, were probably carved out of what remained of this 500-foot plain, after extensive subaërial erosion had taken place. The subparallel bending inward of the shorelines along river valleys, shows that at no later date, however, did the sea obliterate all marks of the previous river erosion.

Conditions Necessary for the Carving of the Terraces.

For the development of a series of terraces such as we find in the Stonington quadrangle, it seems necessary to postulate a number of advances and retreats of the sea. From a study of the Coastal plain, Dr. Barrell has found that there has been a rhythmic rise and fall of the land relative to sea level along the Atlantic coast ever since the Cretaceous period, to account for the unconformities between the marine beds.* The advance of the sea may have gone far on the crystalline rock, as pointed out by Dr. Barrell, and may have done most of the work in developing the flat upland areas found in the Appalachian and New England regions.

In the Stonington quadrangle the exact physiographic history can not be worked out, but the following events seem to have taken place: Formation of an erosional surface on a series of complex igneous and metamorphic rocks, by subaërial and marine agents. This was covered with enough detritus so that on elevation the rivers took courses to the sea independent of their former valleys. This surface is now represented by the upland patches at about 500-feet elevation. Incision of streams resulted, and the region was eroded to submaturity before the next incursion of the sea, which planed off most of the hill tops and divides down to the present 400-foot level. This was followed by successive rises and falls of the land in relation to the sea, which produced the terraces at 300′, 200′ and 100′-levels. A possible stand of the land at 40′ lower than at present may be proved in a region less covered by drift near the coast.

On the whole, subaërial forces were probably more prominent in carving the region into its present form than marine, although wave erosion was probably the agent which planed down the divides and reduced the hills to common levels.

While wave planation was going on along the shore, subaërial forces were doing much to remove the higher land in the interior. Thus the extensive lower surfaces along the Quinebaug and upper Thames rivers (Moosup quadrangle) were probably developed while the waves were attacking the very resistant rocks farther south. The difference in the amount of flat upland north and south of the group of high hills in North Stonington and Voluntown Townships is significant of the difference in the two erosional processes.

Indistinct benches (50-60 feet above the terrace levels) can be seen in the profile of many of the river valleys to the north and in the upper levels of the smaller hills. These probably show the temporary base levels established in the river valleys

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* Bull. Geol. Soc. Am., vol. xxiv, p. 688, 1913; this Journal, vol. xl, p. 9, 1915.

corresponding to the different sea levels shown in the Stonington quadrangle.

Correlation with Other Work.

The question arises as to how the terraces correspond to those worked out in other areas, and what were the probable dates of their formation. A series of terraces has been described by Dr. Barrell as extending from the base of the Berkshire Mountains to the sea. The lower ones he correlates with terraces in Maryland. The writer agrees with Dr. Barrell in finding terraces at 500 feet (which he calls the "Lafayette or Appomatox" level), at 200 feet (or the "Sunderland" level), and 80-100 feet (or "Wicomico" level).

Dr. Barrell also records a rather obscure terrace at 340–380 feet elevation in western Connecticut, which probably corresponds to the 400-foot level in the Stonington quadrangle. The 300-foot terrace has not before been noted, and will be called the "Pitcher Mountain Terrace" to record the name of a place where it is developed (although not as well as in the broader unnamed areas to the southwest).

The Age of the Terraces.

The geological dates at which these terraces were formed is not determined. If the 500-foot terrace corresponds to the Lafayette (Brandywine) in Maryland, as Dr. Barrell suggests, then the lower ones are Pleistocene. In the Westerly region there seems to have been an advance of the glacier when the land stood 60 to 120 feet lower than at present, and this may have been just after the erosion of the 100-foot terrace. This would correspond to the Pensauken of New York and New Jersey and the Wicomico of Maryland. In this case all the terraces noted in this region are pre-Wisconsin in age.*

Until more work has been done on the Pleistocene in this region, little more can be said. The long periods represented by the older drift sheets in the interior of the continent may be represented in this region by marine erosion at the 200-foot, 300-foot and 400-foot levels. The long time necessary for the accumulation of the great ice sheets, with the relative rises of sea level which are presumed to have accompanied their maximum extent in many parts of the northern latitudes, seems amply sufficient for the marine planation of hill tops and divides seen in this quadrangle.

That these lower terraces seem much better developed and

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* The Talbot formation at 40–60′ elevation carries ice-borne bowlders and probably corresponds to the Wisconsin glacial stage. See Tolchester, Md. Folio U. S. Geol. Survey, 1917.

preserved here than at any place to the southwest seems to be due to the absence of the coastal plain and to the hardness of the rocks. Farther west in Connecticut, the coastal plain in Long Island probably caused the waves to spend their force before they could produce much effect on the crystalline rocks, while any effect on the coastal plain has since been destroyed by glaciation.

The rocks in the Stonington region, on the other hand, bore the brunt of the heavy waves rolling in from the southeast. Thus the terrace carving here was perhaps more perfectly done than elsewhere, because of the exposure and relief of the region, and better preserved because of the hardness of the rocks. The working out of the geology over two-thirds of the quadrangle makes it possible to say that in this small region, at least, the terraces are independent of rock structure.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Recovery of Sulphur from the Sulphur Dioxide of Smelter Gases.*—A. E. Wells has described an investigation upon what is called the "Wet Thiogen Process" which is designed for the purpose of disposing of the objectionable, waste sulphur dioxide from smelting operations, and at the same time recovering the sulphur as such. The process is based upon the fact that when barium sulphide, either in finely divided water suspension or in solution, is added to a solution of sulphur dioxide the following reaction takes place :

$$2BaS + 3SO_2 = 2BaSO_3 + 3S$$

or,

$$2BaS + 3SO_2 = 2BaS_2O_3 + S$$

In carrying out the process the gases after being cooled and freed from dust are passed through a tower in which the sulphur dioxide is absorbed by water or mother liquor. To the solution powdered barium sulphide is added to produce the reactions that have been mentioned. The precipitate is settled, filtered, dried, and distilled in order to obtain the free sulphur and one-half of the sulphur of the barium thiosulphate. The liquid is returned to the absorption tower while the residue, consisting of barium sulphite and sulphate, is reduced to sulphide by heating with carbon, and is used again in the process. The operation has been studied both on a laboratory scale and on a scale that may be considered semi-commercial, and the results indicate that it can be carried out successfully, at least at certain localities, and will allow the production of sulphur at a cost of about $12 per ton.—*Jour. Indust. and Eng. Chem.*, ix, 872. H. L. W.

2. *The Use of Large Glass-Stoppered Containers in Autoclaving.*—ROBERT B. KRAUSS has devised a convenient method for heating rather large quantities of liquids or solids under pressure in order to avoid the expense and other difficulties connected with the use of sealed glass tubes and of glass enameled autoclaves. The material to be heated is placed in a glass bottle with a ground stopper, the clean, dry stopper is twisted tightly into the neck of the bottle and fastened securely with a clamp of suitable design. The bottle is then placed in an autoclave which is half-filled with water and the apparatus is then closed and heated to the desired temperature. Bottles used in this way have stood pressures of 5,000 lbs. per square inch when heated in a specially designed autoclave. It is obvious that under proper conditions the internal and external pressures on the bottle are practically equal. The autoclave used was drop-forged from armor-plate steel and then machined. Its walls were two inches thick, and it would take in a bottle of 5 liters capacity. It had a maximum working pressure of 10,000 lbs. per square inch, was provided with a suitable safety-valve, and was heated by a gas burner in a special room provided with very thick, concrete walls.—*Jour. Amer. Chem. Soc.*, xxxix, 1512. H. L. W.

3. *A Cryoscopic Method for the Determination of Added Water in Milk.*—J. T. KEISTER calls attention to the fact that the numerous determinations of the freezing-point of milk found in the literature show a remarkable uniformity. In general, this temperature is from −0·54 to −0·57° C. Hence the value of this determination for detecting added water in milk is evident. No determination of any constituent of milk has given such closely agreeing values as this. It is evident that fat, the most widely varying constituent of milk, has no influence on its freezing-point, while such substances as albuminoids which are present, perhaps, in a colloidal condition, or, in any case, have a very high molecular weight, must have a very small effect upon it. The only constituents, therefore, that exert any appreciable effect upon the freezing-point are the soluble lactose and the salts, which consist largely of the chlorides of the alkali metals. It appears further that there is a more or less constant relation between the lactose and the sodium chloride present, and that when one increases the other diminishes, so that there is a tendency for these substances to balance each other in their effect upon the freezing-point.

By the use of a Beckmann thermometer graduated to 0·01° C the author has examined a large number of samples of milk for their freezing-points, and has found that the results are remarkably uniform, and that the addition of as little as 5 per cent of water can be detected with certainty by this method. It is essential, however, that the test be applied to reasonably fresh milk, since the presence of abnormal acidity lowers the freezing-point. The method is practical in milk control work, but it need be applied only in the case of samples of doubtful character.—*Jour. Indust. and Eng. Chem.*, ix, 862. H. L. W.

4. *The Inadequacy of the Ferric Basic Acetate Tests for Acetates.*—CURTMAN and HARRIS have subjected this old and widely recommended test to a careful quantitative investigation and have found its delicacy to be very unsatisfactory. In the presence of 5 mg. of iron as ferric chloride per cc., boiling at a volume of 50 cc. did not yield a brown precipitate until 20 mg. of $C_2H_3O_2$ in the form of sodium acetate had been added to the neutral liquid, and the sensitiveness of the reaction was much decreased by increasing the amount of ferric chloride as well as by larger dilution. When an effort was made to help the reaction by the addition of an electrolyte (sodium chloride), it was found that the boiling, neutral solutions gave precipitates in the absence of acetates, but when sufficient hydrochloric acid was employed to prevent this interfering precipitation the delicacy of the test was no better than before.—*Jour. Amer. Chem. Soc.*, xxxix, 1315. H. L. W.

5. *The Priestley Memorial Committee of the American Chemical Society.*—At the Urbana meeting of the American Chemical Society, held in April, 1916, a committee was appointed to devise and carry out a plan for a suitable memorial to Joseph Priestley. This committee consists of fifteen gentlemen with Professor Francis C. Phillips of the University of Pittsburgh as Chairman. After careful consideration of various plans, the following recommendations were made to the Society :

1. That a bust portrait of Joseph Priestley be secured, to be a copy of the best available portrait ; that this be retained as the property of the American Chemical Society, but be deposited as a loan in the National Museum in Washington. Also,

2. That a gold medal be awarded at intervals of probably more than one year for superior achievement in chemical research ; the award to carry with it the requirement that the recipient shall deliver an address before the General Meeting of the Society at the time of the presentation or at such other time and place as the Council of the Society may direct.

The Committee further recommends that, in order to carry out these plans, a fund of at least $2000 be secured, and it is requested that subscriptions be sent to the Chairman or to any member of the Committee. Contributions of sums from $1.00 upwards are asked.

Joseph Priestley was born at Fieldhead in England in 1733, and his contributions to chemistry, and in particular his discovery of oxygen in 1774, are too well known to need to be detailed here. It is greatly to be hoped that the plans of the Committee may meet with full success and an adequate sum be secured to do honor to the memory of this great chemist.

6. *The Electron;* by Robert Andrews Millikan. Pp. xii, 268, with 33 figures. Chicago, 1917 (The University of Chicago Press).—"The purpose of this volume is to present the evidence for the atomic structure of electricity, to describe some of the most significant properties of the elementary electrical unit, the electron, and to discuss the bearing of these properties upon the two most important problems of modern physics: the structure of the atom and the nature of electromagnetic radiation." In order to extend the domain of usefulness of the text beyond that of the physicist, the material has been presented in a semi-popular style and all mathematical proofs have been collected in six of the appendixes.

The first chapter deals with the early views of electricity, special attention being given to the growth of the atomic theory of matter and the historical development of electrical theories. The extension of the laws of electrolysis to the conduction of electricity through gases is discussed in the second chapter. The next chapter is devoted to an account of the early attempts at the direct determination of the electronic charge *e*. The methods of J. S. Townsend, J. J. Thomson, H. A. Wilson, and the balanced-droplet method of R. A. Millikan are here taken up in the order named. The next two chapters pertain respectively to the general proof of the atomic nature of electricity and the exact evaluation of *e*. These two chapters are especially illuminating and important, and they contain a very lucid account of the accurate and beautiful experimental investigations of the author. The contents of the remaining chapters may be inferred from their respective titles, which are: "The Mechanism of Ionization of Gases by *X*-Rays and Radium Rays, Brownian Movements in Gases, The Existence of a Sub-Electron? The Structure of the Atom," and "The Nature of Radiant Energy." The volume closes with eight appendixes, and author and subject indexes.

The book merits the attention of all physicists and students of physics because of its authoritative nature, broad perspective, and general accuracy. It should also be added that the author's exceptional clearness of presentation and well-controlled enthusiasm have imparted to the text a freshness and vigor which appreciably increase the pleasure of reading the volume. H. S. U.

7. *Failure of Poisson's Equation.*—In a short mathematical paper, Ganesh Prasad gives some interesting special volume distributions for which Poisson's classical equation fails. Let ρ_0 denote the density at any point P (x, y, z) within the solid. Then Poisson's equation fails at P when $\nabla^2 V$ is either meaningless or has a value different from $-4\pi\rho_0$, V being the potential due to a small sphere of radius a and center P.

Case I. Let the density of the sphere at any point Q (ξ, η, ζ) inside it be

$$\rho = \frac{\cos^2\theta}{\log\dfrac{1}{r}}$$

where θ is the angle made by $\overline{PQ}$ with the axis of z, and r denotes the distance from P to Q. It is shown that, under these conditions $-\frac{\partial^2 V}{\partial x} = -\frac{\partial^2 V}{\partial y^2} = \frac{\partial^2 V}{\partial z^2} = +\infty$. Hence, $\nabla^2 V$ has no meaning, and Poisson's formula fails at P.

Case II. When $\rho = \cos\left(\log\frac{1}{r}\right)$ it is proved that the three second derivatives of the potential are all non-existent, so that Poisson's equation again breaks down.

Case III. When $\rho = \cos\frac{1}{r}$ all of the second derivatives of V are equal to zero, consequently Poisson's equation is not satisfied unless $\rho_0 = 0$. "It should be noted that, in this case, ρ_0 may be assigned *any* value without affecting the value of $\nabla^2 V$."

The last section of the paper is devoted to proving, for the first time, that Petrini's generalization of Poisson's equation is of limited scope, and fails for case II.—*Phil. Mag.*, xxxiv, p. 138, August, 1917. H. S. U.

8. *The Composition of X-Rays from Certain Metals.*—The composition of the X-radiations emitted by anticathodes made of aluminium, copper, iron, nickel, and platinum has been investigated by G. W. Kaye. The quality of the X-rays was tested by placing absorption screens between the aluminium window of the bulb and the ionization chamber. A Wilson tilted electroscope was employed to measure the ionization currents. The experimental data were plotted with thickness of absorbing screen d as abscissa and with the corresponding value of $\log_{10}(I_d/I_o)$ as ordinate. Since $I_d = I_o e^{-\lambda d}$, it follows that the absorption-coefficient λ, at any point on the graph, is obtained by multiplying the slope of the tangent to the curve at the given point by 2·3 (the reciprocal of the modulus). For heterogenous X-rays λ diminishes as d increases, but for homogeneous rays the graph is a straight line. The plan followed in the experiments was gradually to cut down the X-rays until the log-absorption curve indicated that the residual rays were homogeneous or nearly so. This "end-radiation" was subtracted graphically from the total radiation by prolonging backwards the final straight segment of the absorption curve. A second log-absorption curve was then plotted, employing as ordinate the logarithm of intensity-difference derived as stated. The resulting graph proved in practice to be either a straight line throughout its length, or a curve merging into a right line as the thickness of the screen increased. In the latter event, the process of subtraction was repeated.

The following useful facts were brought out by the investigation. The X-rays from a bulb excited by low voltages (10,000 to 50,000 volts) are rich in the characteristic radiation of the anticathode. For copper, iron, and nickel, the percentage of K-radiation lies between 80 and 90. In the case of platinum the proportion of L-radiation is from 40 to 60 per cent. Evidence for the existence of characteristic radiations softer than the K and L series was obtained.—*Proc. Roy. Soc.*, vol. xciii (A), p. 427.

H. S. U.

9. *Relations between the Spectra of X-Rays.*—From simple energy considerations Kossel has deduced the following relations

$$L\alpha = K\beta - K\alpha$$
$$M\alpha = L\gamma - L\alpha,$$

in which the symbols denote the frequencies or reciprocal wave-lengths of the characteristic X-rays of a given chemical element. Since, however, recent experimental work has shown that there are two and sometimes four α lines, two or more β lines, and so forth, doubt arises as to which data should be used in actual calculations. In other words, the formulæ are not written with sufficient exactness. As the writer of this notice has met with this difficulty on several occasions, it may be helpful to others to have reproduced in this place the formulæ given in a recent paper by Jun Ishiwara. According to I. Malmer the first relation should read

$$L\alpha_1 = K\beta_1 - K\alpha_2.$$

The wave-lengths given in M. Siegbahn's tables also lead to the equations

$$M\beta = L\gamma_1 - L\beta_4$$
$$M\ _1 = L\gamma_2 - L\beta_1.$$

The author says: "I will here also remark that the following relations hold very exactly through all the elements :

$$\left.\begin{aligned} L\alpha_2 - L\beta_2 &= L\beta_1 - L\gamma_1 \\ &= L\beta_3 - L\gamma_2 + \Delta \end{aligned}\right\} \qquad (4)$$

where Δ is a constant."

"In order to account for these relations, especially (4), Bohr's theoretical formula should be modified as follows :

$$\nu = \nu_0 \left\{ \frac{(N - C_1)^2}{(n_1 + \mu_1)^2} - \frac{(N - C_2)^2}{(n_2 + \mu_2)^2} \right\}$$

N being the atomic number, n_1 and n_2 certain integers. It should be supposed that $N - C_1$ and $N - C_2$ represent the numbers of electric quanta contained in the "effective" nucleus charge. The curve in Moseley's diagram shows further that μ_1 and μ_2 are not absolute constants, but vary gradually from element to element."—*Nature*, xcix, p. 424, July 26, 1917.

H. S. U.

II. GEOLOGY.

1. *Grundzüge der Paläontologie* (*Paläozoologie*); by KARL A. VON ZITTEL, revised by F. BROILI. I. Abteilung: Invertebrata, 4th edition, vi + 649 pp., 1458 text figs., Munich and Berlin 1915 (R. Oldenbourg).—This standard text-book of invertebrate paleontology has now appeared in the fourth edition. It seems to have been issued from the press during the latter part of 1915, but was not received by the reviewer until August, 1917, and was sent through the International Exchange Bureau of the Smithsonian Institution. The book is much improved over the third edition, having 44 new figures, 87 more text pages, and about 1700 additional generic and other names. The Monticuliporidæ are no longer grouped among the tabulate corals, but are now properly placed among the trepostomatous Bryozoa. On the other hand, the classifications are still conservative and in general much like those of the former edition. C. S.

2. *Palæozoic Crustacea, the publications and notes on the genera and species during the past twenty years, 1895–1917*; by ANTHONY WAYNE VOGDES. Trans. San Diego Society Natural History, 1917, 141 pp., 5 pls.—In 1890 and again in 1893 Vodges presented bibliographies of Paleozoic "Crustacea" from 1698 to 1889, and in 1895 he issued a supplement comprising the literature up to that date. Now he gives us another catalogue of the literature on the Paleozoic Crustacea from 1895 up to 1917. These bibliographies are annotated and give the genera and species discussed in each work, and they will therefore always be of the greatest aid to paleontologists. Now if some one would publish an index to all the names in these four publications, our cup of joy would be full. The whole work has been one of love, and all through the author's military career he has devotedly applied himself to these bibliographies and has in addition assembled one of the best libraries on paleontology. We salute the general, and he has our congratulations on making the work of paleontologists easier and more certain of good results. C. S.

3. *The Lower Cambrian Holmia fauna at Tømten in Norway;* by JOHAN KIÆR. Videnskaps. Skrifter, I. Mat.-Naturv. Klasse 1916, No. 10, 112 pp., 14 pls., 15 text figs., 1916 (= 1917). —In this very important and far-reaching contribution to invertebrate paleontology and stratigraphy, the author describes the Lower Cambrian fauna of twenty-one species found at Tømten in southern central Norway. The greatest value of the study lies in the very detailed description of the trilobites and in the critical analysis of this fauna, with others, as to its time and provincial relations. His restorations of the trilobites *Holmia* and *Kjerulfia* (new) are excellent. Good reasons are given showing that *Paradoxides* could not have originated in *Olenellus* or in any allied genus, but that they are parallel families having origi-

nated in the oldest Lower Cambrian, "or at a still earlier period," in a stock ancestral to both (p. 92).

The author further differs with Walcott, holding that the Olenellus zone of the Lower Cambrian probably does not overlie the Callavia zone. Rather that both are practically of one time but of two basins. The proof for this he sees especially in that "a profile has never been found in North America in which an Olenellus zone succeeds above a Callavia zone" (109).

Kiær also discusses the probability that the unfossiliferous, widely extended, and thick Sparagmite formation of central Scandinavia is a continental deposit, and that instead of its being of latest Proterozoic age it is more likely of earliest Lower Cambrian time. His interpretation of the succession is as follows:

Upper part of Lower Cambrian. Marine. About 50 meters thick

Zone of *Strenuella linnarssoni*
Zone of *Holmia kjerulfi*
Zone of *Discinella holsti*
Sandy shales with trails and *Torallella*
} Equivalent to Callavia time in the Atlantic province of North America

Middle and lower part of Lower Cambrian. Sparagmite formation. Continental deposits. Very thick.

Kiær holds that the Strenuella zone passes unbroken from the Lower into the Middle Cambrian (99), and refers it to the former division even though no Mesonacidæ occur here. He does this because it has a few species, other than trilobites, of the older horizons, none of which, however, appear to the reviewer to be of stratigraphic value. The author admits the great difficulties here, but seems to give little value to his conclusions that the earlier faunas invaded Scandinavia from the opposite direction to that of the Strenuella assemblage. In other words, that the paleogeographies of these times were markedly different. He also plainly shows that the Middle Cambrian sea is an overlapping sea across an irregular topography, and further, that the terminal Lower Cambrian Protolenus zone of the Atlantic realm is absent in Scandinavia. For the present the reviewer would therefore rather believe that the Strenuella zone is of Middle Cambrian age and of Atlantic faunal affinities. Further, that the Lower Cambrian is separated from the Middle Cambrian by a time break of considerable magnitude, during which time there was enough warping of the land to bring about wholly different sea invasions.

C. S.

4. *Recurrent tetrahedral deformations and intercontinental torsions;* by B. K. Emerson. Proc. Amer. Philos. Soc., lvi, pp. 445–472, 1917.—This is a very interesting article, and should be read in connection with the author's presidential address before the Geological Society of America, printed in volume 11 of the Bulletin of that society under the title "The tetrahedral earth and zone of the intercontinental seas." C. S.

5. *On the crinoid genus Scyphocrinus and its bulbous root Camarocrinus;* by Frank Springer. Smithsonian Institution,

Publication 2440, 55 pp., 9 pls., 17 text figs., 1917.—This splendid memoir demonstrates that not only the European genus *Scyphocrinus* but even the highly specialized Bohemian species *S. elegans* Zenker occurs abundantly in the Devonian of the United States. Further, that the bulbs long known as *Camarocrinus* are the roots and not the floats of *Scyphocrinus*. C. S.

6. *On a new hydrozoan fossil from the Torinosu-limestone of Japan;* by ICHIRÔ HAYASAKA. Science Reports, Tohôku Imperial University, Sendai, Second series (Geology), iv, No. II, pp. 55–59, pl. 14, 1917. *Geological and geographical distribution of Gigantopteris;* by HISAKATSU YABE. Ibid., pp. 61–73, pls.15, 16. *Problems concerning the geotectonics of the Japanese islands: critical reviews of various opinions expressed by previous authors on the geotectonics;* by H. YABE. Ibid., pp. 75–104.

Hayasaka describes a new genus of stromatoporid related to the Permian (India) *Circopora* and he therefore calls it *Circoporella semiclathrata.* It is from the Lower Cretaceous.

In the second paper Professor Yabe discusses the distribution of the three Asiatic and the one American species of *Gigantopteris.* This most interesting cycadofilic genus ranges from the Lower Permian into the Lower Triassic. Mr. Koiwai describes and illustrates the three Asiatic species, one of which is thought to be new but not named because of its very fragmentary preservation.

The third paper, a most valuable one, sets forth the geotectonics of the Japanese islands as understood by Naumann, Harada, Suess, Ogawa and Von Richthofen, beginning in 1885 and now brought more or less up to date by Yabe. We are soon to receive from Professor Koto his great work on the Geology of Japan, and then Yabe is to return to the subject here so well compiled.

C. S.

OBITUARY.

DR. ADOLF VON BAEYER, the distinguished German chemist, to whom is due the credit of synthetic indigo, died in August last at the age of eighty-two years.

DR. EDUARD BUCHNER, professor of chemistry at the university of Würzburg, has died as the result of wounds received in battle. He received the Nobel prize for chemistry in 1907.

M. EDUARD SARASIN, editor of the *Archives des Sciences physiques et naturelles*, and author of numerous original papers in physical science, died in August last.

DR. ROBERT BELL, formerly chief geologist of the Geological Survey of Canada, died recently at the age of seventy-six years.

DR. DELORNE D. CAIRNES, a graduate of Queens (1905) and of Yale (Ph.D., 1910), and an active member of the Canadian Geological Survey, has died.

CHARLES WALES DRYSDALE, a graduate of McGill and Yale Universities and one of the most promising of the young geologists of the Geological Survey of Canada, was drowned along with his assistant Mr. Gray in trying to cross the Kootenay river about 30 miles from Sinclair, B. C., on the evening of July tenth.

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THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XXVIII.—*The Great Barrier Reef of Australia*; by W. M. DAVIS.

THE Great Barrier reef of Australia, which fronts the eastern coast of Queensland for a distance of over 1,000 miles, has been interpreted according to Darwin's theory by Jukes, the first geologist to study it (1847), and by several later observers, and therefore regarded as a great upgrowth of reef and lagoon deposits upon a slowly subsiding foundation. The lagoon being from 30 to 70 miles wide, a vast thickness has been ascribed to the reef, as in section A, fig. 1. Other observers have denied that Darwin's theory is applicable in explaining this greatest of barrier reefs; thus Gardiner, the most experienced English student of the coral-reef problem, says that the theory of subsidence is here "absolutely excluded," and replaces it by the theory of veneering reefs on sea-cut platforms.* This is an impossible theory because the shore line is not clift. Unfortunately, in reaching his opinion Gardiner overlooked the indisputable evidence for submergence, presumably due to subsidence, that is afforded by the strongly embayed mainland coast, to which Penck first drew attention in 1896. A sample of the coast in latitude 20°, S., is given in fig. 2, reduced from British Admiralty chart No. 347. Several sketches of the mountainous coast and its embayed shore line are given in fig. 3: sketches A and B are of islands outside of the Whitsunday passage (see fig. 2); sketch D shows the mainland coast of the passage; sketch C is Magnetic island, near Townsville; sketch E is a part of the coast south of Cairns. As the sketches were made from the deck of a passing steamer, the embayments are much foreshortened.

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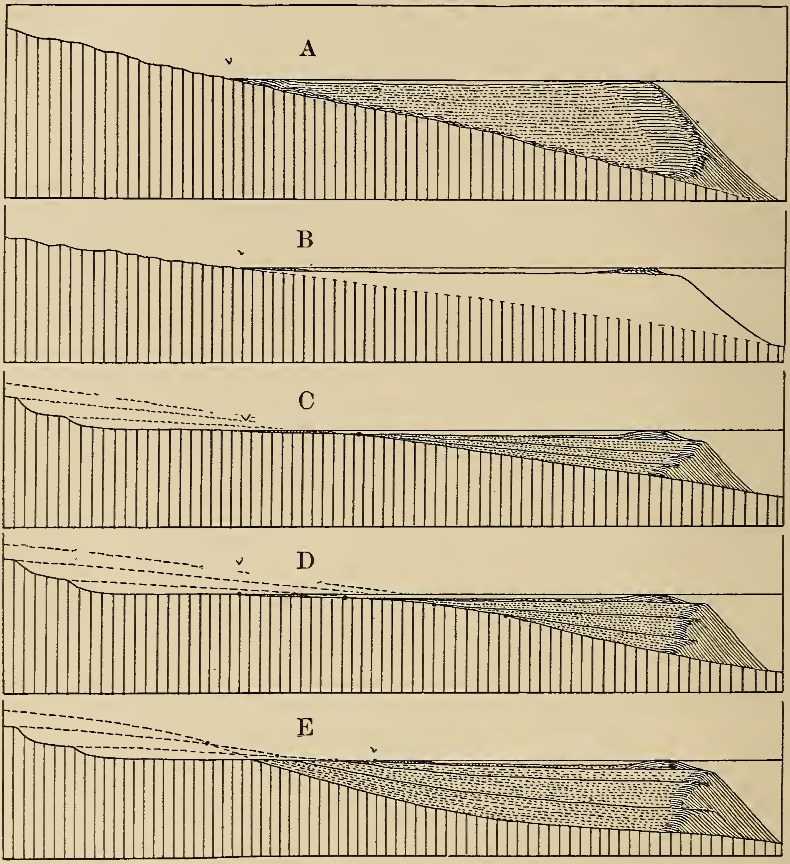
* J. S. Gardiner, The Building of Atolls, Proc. Internat. Congr. Zool., 1898, 119–124.

On the other hand, Vaughan, while recognizing recent submergence of small amount as the cause of upgrowth of the visible barrier reef from a platform now about 30 fathoms below sea-level, has excluded coral-reef agencies from any part in forming the platform itself, and has thus limited the thickness of the reef to a small fraction of the thickness that is implied by Darwin's theory: Vaughan concludes that "the living barrier reef is growing on what was a land surface in Pleistocene time;" hence "the idea that the platform was formed by infilling behind the reef may be permanently set aside."* Both Gardiner's and Vaughan's views as to the thick-

Fig. 1.



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* T. W. Vaughan . . . The Virgin Islands . . . and their bearing on the coral-reef problem. Bull. Geol. Soc. Amer., xxvii, 41–45, 1915.

ness of the reef are represented in section B, fig. 1, the unshaded part of the section beneath the reef being regarded as part of the continental mass, although the origin of its form is not

FIG. 2.

satisfactorily explained. Vaughan's view is based on the physiographic investigations of parts of the eastern coast of Australia by Andrews (1903); but a careful review of Andrews' papers and a brief inspection of the region itself in 1914 have convinced me that the explanation just quoted is not the only one that deserves consideration, and that upgrowing coral

Fig. 3.

reefs may have bordered the Queensland coast not only during its recent moderate submergence, but during a long antecedent period of great downwarping, as a result of which the total thickness of successive reef growths and of the lagoon deposits behind them may be as much as one or several thousand feet. The reasons for this interpretation are here set forth.

Andrews was the first to apply modern physiographic methods to the explanation of the coastal highlands of eastern Australia. The region that he more particularly studied is locally known as "New England," and lies in the northeastern part of New South Wales, not far south of the southern end of the Great Barrier reef which fronts the Queensland coast farther north. The history of the highlands indicates the history of the off-shore sea bottom or reef foundation also. Andrews' chief results are that the New England region, of complicated structure and once of mountainous form, as in block A, fig. 4, was reduced to an extensive peneplain, FF′, in Cretaceous time, and that as a result of successive broad uplifts of a north-south belt, GG′, MJ′, RK′, after shorter and shorter intervals of time, three coastal peneplains of less and less extent, LL′, QQ, UU′, have been eroded on the eastern slope of the uplifted belt at lower and lower levels, so that they now form a series of benches, each one a number of miles in breadth, separated by irregularly dissected escarpments, K, O, S, independent of rock structure, and from several hundred to a thousand feet in height. The lowest and youngest of the peneplains, UU′, now diminished in breadth, VV′, by subrecent submergence, constitutes the present coastal lowland; like the earlier peneplains it is often surmounted by monadnocks, large and small.

Andrews gives only a brief discussion of the off-shore changes attendant upon the successive uplifts of the highland. His most significant statements on this point are as follows: "During late Pliocene and Pleistocene times, a differential subsidence took place for the coastal area . . . The formation of the present Great Barrier reef probably does not antedate this last movement of subsidence, although reefs doubtless existed prior to the cycle of subsidence. Unless the movements of subsidence were accentuated in an easterly direction, the depression which determined the Barrier Reef must have been very moderate in amount . . . The effect of the late subsidence was . . . to give birth to the Great Barrier reef."*

It is to the extension of this discussion, particularly with regard to an eastward accentuation of subsidence, that the present paper is directed. The successive uplifts of the coastal region must have been of diminishing measure eastward: for

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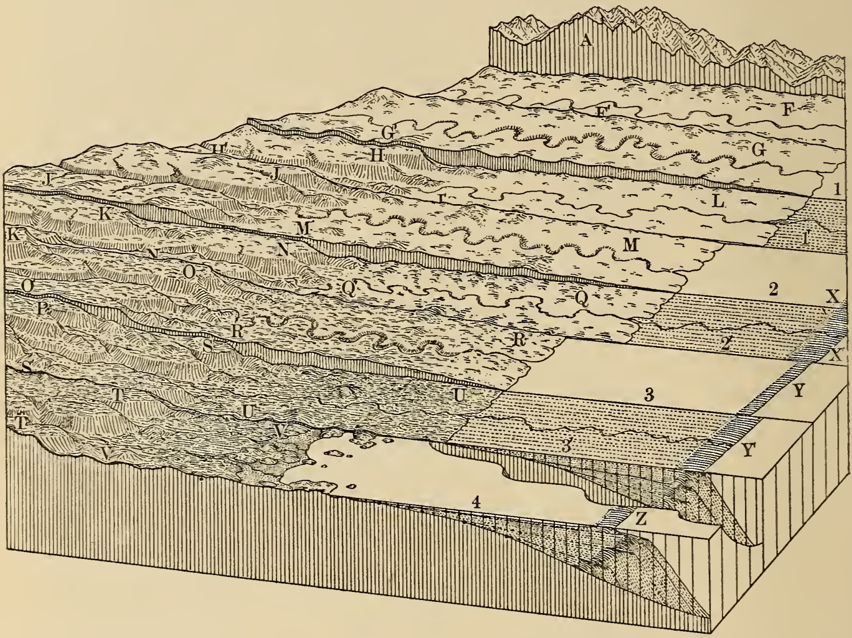
*E. C. Andrews, An outline of the Tertiary history of New England. Rec. Geol. Surv. N. S. W., vii, 1903, 140-216; see pp. 214-215.

if the uplifts had been everywhere of the same amount, the continent would have been broadened thereby, and the coastal lowland today would show successive littoral belts of younger and younger marine sediments, more or less eroded. The absence of such belts indicates that, while the interior highlands were uplifted, the adjoining sea floor either stood still or subsided.

Let it be noted in passing that the absence of littoral belts of marine sediments suffices to disprove the possibility to which some credence appears to be given by Australian investigators, that the uplift of the highlands was not actual but only apparent, and that the sloping land really stood still while the sea sank to lower and lower levels; for in such case at each sinking the marine sediments previously deposited would be laid bare, and although they would be worn down to lowlands in each interval of local peneplanation, they would still be visible today in the littoral zone. No such belts are to be seen; hence the supposition that the land gained height because the sea surface sank is excluded; the continental mass, not the sea surface, must be the chief seat of movement.

Fig. 4.



Furthermore, had the coastal lowland and the adjoining sea bottom stood still while the inner highlands rose, the present shore line would not be embayed, and a broad fluviatile plain, composed of the confluent deltas of many rivers, would border the coast; but as a matter of fact, the shore line is well embayed and the delta plains are relatively small and discontinuous, as at V, fig. 4. Hence the sea floor but not the sea surface probably subsided each time that the highland rose; in other words, the littoral belt was gently and intermittently tilted eastward between a broad highland anticlinorium on the west and a deep sea-bottom synclinorium on the east: in short, the littoral belt occupies a zone of intermittent flexure.

The line of no change of level or axis of flexure cannot have advanced seaward as the successive flexures took place, as in section E, fig. 1, for in that case as well as in the case of uniform uplifts, belts of marine sediments would now be found in the coastal lowland. The line of no change cannot have remained fixed, for this would entail a non-embayed coastal lowland bordered by fluviatile deposits; of less breadth, to be sure, than if no down-flexing had taken place off shore, yet much greater breadth than is actually found in the discontinuous deltas of today. Hence, as these various possibilities are excluded, the line of change probably shifted westward, as in section D.

This interpretation is adopted in fig. 4, in which nine stages in the physiographic development of the region are represented in successive east-west blocks from background to foreground. The disordered structure of the region demands, as above noted, that it was once mountainous, as in block A. The mountainous mass must have remained long quiescent, for it was reduced in Cretaceous time to an extensive peneplain, FF′. Then as a result of a gentle flexing the seaward area was submerged and the interior area was elevated as in block GG′; and in this position the seaward slope was reduced to a second but less extensive peneplain, LL′, separated from the unconsumed part of the uplifted peneplain, HH′, by a ragged retreating escarpment. This escarpment of differential erosion is analogous to the mountainous escarpment in North and South Carolina known as the Blue Ridge. Similar changes occurred twice again, resulting in the formation of a third peneplain, QQ′, and a fourth peneplain, UU′. But as the present shore line is much embayed, and as many subdued hills rise as islands from the shallow sea bottom, the eastern part of the fourth peneplain, UU′, must have been slightly downflexed and submerged at a recent date: the interior part of the peneplain, constituting the present coastal lowland, VV′, together with the benched highland, TT′, back of it, were probably upflexed at the same time, for the lowland, where I saw it, is now trenched by narrow valleys. Hence the latest movement of the coastal region seems to be of the same nature as, but of smaller amount than the movements inferred to have taken place at much earlier periods. A slight emergence of very recent date need not be considered here; it may be the result of the latest upflexing, or it may, following the principle of shore line changes demonstrated by D. W. Johnson, be the result of diminished tidal range in consequence of the enclosure of the lagoon by the present barrier reef.

The problem before us is to determine what opportunity for reef formation may have been offered during the successive down-flexures of the sea floor and during the long intervening periods of rest as indicated by the successive peneplanations of the coastal belt; but as this inquiry involves the conception of young barrier reefs, mature reef-plains, and abraded reef-plains, two paragraphs will be given to that aspect of the subject, following and extending a view of reef development first clearly enunciated by Hedley in 1907.

Imagine a recently uplifted and reef-free coast, or for convenience of graphic illustration imagine a recently constructed, reef-free volcanic cone, of which an undissected sector is shown at D, fig. 5. The shore is attacked by waves and a cliff and platform are developed, sector E, on which no reefs can be formed* until submergence embays the radial valleys, sector F, when a narrow young reef will make its appearance, enclosing a lagoon where aggradation takes place. Tahiti, I believe, exemplifies this sequence of development. Let it be supposed that the reef thus initiated is maintained in a narrow or youthful stage with a widening lagoon by continued subsidence, until in sector G a long enduring still-stand period sets in. The youthful reef will thereupon widen to more mature form by outgrowth and overwash; the embayed valleys will be filled by deltas, which will advance farther and farther into the lagoon, as in sectors H, J, and K; and the lagoon will be at last converted into a mature reef-plain, as in sector L.

The mature reef-plain is not, however, the limit of orderly change if the island suffers no variation of level. The detritus from the central island will be delivered by the streams to the outer face of the mature reef, and the growing corals may thus be smothered. When that eventuality is reached the waves will cut the dead reef farther and farther back, reducing it to a shallow submarine platform, as in sectors M and N. Finally the central island itself will be again attacked, unless before that goal is reached subsidence sets in anew, whereupon a rejuvenated reef will make its appearance on the outer edge of the widening platform, or on the outer edge of the narrowed

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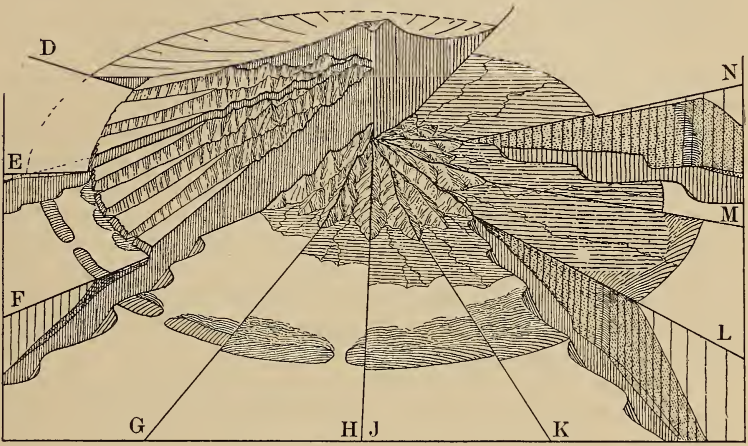
* See Clift Islands in the Coral Seas, Proceedings Nat. Acad. Sci., ii, 1916, 284–288.

plain, or on the island border, according as the submergence is large and rapid or not. It is interesting to note in passing that Darwin foreshadowed the idea here presented: he noted that, should atolls "remain at their present level, subjected only to the action of the sea and to the growing powers of the coral, ... it cannot . . . . be doubted that their lagoons and the islets on their reef would present a totally different appearance from what they now do. This consideration leads to the suspicion that some agency (namely, subsidence) comes into play at intervals, and renovates their original structure" ('42).

Fig. 5.



In applying this scheme of reef development to the Queensland coast, it will be convenient to trace the sequence of events backwards from the present into the past. But let it first be noted that the Great Barrier reef is already a mile or more wide in part of its length, and that the coastal embayments are already somewhat encroached upon by deltas; hence the present reef, Z, fig. 4, formed after the fourth flexure of the littoral belt, has passed the stage of earliest youth and is advancing toward maturity; if the coast should stand still for a long time to come, the broad lagoon would be converted into a mature reef plain.

Now as to the origin of the present reef, there can be little doubt that the opportunity for its upgrowth was given by the latest or fourth flexure of the continental border, whereby the formerly wider coastal lowland, UU′, was reduced to the present narrower lowland, VV′. But the wider coastal lowland must, before flexure and submergence, have been fronted by a mature reef plain, Y′, formed during the fourth peneplanation of the coastal slope, UU′; and the mature reef plain must have been developed from a young, upgrowing barrier reef, Y, that had been initiated by the flexure which tilted the peneplain, QQ′, into the coastal slope, RR′, just as the present reef, Z, was initiated by the flexure which tilted the peneplain, UU′, into the coastal slope, VV′. Again, the foundation from which reef Y grew up must, with large probability, have been a down-flexed and submerged mature reef-plain, X′, of an earlier cycle; and so on backwards through the series of flexures.

Thus, as far as present features can be genetically linked to the chain of antecedent features, the platform, shown in foreground section, from which the visible Great Barrier reef, Z, has grown up, appears, in its outer part at least, to be in large measure the product of coral-reef agencies that were directly or indirectly in operation through a considerable period of past time; for it must be remembered that reef-forming agencies contribute to the formation of a mature reef-plain not only directly by the constructive growth of the reef organisms and by supplying overwashed waste, but also indirectly by serving as a breakwater which encloses a lagoon where a large amount of land waste is locally deposited, instead of being swept offshore as is the case where unimpeded ocean waves wash and attack the land margin.

It is believed that this sketch of reef development takes fuller account of the accepted physiographic history of the adjoining coastal highlands than has been taken by other sketches; and that reef-forming agencies are thus shown to have been, with large probability, so long associated with the development of the off-shore structure of this part of the Australian continent that they cannot be reasonably limited to the brief period needed for the upgrowth of the present barrier reef from a depth of only 30 fathoms; but it is not intended to imply that the above-outlined sketch of the development of the Great Barrier reef embodies unescapable conclusions, for it is easy to suggest alternative possibilities, one of which is mentioned below.

It is furthermore believed that, in as much as the development of an off-shore continental shelf along the cooler coast of New South Wales is now contemporaneous with the development of the Great Barrier reef in the warmer waters along the Queensland coast, the contemporaneous development of these two unlike features, one largely by inorganic, the other largely by organic processes, may have been similarly contemporaneous each in its own latitudes, for a long time in the past. It is true that this view traverses the opinions of Guppy,* Forbes,†

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* H. B. Guppy, The Origin of Coral Reefs, Proc. Vict. Inst., xxiii, 1890, 51–68.

† H. O. Forbes, The Great Barrier reef of Australia, Geogr. Jour., ii, 1873, 540–546.

Vaughan* and others, who seem to have thought that only in recent times could these two unlike features be developed on a single coast line, and that in earlier times an inorganic continental shelf fronted the whole coast; but no good reason has been shown why a continental shelf and a barrier reef can not have been formerly developed contemporaneously along the cooler and the warmer parts of any continuous continental coast, just as well as they are now contemporaneously developed along the Australian margin, and just as well as they are now developed on many discontinuous coasts; hence I am inclined to regard the present juxtaposition of shelf and reef as a normal and not as an exceptional relation, and therefore as a characteristic of the past as well as of the present.

As to alternative explanations for the Great Barrier reef:—it is easily conceivable that, until the latest flexure of the coast took place, whereby the coastal lowland was narrowed as in the change from UU′ to VV′, fig. 4, no previous shift of the axis of flexure occurred, as in section C, fig. 1; or if such a shift occurred, the axis of no change of level may have advanced not landward as in section D, but seaward as in section E. In this case, reefs may not have been formed, for they do not as a rule occur along coasts that are bordered by recently formed, unconsolidated sediments. Then, in the absence of off-shore barrier reefs, the unimpeded waves may have formed an inorganic continental shelf along the northern half of the Australian coast, just as they are now and long have been forming a shelf along the southern half of the coast; and finally after the latest flexure took place, the present barrier reef may have grown up on a continental shelf in the formation of which earlier reefs had taken no part. But in view of the various lines of geological evidence which suggest a large diminution of land areas in the Australasian region during Tertiary time it seems not unreasonable to assume that, on the whole, the earlier flexures of the Queensland coast have, like the latest flexure, involved a westward shift of the axis of flexure and caused an encroachment of the sea on the land, as in section D; and in view of the occurrence of greatly uplifted and elaborately dissected coral reefs on the neighboring islands of Australasia, which imply the presence of corals in this region for a considerable period of past time, it seems unreasonable to assume that reefs have occupied the Queensland coast only for the brief period demanded for the formation of the superficial part of the Great Barrier.

The Great Barrier reef of today does not in all parts of its extraordinary length rise from the outer margin of its platform,

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* T. W. Vaughan, The Platforms of Barrier Coral Reefs, Bull. Amer. Geogr. Soc., xlvi, 194, 426–429.

and this has been taken to show that the platform is an inorganic continental shelf and not an antecedent reef plain. But no reason has been adduced to show why a reef should grow up at a moderate distance back from the margin of a smooth continental shelf, and why it should not grow up at a similar distance back from the margin of submerged and almost equally smooth mature reef-plain. On the other hand, reasons for the upgrowth of a young barrier reef at a certain distance back from the margin of a submerged reef-plain are suggested in sectors M and N of fig. 5:—a partly abraded reef-plain might, after rapid submergence, be too deep for coral growth at the outer margin of its abraded platform, but not too deep at the margin of the unconsumed part of the plain. Hence the control of the location of the present barrier reef may well have been the result of other conditions and factors than those which formed the platform that serves as its foundation.

There is one way, to which attention has not hitherto been called, in which the inorganic processes now at work in developing the continental shelf of New South Wales may be in the future, and may have been in the past, unfavorable to the development of a mature reef-plain along the Queensland coast. In that part of the coast where the Great Barrier reef of Queensland and the great continental shelf of New South Wales adjoin, the 'long-shore currents are at present engaged in forming extensive sand reefs, which appear to be extending northward. The sand reefs have already, in the relatively short interval since the latest flexure by which the coast was embayed, gained lengths of scores of miles. Hence in an earlier and much longer interval, sufficient for the partial peneplanation of an upflexed coastal belt, similar sand reefs might have extended much farther northward along the coast than they now reach; as fast as they advanced they would certainly kill all the reef-building organisms, and thereafter the waves might be able to cut away the reef. It is, therefore, conceivable that, toward the close of the several still-stand periods in which the lowlands, LL′, QQ′, UU′, fig. 4, were developed, the coral reefs (W′,) X′, Y′, of the Queensland coast may have been encroached upon for a few hundred miles by sand reefs from the south; but inasmuch as the present immature reef has its southern end determined chiefly by temperature, however far its mature predecessors were encroached upon by shore sands, it is quite possible that earlier young reefs (W,) X, Y, may also have been able in their youth to extend as far south as their successor of today. But this transcendental aspect of the problem need not be pursued further.

Art. XXIX.—*Wave Work as a Measure of Time: A Study of the Ontario Basin*; by A. P. Coleman.

The Pleistocene of the Toronto region has been studied as long and as carefully as that of any part of North America, and the work of waves on lake shores, ancient and modern, and of rivers entering the successive lakes in the Ontario basin has been of great importance in determining the geological relationships. Its study may be said to have begun with the visit of Sir Charles Lyell to the raised beaches (Iroquois) north of the town in 1842;* and to have been continued by the distinguished engineer, Sir Sandford Fleming, who in 1850 described the growth of Toronto island by the transport of materials from Scarboro' Heights,† and in 1861 gave an excellent account of a part of the Iroquois beach to the north of Toronto.‡ In 1880 Dr. Spencer and Dr. Gilbert showed that the beaches of the ancient lake were deformed, and the appropriate name of the Iroquois Water was given to the predecessor of Lake Ontario by Dr. Spencer.§ Since then various papers have been published by the present writer on matters connected with Lake Iroquois and other lakes and rivers which formerly played a part in the history of the region, the latest in 1913.‖ In this paper an attempt was made to work out the age of Lake Ontario from the rate of recession of the Scarboro' cliffs and the distance they had receded, additional, though less reliable, evidence being deduced from the growth of Toronto island. The results thus obtained have recently been criticised by Dr. Spencer in an article on the "Origin and Age of the Ontario Shore Line."¶ Dr. Spencer's pioneer work on Lake Iroquois was so good that his views on the history of the Ontario basin will naturally receive careful consideration. The question of the age of Lake Ontario is of so much interest that a further discussion of the matter is desirable, since the difference between 8,000 years, as determined by myself, and 2,000, as worked out by Dr. Spencer, is far too great to be accidental. In reading his paper carefully it appears that through lack of personal knowledge of the region he has made some incorrect assumptions which lead to wrong conclusions, and it is proposed to restate the problem and show how the errors occurred.

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* Travels in North America, vol. ii, pp. 103–8.

† Jour. Can. Inst., 1854, pp. 107–223.

‡ Ibid., 2d Series, vol. vi. pp. 247–253.

§ The Iroquois Beach, Trans. Roy. Soc. Can., 1889, p. 121, etc.; and other publications.

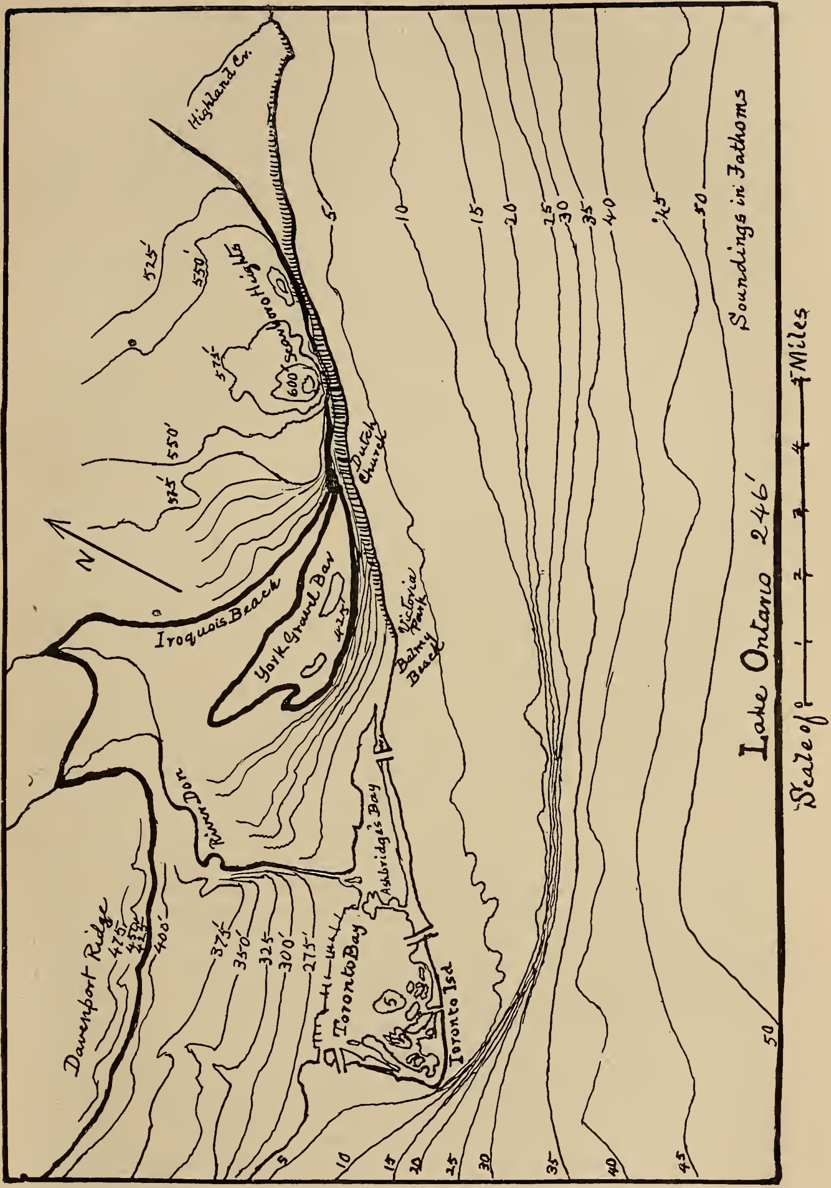
‖ An Estimate of Post-glacial and Interglacial Time in North America, Congrés Geologique, XIIe Session, Compte-Rendu, pp. 435, etc.

¶ This Journal, vol. xliii, No. 257, pp. 351–362, May, 1917.

The most striking physiographic feature in the vicinity of Toronto is Scarboro' Heights to the northeast of the city, extending as bold cliffs of stratified clay and sand capped with bowlder clay, for a distance of nine-and-a-half miles in a nearly straight line, and rising for a short distance near the center to 350 feet above Lake Ontario. These cliffs have been studied by the present writer every year since 1890, and the undercutting by waves and the land slips occurring in the spring give clear evidence of recession. During the time of observation the shore has receded in a nearly straight line, and the most satisfactory mode of determining the rate of recession would be to compare the results of careful mapping of the shore, repeated after a lapse of years. Unfortunately no such map has been made, the only accurate measurements available having been carried to the top of the cliff and not to the shore. However, it has been found in more than 20 years of observation that the slope of the cliffs has remained very uniform, so that results obtained from the edge of the heights must correspond closely on the whole with the recession of the shore beneath.

It has been noted also that, with the clearing of the forest ravines due to rain, erosions have become more frequent and are cut backwards more rapidly than formerly. In some cases such rain gullies have advanced more than fifty feet inland in a single season, and it is evident that only the actual edge of the cliffs, corresponding to the nearly straight shore beneath, can be taken into account in determining the rate of recession.

The first survey of Scarboro' was made in 1792, as shown by plans at the Crown Lands Department of Ontario, but no accurate work was done until 1862 and '63 when Mr. F. F. Passmore carefully re-surveyed the township, planting corner stones to fix the road allowances and the boundaries of properties. In 1912 I was asked by the City Commissioner of Toronto, Mr. R. C. Harris, to report on the rate of recession of the cliffs, since the location of a reservoir on the heights was under consideration. On my recommendation Messrs. Speight and Van Nostrand repeated Passmore's measurements toward the end of 1912, fifty years after the original survey. Beginning at the southwest, the recession at the seventeen points where corner posts were available is as follows: 8, 98, 93, 120, 85, 55, 198, 31, 76, 50, 167, 199, 127, 128, 62, 39, and 89 feet. An examination of the edge to which the measurement was made at these different points showed that the three largest recessions, 198, 167 and 199, occurred where ravines were being actively cut, and so should not be included in the computation. The first one, of 8 feet, was on low ground at the end of the cliff where little wave work was going on and was left



Map of Toronto Region.

out of consideration also. The thirteen measurements that appear to be normal give an average of 81 feet in the fifty years, which works out to 1·62 feet per annum.

The rate of recession having been settled, the next problem to determine is the distance through which the cliffs have been cut back. At first sight this might appear to be almost insoluble, but a study of the history of the former lakes of the Ontario basin and of the mode of action of waves in such lakes gives quite definite information as to the point where the work began.

The earliest lake of which there is positive evidence occurred in interglacial times, when the water stood 150 feet or more above the level of the present lake and a great river flowing from the northwest entered at Scarboro'. This river, an interglacial successor of Dr. Spencer's preglacial Laurentian river, built a delta of clay and sand out into the lake causing an obstruction to the next advance of the ice. This delay in the motion of the glacier was repeated at each successive advance, and the result was the building of a ridge of bowlder clay and interglacial materials, which begins at the interlobate moraine between the Ontario and Georgian Bay basins and extends with a fairly uniform elevation to Scarboro' Heights, making the highest point on the whole shore of Lake Ontario. The transformation from a river valley into the highest ridge in the region is an impressive one.

That such a long and uniform ridge did not end suddenly but once extended farther into the Ontario basin is in itself probable; and to determine just how far it reached beyond the present shore will give a measure of the length of time during which wave work has gone on under present conditions.

It is a well-known fact that a cape projecting into a body of water is more strongly attacked than the rest of the shore, and that the materials removed by the waves are shifted in the direction of the greatest reach of the prevalent storm winds and built out across the next bay as a spit. If the bay is shallow the spit may grow across its whole width and form a bar. If the bay is deep the spit advances only so far across as the lower limit of wave action permits and then bends shorewards forming a hook. Successive hooks are built out into the deeper water forming a platform which rises a few feet above the water and encloses shallow depressions or lagoons. As the work continues and the cape is cut back farther and farther, a gently sloping terrace is carved from it, and at the same time the spit or hook is shifted in a direction inland forming a terrace also, but in this case one that was first built up from the bottom and afterwards cut down a little by wave action. These two varieties of terrace, though formed in different ways, join and make a continuous subaqueous shelf along the coast where the process is at work. The under-water forms of the two portions of the shelf may be studied by means of soundings, and it is found that the part carved from the projecting shore has a gentle slope to the edge where the attack began, and a steeper slope beyond towards the depths of the lake; while the built terrace terminates outwards in a much more rapid descent into deep water. The slope just mentioned is usually about at the angle of stability for the materials of which it has been built.

Such a shelf consisting of two distinct parts formed in different ways and having different contours may be recognized under water by soundings, and the edge where the more rapid descent into deep water occurs represents the end of the promontory before the carving of the waves began.

Fortunately ancient Lake Iroquois did the same kind of work as Lake Ontario and carried its work to about the same degree of completion, so that one may study these subaqueous earth forms conveniently on dry land. An old shore cliff of Lake Iroquois is well seen at Davenport ridge in Toronto, rising from 50 to 75 feet above a terrace carved from rolling bowlder-clay country, and sloping down for nearly 170 feet to the shore of Lake Ontario. This descent is pretty uniform, and the contours are fairly evenly distributed over the three miles of distance between the old shore cliff and the present water front. The carved portion of the terrace, sometimes veneered with more or less stratified sand, joins on the east the terrace built up of cross-bedded sand of great thickness south of the old Humber bar. These relationships were described by Sir Sandford Fleming in 1864 and a comparison was made between them and the relations of Toronto island to Scarboro' Heights.*

We are now ready to consider the extent of the recession of Scarboro' Heights by the wave action of Lake Ontario. It will be seen from Dr. Spencer's map, in spite of the fact that it is taken from an old and very imperfect survey, that the shelf carved from the cliffs extends with a gentle slope for 2 or 3 miles to about 100 feet in depth and then falls off rapidly to greater depths. The southward projection of the contours shown on his map near the middle of the water front is due to an error. The edge of the shelf is in reality very uniform as may be seen on the map accompanying my former paper, or the one given here, which has been prepared from the last Hydrographic Chart published in 1916. The point where the carved terrace joins the built terrace, with its steeper slope, is well marked and the extent of the promontory removed by the

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* Journ. Can. Inst., 2nd Series, vol. vi, pp. 247–253.

waves measures from 2¼ miles to about 3 miles. In my earlier account it was given as 2½ miles or 13,000 feet in round numbers, which corresponds with the average distance from shore of the 15-fathom line of the new chart.

Dr. Spencer casts this measurement aside and replaces it in his own paper by a line drawn at a distance of 4,000 or 4,400 feet, his only assigned reason for this being that "its slope should correspond to that of the country between the Iroquois beach and the low shore just west of Victoria Park." As this slope is on the rapid lakeward descent of an Iroquois gravel bar and not on a carved terrace cut in the clay, such as that south of Davenport ridge a few miles to the west, it is evident that he has not distinguished between the two quite different forms produced by wave-action. As shown before, the carved terrace slopes only 170 feet in 2½ or 3 miles, while the built terrace descends much more steeply. As we are dealing with a terrace carved from interglacial clay and sand and the successive bowlder clays above, it is clear that the slope should correspond, and the more rapid descent 2½ miles from shore must be considered the lakeward end of the promontory.

Thirteen thousand feet divided by 1·62 feet, the rate of annual recession shown in 50 years, gives 8,000 years as the length of time required to cut back the old Scarboro' promontory.

When the time required to cut back Scarboro' Heights to its present position had been worked out, it seemed advisable to take up the other end of the problem, i. e., the length of time needed to build Toronto Island out of the sand transported from Scarboro'. For this purpose an estimate was made of the amount of sand deposited northeast of a pier at the eastern channel into Toronto bay during the thirteen years since it had been constructed. The annual increment of sand against the pier was estimated at about 42,000 cubic yards, and the bulk of the island was roughly put at 337,000,000 cubic yards, which works out to a little over 8,000 years. Owing to the short number of years during which sand had accumulated east of the pier and to other uncertainties no great stress was laid on this computation, though it seemed to corroborate the conclusion drawn from the Scarboro' recession. For some reason not very clear to me, Dr. Spencer has reversed things and assumed that my time estimate depended on the growth of the island rather than the recession of the cliffs and states that "the enormous mass of sand deposited here is of more than local interest, having given rise to fatal chronological speculations." He proceeds to demolish my line of argument by stating that only the upper 30 feet of the island belong to the Ontario beach, the materials beneath being delta deposits from the river Don.

Toronto island is one of the most characteristic examples of wave-work on the Great Lakes, its form both above and below water agreeing perfectly with those of a succession of hooks built into deep water. The only evidence Dr. Spencer gives of its delta character is the small amount of clay occurring interbedded with sand; and this is easily explained when one has seen the waters opaque with clay for miles from shore during an easterly storm. This drifts right past the island at present and must have been deposited in earlier days over the growing shoal in advance of the island.

That the Don has deposited delta materials to a depth of 80 feet or more in an old deep channel beneath the present Don flats is proved by wells sunk near its mouth, but its rather insignificant delta ends a mile northeast of Toronto island where marshy shoals occur in Ashbridge's bay. The whole of the small delta is northeast of the pier against which sand is accumulating and the main structure of the island is clearly due to the southwesterly drift of sand from Scarboro'. Why should the little river Don build a huge hook-shaped delta when the much larger Humber and Rouge rivers flowing through the same type of country have done nothing of the kind? There is no hook near the mouth of the Rouge or the Humber because there was no great promontory of sand and clay just to the east from which the storms could obtain building material. This is the only difference between them and the Don.

If Lake Ontario has lasted at least 8,000 years it is probable that Lake Iroquois, of about the same size and with shores of about the same maturity, lasted in the neighborhood of 8,000 years, also; though an argument from analogy must of course be received with caution.

The lapse of time between the end of Lake Iroquois and the beginning of Lake Ontario is more uncertain. The thawing away of the ice from the St. Lawrence region, after it had sunken so far as to allow the waters to drain past the Adirondacks, seems to have gone on rapidly, since no prominent shore lines are found between those of Lake Iroquois and the marine beaches formed when the St. Lawrence valley became free from ice. Again, the length of time during which the Ontario basin was below sea-level, forming a fresh water extension of the Gulf of St. Lawrence, is not certain. The old marine shores are much less mature than those of Lake Iroquois and of Lake Ontario; which would seem to imply a much shorter time in their construction, perhaps not more than half as long, say 4,000 years. How long a time was required to elevate the outlet of the basin and cut off Ontario from the sea, and afterwards to raise the outlet until the water was ponded back as far as the Toronto region, so that wave work could begin at Scarboro', is very hard to estimate. The guess hazarded in my last paper, that the events occurring in the interval between the two lakes might require about 8,000 years, is objected to by Dr. Spencer, who thinks the time much too short. In this he may be right, in which case the 8,000 years suggested should be looked upon as a minimum; and the whole period since the ice left the Ontario basin may be considered to have been at least 24,000 years, but probably somewhat longer.

There are two other points of interest raised in Dr. Spencer's paper, that of the constancy of level in Lake Ontario in recent times; and that of the limit to be assigned for the end of the ice age. These may be discussed briefly.

He suggests that "researches as 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 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 fact that all the streams flowing into Lake Ontario near the southwestern end have dead water for two or three miles while their courses are rapid above this point, strongly suggests that the water has been backed up by the differential elevation of the outlet of the lake; and the further fact that the lagoons behind the meanders are not yet filled up with mud from the spring floods, nor with peat or other vegetable matter, suggests that the change of level has been much more recent than 3,500 years.

The other point is raised in the following rather curious manner: . . . . . "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."

The suspicion suggested that I had "some speculation to support" need not be replied to, but the question as to when one geological period ends and another begins is of considerable interest. When did the Glacial Period end? When the ice began to disappear, when it had half disappeared, or when it had wholly disappeared? If the last assumption is made the ice age still continues, for there are still small glaciers in Labrador, larger ones in the Rocky Mountains, still larger sheets in Alaska and the Arctic islands, and an ice cap in Greenland.

Can the question be settled by a reference to climates, the Glacial Period implying Arctic conditions and ending when the climate became cold temperate? If that is the case the Glacial Period ended for the Ontario region at the beginning of Lake Iroquois, for large spruce and tamarack trees grew at Hamilton while the lake was still young, the beaver, the bison and the wapiti, as well as extinct mammals, inhabited its shores before the great gravel bar in front of Dundas marsh had been built, and unios, campelomas, plueroceras and sphæriums like those in the waters of Lake Ontario occur in an Iroquois gravel bar at Toronto.

The climate was not Arctic but cold temperate on the shores of Lake Iroquois and the shells and other remains found in the old beaches of Lake Agassiz and of Lake Algonquin in the more northern parts of the province of Ontario point to similar climatic conditions, since they are the same as live in the present waters of those regions.

In spite of the presence of a stagnant, slowly thawing mass of ice, reaching from the Adirondacks northwards and blocking the waters of Lakes Iroquois and Algonquin, the climate was not Arctic any more than that of southern Alaska, with great ice sheets not far off, is Arctic at the present day.

Probably the most satisfactory account of the close of the Glacial Period is to make it a progressive event beginning in Iowa and adjoining states thousands of years before it reached Ontario and taking place on the shores of Lake Iroquois thousands of years before it reached James Bay and Hudson's Bay and the last remnant of the continental ice sheet finally disappeared.

To the stratigrapher striving to establish sharp boundaries between formations this account of the slow and progressive ending of one geological period and beginning of the next may appear unsatisfactory; but in reality most physical changes on the earth have been gradual, spreading from point to point, from region to region, requiring many thousands of years for completion. It is only when looking back upon them from far off that these events appear sudden and instantaneous for the whole world. A discussion therefore as to the precise year in which the Ice Age ended is not of much value since it really ended at different times in different places.

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Art. XXX.—*Arthropods in Burmese Amber;* by T. D. A. Cockerell.

In the August number of this Journal for 1916, I recorded the occurrence of insects in Burmese amber, obtained from beds of Miocene age. Mr. Swinhoe has since sent additional material, and the species found appear on the whole remarkably primitive. They are, indeed, related to living forms; but in practically every case to precisely those forms which we have thought of as ancient, as remnants of a very old fauna. So far, no ants, bees or wasps have been found; the Hymenoptera are Evaniids and Bethylids. The Hemiptera so far examined belong to the archaic family Enicocephalidæ. It is too early to express a positive opinion, but it is difficult to avoid a strong suspicion that the amber, though found in Miocene clay, is actually very much older, conceivably even Upper Cretaceous. The species described in the present paper all come from a very large block which has been cut into slabs; they therefore all lived at the same exact time and place.

Pseudoscorpiones.

Electrobisium new genus (Obisiidæ).

Cephalothorax remarkably long and narrow; apparently no eyes; pedipalps very long and slender, with large trochanter, stout femur, very slender tibia, and long slender hand with bulbous base; first pair of legs with femur very stout, the others ordinary, but all the legs quite long; abdomen broad and rounded, the scutes entire; body and appendages not hairy. Type the following.

Electrobisium acutum new species.

Wood brown; abdominal segmentation marked by darker lines. The following measurements are in microns: Length 1040; width of abdomen 530; pedipalp with femur 304 long, tibia 256, and hand 368; first legs about 496 long, second the same, third about 544, fourth extending about 770 beyond margin of body.

Burmese amber, from R. C. J. Swinhoe. In the same slab as type of *Electrofœnus*, but on opposite side, and close to edge of thickest part. This is quite unlike the pseudoscorpions described from Baltic amber, though there is a slight superficial resemblance to *Chelifer ehrenbergii.*

Thysanura.

Lampropholis (?) *burmiticus* new species (Lepismatidæ).

Male. Length 3^{mm} (not counting cerci), parallel-sided, the form as in *Lampropholis dubia* Koch and Berendt (from Baltic amber), but body apparently without scales; stili can only be seen at apex of abdomen, and certainly are absent from the middle segments. In the following descriptions the measurements are all in microns:

Antennæ as usual in the family, with short setæ; maxillary palpi 5-jointed, the first joint short, the others measuring, (2) 96, (3) 88, (4) 96, (5) 160; width of head about 400; width of thorax in middle about 640; width of abdomen about 528; long slender hairs project from sides of thorax as in Silvestri's figure of *Lampropholis*, only they are more numerous; coxæ and femora stout, the legs essentially as in *Lepisma*, the only noteworthy feature being the extremely oblique end of first tarsal joint; hind tibiæ 304 long, their tarsi 320; cerci about 1440 long, with fine bristles, and three very long bristles, more or less broadened apically, placed about 320 apart; caudal stili about 240 long, not counting the apical bristle, which is about 65; inner process of caudal subcoxæ long and pointed, its length about 160.

Burmese amber, from R. C. J. Swinhoe; in the same piece as the type *Electofœnus*, and 28^{mm} from it. This may have lost all its scales, but if it was a scaly form, it is surprising that no scales are to be found, even in the amber round about it. *Lepidothrix*, from Baltic amber, is without scales, but is in other respects very distinct from our insect. Possibly the Burmese species should be placed in a new genus.

HEMIPTERA.

Disphœrocephalus new genus (Enicocephalidæ).

Related to *Enicocephalus*, but differing thus: head strongly constricted behind eyes, so that there is a slender neck before the bulbous expansion; thorax long and relatively slender, much longer than wide, with a marked posterior constriction; wings (the specimen apparently adult) not developed, represented by pads; rostrum long, in specimen seen extending straight out from head; antennæ long and very slender; anterior tibiæ (shown greatly foreshortened in figure) broadened and angularly produced apically, much as in *Enicocephalus*, but their tarsi long and narrow, with two slender straight claws, one much longer than the other; hind femora very stout, with an obtuse angle beneath. The head and thorax are delicately hairy; the antennæ are not hairy. Type the following.

Disphœrocephalus constrictus new species.

Length (to end of extended proboscis) 5^{mm}; the following measurements are in microns: Eyes to end of first antennal joint 640 (it is not possible to see quite clearly where the joint begins, but 400 of this is antenna, at least); second antennal joint, 750; third, 576; fourth, 480; width of thorax about 496; eyes to end of rostrum about 960; width of abdomen about 1070; anterior legs with long claw 192, short 128; length of middle tibia, 960; middle tarsus, 336; width of hind femur 208. The claws of middle legs are ordinary, slender and simple. It is assumed that the antennæ are four-jointed, but the region at base is obscured, and there may be a small basal joint.

Burmese amber, from R. C. J. Swinhoe. In the same slab as the type of *Cryphalites*, and 22$^{\text{mm}}$ from it. I at first thought this singular insect must be a Reduviid, but although the wings are not developed, the structure indicates the primitive family Enicocephalidæ. Owing to the inclusion of air, the details of the dorsal surface cannot be clearly made out. *Phthirocoris* Enderlein, from the Crozet Is., is apterous, but is in other respects very different.

The following key separates the principal genera of this group:

Wings not developed; anterior tarsi with two claws 1
Wings developed 2
1. Antennæ very short and stout; rostrum short and stout; middle and hind legs with 1-jointed tarsi .... *Phthirocoris* Enderlein
Antennæ very long and slender; rostum slender .... *Disphærocephalus* Ckll.
2. Anterior tarsi with one claw only ... *Enicocephalus* Westwood
Anterior tarsi with two claws 3
3. Posterior lobe of head transverse; insect strongly pubescent; discal cell closed .... *Hymenocoris* Uhler
Posterior lobe of head elongate; insect little pubesceut .... *Stenopirates* Walker

Enderlein also distinguishes two other genera. *Sphigmocephalus* Enderlein, from Africa, is separated from *Enicocephalus* by the middle and hind tarsi, which are 2-jointed instead of 3-jointed; the venation does not differ in any important particular. *Henschiella* Horv., from Europe, has the 3-jointed middle and hind tarsi; but there is only one cross-vein between the media and cubitus. *Hymenocoris* was based on the Californian *H. formicina* Uhler; another species is *Hymenocoris barbatus* (*Henicocephalus barbatus* Bergr.) from Ceylon. *Hymenodectes* Uhler is here considered a synonym of *Stenopirates*; but Van Duzee, in his recent Check List, places it together with *Henschiella*, under *Systelloderus* Blanch. Various arrangements are possible, according to the emphasis placed on the venation, form of head and thorax, or the

Fig. 1.

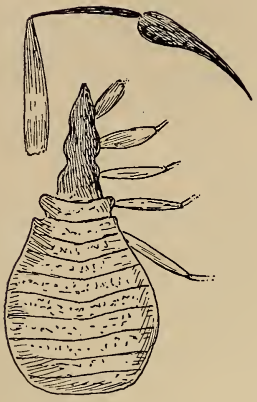

Fig. 3.

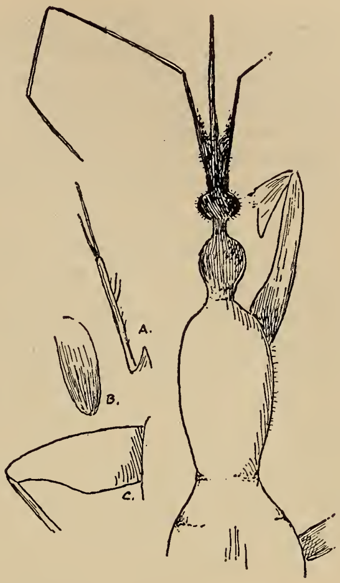

Fig. 2.

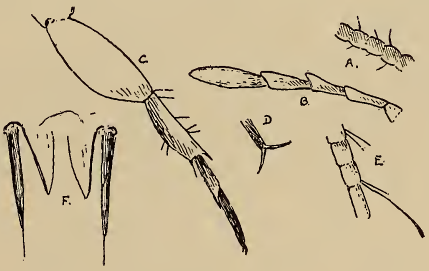

Fig. 4.

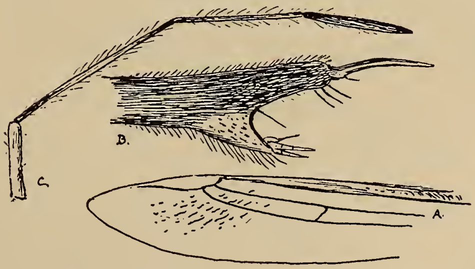

Fig. 1. *Electrobisium acutum.*
Fig. 2. *Lampropholis* (?) *burmiticus.* A. Part of antenna; B. Maxillary palpus; C. anterior leg; D. Claws of hind leg; E. Part of cercus; F. Caudal stili and subcoxal processes.
Fig. 3. *Disphærocephalus constrictus.* A. Anterior tarsus; B. Wing pad; C. Hind femur.
Fig. 4. *Enicocephalus swinhoei.* A. Hemelytron; B. Anterior foot; C. Antenna.

structure of the legs. The general tendency has been to recognize only one or two genera, but we have in the living Enicocephalidæ the remnants of a once numerous group, and it seems reasonable to consider the more striking morphological distinctions generic. *Disphærocephalus* is not generically separable on account of the undeveloped wings, but the other characters cited above are sufficiently distinctive.*

Enicocephalus swinhoei new species.

Length about 3^{mm}: brown, the hemelytra dilute brown, coriaceous; venation apparently as shown in figure, but the hemelytron figured is seen in very oblique view, and is actually no doubt considerably broader; head and thorax dorsally with much erect fuscous hair; anterior part of head separated from posterior bulbous portion by a distinct though thick neck, the posterior part strongly elevated dorsally; costa angulate near base, the costal region broadened basally much as in *Hymenocoris barbatus;* antennæ hairy, long and slender, flattened, so that they appear extremely thin in one view; middle and hind tarsi very slender, apparently two-jointed (the basal joint very short), terminating in two long simple claws. In *Systelloderus* or *Stenopirates biceps* (Say) these tarsi are short and stout, entirely different from those in our fossil.

The following measurements are in microns: Length of hemelytra about 1760; length of rostrum about 640; antennal joints, (1) 192, (2) 690, (3) 528, (4) 512, the last joint 40 wide on the flat side, but only 16 seen on edge; middle tarsus 320 long, hind tarsus 448 (both excluding claws). The anterior legs have only one claw.

Burmese amber, from R. C. J. Swinhoe. Very distinct from *E. fossilis* Ckll., also from Burmese amber, by the venation and long antennæ. The specimen is in the same slab as the type of *Disphærocephalus*, and 39^{mm} from it.

Judging from the Burmese fossils, the modern Enicocephalidæ average much larger than the ancient ones.

HYMENOPTERA.

Electrofœnus new genus (*Evaniidæ*).

Anterior wings folded longitudinally, as in Foeninæ, but venation of Aulacinæ. Stigma well developed, approximately as in *Hyptiogaster;* marginal cell large, its face on first submarginal about as great as that on second; two submarginal

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* Since the above was written, a second species of *Disphærocephalus* has been found. It is about 3^{mm} long, and has well developed wings, 2688 microns long; the anterior tarsus is shorter than the long claw; middle and hind tarsi two-jointed, first joint very short. This is named *D. macropterus* n. sp.

cells, but the outer side of second without any darkened or distinct bounding nervure; first submarginal very large, formed as in *Foenus;* second pentagonal, pointed basally, truncate apically, shaped as in *Interaulacus;* first discoidal very small, long and narrow, its oblique apical and basal sides parallel; second discoidal large, formed approximately as in *Psammegischia;* brachial cell large, triangular. Hind wing as in *Hyptiogaster.* Head large and broad, with very prominent eyes; mandibles projecting, stout, strongly elbowed, apparently bidentate; thorax elongated, the mesothorax in lateral profile flat, but anteriorly the thorax is bulging; no evident pubescence; antennæ slender, the joints long; legs very long and slender, posterior femora and tibiæ neither swollen nor clavate; hind tibiæ with two short but well-formed spurs; claws extremely small. Abdomen missing.

This peculiar genus appears to connect the Foeninæ with the Aulacinæ, but it is to be referred to the Foeninæ as a new tribe Electrofœnini, contrasted with the modern Foenini, typified by *Foenus* and allied genera. Type the following species.

Electrofœnus gracilipes new species.

Head, thorax, antennæ and legs black; wings hyaline, with dark red-brown stigma and nervures. Length of head and thorax about 3^{mm}; of anterior wing 4. Claws quite simple, as in *Psammegischia*, but more slender. Hind femur and tibia each about 1665 microns long; hind tarsal joints measuring in microns, (1) 800, (2) 240, (3) 175, (4) 80, (5) 145.

Burmese amber, from Mr. R. C. J. Swinhoe. The dominant Oriental Evaniids to-day are such genera as *Evania* and *Prosevania*, very different from the amber fossils.

Bethylitella new genus (Bethylidæ).

Head elongate, subcylindrical, much as in female *Isobrachium;* eyes very small; mandibles large, parallel-sided, with five equal small teeth on apical margin; antennæ 13-jointed, the scape stout and placed on a conical elevation, the flagellar joints stout, successively longer, the last considerably the longest; thorax long and cylindrical, abruptly obliquely truncate posteriorly; anterior legs with coxæ very stout, with a sharp but short tooth behind; their trochanters long and slender; their femora stout, concave above and convex below; their tibiæ stout and short, with a long spur and two short spines at apex; their tarsi five-jointed, the first joint a little longer than the next three together, strongly curved; the next three joints small, successively decreasing in size, the last slender, as long as the third and fourth together, with rather large simple claws and a large pulvillus; hind femora very stout, their tibiæ slen-

FIG. 5.

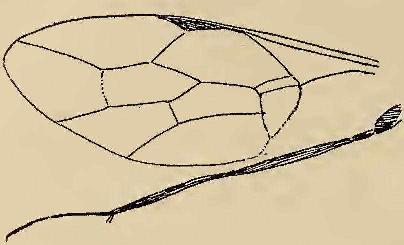

FIG. 5. *Electrofœnus.* Anterior wing and hind leg.

FIG. 6.

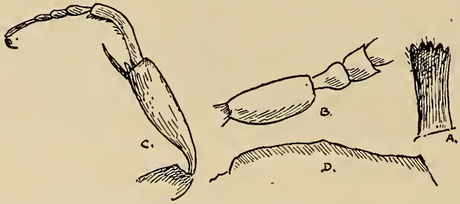

FIG. 6. *Bethylitella cylindrella.* A. Mandible; B. Base of antenna; C. Anterior tibia and tarsus; D. Dorsal profile of thorax.

FIG. 7.

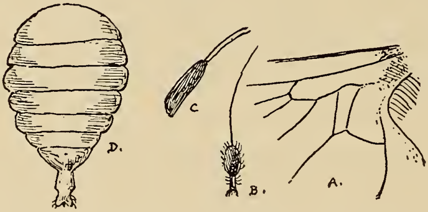

FIG. 7. *Burmitempis halteralis.* A. Base of wing; B. Antenna; C Halter; D. Abdomen.

FIG. 8.

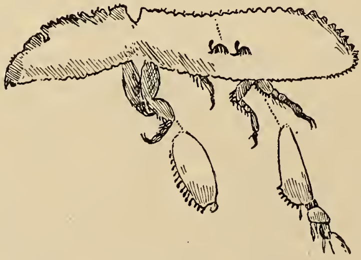

FIG. 8. *Cryphalites rugosissimus.*

der basally, gradually widening to a thick apex, with one long and one short spur; hind tarsi longer than tibiæ, the basal joint not curved; middle legs apparently much smaller than the others; wings ample, minutely hairy, venation not appreciably differing from that of *Mesitius*. Abdomen not preserved, but enough is left to show that the petiole was short. The submedian cell is open at its lower apical corner, and its apical side is very oblique. Type the following species.

Bethylitella cylindrella new species.

Head and thorax black; legs, antennæ and mandibles ferruginous. Head about 560 microns long and 320 broad (in a sublateral view); thorax about 880 microns long and 288 broad. Anterior tibia about 240 microns long, its tarsus fully 320; length of mandibles 192. Burmese amber, from Mr. R. C. J. Swinhoe. In the same piece as *Electrofœnus gracilipes*, and very close to it. A genus of Bethylinæ related to *Mesitius*, but distinct by the formation of the head and thorax. In the long prothorax it resembles *Palæobethylus* of Brues, from Baltic amber, but the venation is much more reduced.

DIPTERA.

Burmitempis new genus (Empididæ).

Apparently nearest to *Microsania* Zett. Minute flies with broad head, rather narrow thorax with subparallel sides, and oval abdomen; eyes widely separated; antennæ with first joint broad and rounded, second narrow and hairy, third very large, oblong-oval, obtuse at end, hairy, with a very long simple arista; wings large and broad, extending beyond abdomen; first basal cell long, emitting three veins from apex; second posterior cell somewhat contracted apically; no discal cell; second basal small and narrow, its long axis nearly vertical, and its apex considerably basad of end of first basal; anal larger than second basal, very obtuse apically, its outer margin not in a line with end of second basal; anal angle of wing projecting (about as in *Syneches*); lower margin of wing at base with long hairs; legs long, ordinary, with only very short hairs, femora not incrassate; male genitalia relatively small and simple, much as in *Rhamphomyia ungulina* Lw., from Baltic amber. Halteres enormous, the knob very long and thick. Type the following.

Burmitempis halteralis new species.

Black, including legs and knobs of halteres. Wings hyaline. The following measurements are in microns: length about 1040; length of wing 750; breadth of wing about 370;

width of second posterior cell in middle 80, and at end 60; depth of first posterior cell at vertical level of end of submarginal 96; apex of first basal cell apicad of apex of anal 76; width of anterior part of thorax about 160; length of halteres 240 (the knob being 128); anterior femur about 240; antennal arista about 256.

Burmese amber, from R. C. J. Swinhoe. On the same slab as the type of *Electrofœnus* but on the other side, close to the thickest part of margin, 32^{mm} from type of *Electrobisium* and nearly 6^{mm} from margin. This is a remarkable little fly, suggesting the Tachydromiinæ in some of its characters, but excluded from that group by the possession of an anal cell.

COLEOPTERA.

Cryphalites new genus (Ipidæ).

Small cylindrical beetles of the subfamily Cryphalinæ; thorax and elytra strongly tuberculate, and with small clavate hairs; elytra rounded posteriorly; head, seen from above, not concealed; anterior femora very stout; anterior tibiæ stout, the outer margin strongly convex, the inner with small clavate spines from base to apex (these tibiæ are seen in very oblique view, so the figure may not be quite correct as to proportions); hind tibiæ stout, subcuneiform, with seven spines (not clavate) on inner side near apex; on inner side of tibiæ at apex, and of small tarsal joints, are long flattened hairs; small joints of tarsi short and thick, third joint simple, fourth so small as to be invisible, so that the tarsi seem four-jointed; fifth joint long and stout, fully as long as the others taken together, with large simple claws. Unfortunately the antennæ cannot be seen. Type the following.

Cryphalites rugosissmus new species.

Black. The following measurements are in microns: length of thorax dorsally, 800; length of elytra, 1600; length of last joint of hind tarsus, 96, and of its claws, 80.

The flattened tarsal hairs are homologous with the remarkable fimbriate hairs figured by Hopkins in *Ptilopodius*. The spines of hind tibiæ are also essentially as in female *Ptilopodius*, a genus from the Philippine Islands. The rugose sculpture is wholly unlike that of *Ptilopodius*.

Burmese amber, from R. C. J. Swinhoe. In a slab cut from the same large piece as that containing the type of *Electrofœnus*.

University of Colorado, Boulder, Col.

Art. XXXI.—*A Calcium Carbonate Concretionary Growth in Cape Province;* by C. J. Maury.

The origin of the lime deposit owned and quarried by Mr. Stephen Dahse, near Hermon, forty miles north of Cape Town has been accounted a baffling puzzle of Cape geology. The lime lies in the Malmesbury shales and forms a small dome occupying the center of a low hillock rising from the surrounding level veldt. A few calcareous bowlders chanced to be found on the top of the hill and led to the exploitation of the dome beneath. Near the surface the lime rock is weathered into odd, fantastic shapes, but deeper down it becomes hard, crystalline, and of great purity. It may be noted that the last characteristic alone marks the deposit as rather unique, for pure lime free from magnesia or silica is a valuable rarity in South Africa. On chemical analysis the Hermon deposit yields 99 per cent $CaCO_3$. The rock is so handsome that efforts were made to cut it into ornamental slabs, but its tendency to break along the rhombohedral cleavages could not be overcome; hence it is roasted in kilns and serves for plastering and whitewashing the fine old Cape Dutch houses.

At the time of my visit the lime quarry had been exploited to a depth of about seventy-five feet and a diameter of about two hundred. The circular form of the calcium mass was completely revealed as it lay encircled by the Malmesbury shales. These are typically laminated, much fractured, and steeply inclined. They constitute the oldest rocks of the Cape region. In the vicinity of their contact with the lime dome they are greatly decayed and disintegrated into a very unctuous clay. The plane of contact was very markedly slickensided.

It is my belief that this singular formation is a concretionary growth parallel in origin to the salt domes of Louisiana. Professor G. D. Harris,* then State Geologist of Louisiana, originated the ingenious theory that these domes or "salt islands" are huge concretions formed by crystal growth from material in aqueous solution.

This theory was rendered still more convincing by the experiments of Mr. Stephen Taber † and those of Miss Long,‡ both series demonstrating the force that growing crystals exert in overcoming external resistance. Mr. Taber was led to conclude that the force thus arising may have played an important rôle in the formation of veins and concretions.

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* Louisiana Geological Survey, Bulletin No. 5; also Bulletin No. 7, pp. 75–83, 1908.

† This Journal (4), vol. xli, pp. 532–556, June 1916.

‡ Ibid., vol. xliii, pp. 289–292, April 1917.

Pure concretions like that at Hermon, differing from the surrounding rock, are characteristic of shales. The fact that the Malmesbury shales contain a low percentage of lime might seem an objection to this theory of the concretionary origin of the lime dome they inclose, but Professor R. B. Young of the Johannesburg School of Mines assures me that his observations have shown that particles may segregate from astonishingly great distances.

The slickensided plane of contact between the Hermon dome and the Malmesbury shales is also very suggestive of the concretionary origin of the dome, since Professor Harris tells me that this is commonly seen in the case of concretions in the Southern States. The pressure causing the motion is apparently chiefly due to the increasing bulk of the growing concretion.

At Piquetberg, north of Hermon, is what may be a similar dome, but Mr. Dahse had not then exploited it. In the vicinity of Worcester, Cape Province, are a number of lime deposits, but they lack the purity of the Hermon deposit and their origin is doubtless different.

In conclusion, the writer believes that the Hermon deposit represents a dome of calcium carbonate formed by the segregation and crystallization of lime particles from the surrounding and underlying Malmesbury shales, and corresponds in its mode of origin to the sodium chloride domes of Southern Louisiana and Texas, and the conical "salt mountains" of Rhang el Melah, Ain Hadjera and Djebel el Melah in Algeria.

Hastings-on-Hudson, N. Y.

Art. XXXII.—*On the Preparation and Hydrolysis of Esters Derived from the Substituted Aliphatic Alcohols;* by W. A. Drushel and G. R. Bancroft.

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

In 1894 de Hemptinne,* working under the direction of Van't Hoff, determined the velocity constants for the hydrolysis of eleven of the lower aliphatic esters. These included methyl, ethyl, propyl acetates, propionates, butyrates, also ethyl isobutyrate and ethyl valerate. This work of de Hemptinne showed that the unsubstituted alcohol radical has very little influence upon the rate of acid hydrolysis. Later in the same year Löwenherz,† also under Van't Hoff, determined the velocity constants for the acetates of glycerol and phenol. By a comparison of these results with those obtained by de Hemptinne for methyl, ethyl, and propyl acetates, it was shown that although the alcohol radical has little influence in determining the rate of hydrolysis, its chemical nature is of considerable importance.

In 1897 and 1898 Geitel‡ studied the velocities of the hydrolysis of mono-, di-, and triacetates of glycerol when catalyzed with decinormal hydrochloric acid at 25° and found them to be in the ratios of 1 : 2 : 3. In 1907 Julius Meyer§ investigated the reaction velocity of the hydrolysis of ethylene glycol monoacetate and diacetate, working at 25·2° and catalyzing the reaction with N/50 and N/100 hydrochloric acid.

The reaction with the glycol diacetate was found to proceed in two stages, the monoacetate being formed as an intermediate product, and this finally decomposing forms ethylene glycol. The rate of hydrolysis in the first stage was determined to be double that of the second stage. E. Abel‖ and R. Kremann¶ also have studied the acid and alkaline hydrolysis of esters of the polyhydric alcohols. Their results seem to agree with those of Geitel in that they found the rate of hydrolysis in the case of tri-, di-, and monoacetates of glycerol to be in the ratio of 3 : 2 : 1.

In 1910 a study of the effect of constitution on the rate of ester hydrolysis was begun in Kent Chemical Laboratory of Yale University. A series of articles** dealing with the hydrolysis of esters of substituted aliphatic acids has already appeared. In this paper, and others which may follow, the investigation is concerned with the study of the effect of sub-

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* de Hemptinne, Zeitschr. phys. Chem., xiii, 561, 1894.

† Löwenherz, Zeitschr. phys. Chem., xv, 389, 1894.

‡ Geitel, J. pr. Chem. (2). lv, 417–429, 1897. Ibid. (2), lvii, 113–131, 1898.

§ Meyer, Zeitschr. Elektrochem., xiii. 186, 1907.

‖ Abel, Zeitschr. phys. Chem., lvi, 558, 1906.

¶ Kremann, Zeitschr. Electrochem., xiii, 307, 1907.

** Drushel and Hill, this Journal, xxx, 72–78, 1910.

stitution in the alkyl radical of an ester upon the rate of hydrolytic cleavage.

Preparation of Materials.

The *a*-chlor-ethyl acetate was prepared by the method of Simpson,[*] by heating equimolecular quantities of acetyl chloride and water-free acetaldehyde in a sealed tube at 100°. The ester, boiling at 120°–124°, was purified by fractionation. As a further criterion of purity it was analyzed for halogen. Weighed portions of the ester were hydrolyzed with sodium hydroxide on a steam-bath. The formation of aldehyde resin indicated the presence of acetaldehyde. After filtering off and carefully washing the resin, the filtrate was neutralized with nitric acid and the halogen estimated by titrating with decinormal silver nitrate, using potassium chromate as an indicator.

Chlorine found—I. 28·27%, II. 28·62%.
Chlorine calculated—28·94%.

The *a*-chlor-ethyl propionate was prepared by the method of Rubencamp.[†] Equimolecular portions of water-free acetaldehyde and propionyl chloride were heated in a sealed tube at 120°. The ester, boiling at 134°–136°, was purified by fractionation and its halogen content was shown to correspond to theory using the method outlined above for the *a*-chlor-ethyl acetate. Here, as in the preceding case, aldehyde resin was formed in the hydrolysis.

The *a*-ethoxy-ethyl acetate was obtained[‡] by heating equimolecular portions of the diethyl acetal of acetaldehyde and acetic anhydride in a sealed tube at 150°. The reaction product was washed with a solution of potassium carbonate, then separated and dried over freshly fused potassium carbonate. That portion distilling over at 125°–130° was collected as the pure ester. The acetal from the above preparation was prepared by the method of Fischer and Giebe.[§]

As a preliminary to the preparation of the *β* substituted esters the following compounds were prepared in considerable quantity: ethylene dibromide, ethylene glycol diacetate, and ethylene glycol. The ethylene dibromide was prepared by the method of Balard.[‖] The ethylene glycol diacetate was obtained by refluxing a mixture of one mole of ethylene dibromide with two moles of fused anhydrous potassium acetate in the presence of a mole of glacial acetic acid.[¶] A second method[**]

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[*] Simpson, Compt. rend., xlvii, 874, 1858. Ann. d. Chem. u. Pharm., cix, 156, 1859.

[†] Rubencamp, Ann. d. Chem., ccv, 276, 1884.

[‡] Claisen, Ber. d. d. Chem. Gesell., xxxi, 1018, 1898.

[§] Fischer and Giebe, ibid., xxx, 3053. 1897.

[‖] Balard, Ann. d. chim. et d. Phys. (2), xxxii, 375, 1826. Erlenmeyer and Bunte, Ann. d. Chem. u. Pharm., clxviii, 64, 1873.

[¶] Gattermann, Prac. Methods of Org. Chem. 3d ed., p. 196, 1915.

[**] Henry, Ann. d. chim. et d. Phys. (4), xxvii, 250, 1872.

was also used in the preparation of the glycol diacetate. One mole of ethylene dibromide and two moles of freshly fused potassium acetate were refluxed in a solution of eighty-five per cent alcohol on a water bath for eighteen to twenty hours, and filtered to remove the potassium bromide. The filtrate was fractionated to remove the alcohol and the glycol diacetate was collected at 185°–187°.

The ethylene glycol was produced by the hydrolysis of ethylene glycol diacetate according to the method of Haller,[*] the process being carried out as described by Louis Henry,[†] and the yields corresponded to those given by Gattermann.[‡]

β-Hydroxy-ethyl acetate was first prepared by Atkinson[§] by heating on a boiling water bath for two days equimolecular quantities of ethylene dibromide and potassium acetate in a solution of eighty-five per cent ethyl alcohol. De Mole[‖] claimed a considerable yield of the monacetin of ethylene glycol by heating for eighteen hours at the boiling temperature an equimolecular mixture of ethylene dibromide and freshly fused potassium acetate in an eighty to eighty-five per cent solution of ethyl alcohol. Lourenço[¶] obtained this ester by heating equimolecular quantities of ethylene glycol and glacial acetic acid for one day in a sealed tube at 200°.

The above method of Atkinson and De Mole was employed with the hope of obtaining the β-hydroxy-ethyl acetate. Three hundred grams of ethylene dibromide were treated with 155 grams of water-free potassium acetate in 300 grams of 85 per cent ethyl alcohol. This mixture was digested for twenty hours in a flask fitted with a reflux condenser on a boiling water bath. The potassium bromide which precipitated was filtered off, and the filtrate fractionated to remove the alcohol. A yield of 83 grams of diacetate was obtained, but no monacetin was formed, as no reaction took place on treatment of a portion with acetyl chloride.

On treating 300 grams of ethylene dibromide with 310 grams of anhydrous potassium acetate in 300 grams of 85 per cent ethyl alcohol, digesting for twenty-four hours, filtering, and fractionating the filtrate, a yield of 174 grams of glycol diacetate was obtained. This result is in accordance with the experience of Louis Henry,[**] who states that the diacetate is obtained by treating ethylene dibromide with fused potassium acetate, as described above. This method was tried repeatedly,

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[*] Haller, Compt. rend., cxliii, 657, 1906.

[†] Henry, Bull. Acad. Roy. Belg. cl. sci. (3), xxxii, 402–417, 1896.

[‡] Gattermann, Prac. Methods of Org. Chem. 3d ed., pp. 197–198, 1915.

[§] Atkinson, Ann. d. Chem. u. Pharm., cix, 232, 1859.

[‖] De Mole, Ber. d. d. Chem. Gesell., vii, 641, 1874. Ann. d. Chem. u. Pharm. clxxiii, 117, 1874; clxxvii, 147, 1875.

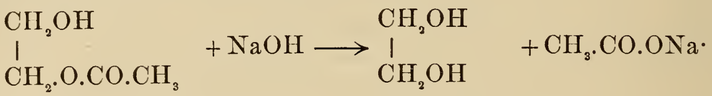
[¶] Lourenço, Compt. rend., l, 91, 1860 Ann. d. Chem. u. Pharm., cxiv, 122, 1860.

[**] Henry, Ann. d. chim. et d. Phys. (4), xxvii, 250, 1872. Rec. d. trav. chim. d. Pays-Bas, xx, 243–254, 1901. Bull. Acad. Roy. Belg. cl. sci. (3), xxxvii, 236–248, 1901.

always with the same result, and the product was used in the preparation of ethylene glycol. Also on saturating a portion of the product with dry hydrobromic acid gas the β-brom-ethyl acetate was formed.

Finally, a direct esterification method was devised for the preparation of the β-hydroxy ethyl acetate, which is really a modification of that given by Lourenço,* to which reference has already been made. Equimolecular portions of ethylene glycol and glacial acetic acid were digested over twice the theoretical quantity of anhydrous copper sulphate in a flask over a free flame for eight hours. In order to keep track of the esterification, one cubic centimeter of the reaction mixture was pipetted into a graduated flask before heating and the volume made up to 250^{cm^3}. Aliquot portions of fifty cubic centimeters were withdrawn and titrated with decinormal sodium hydroxide. Other portions of the reaction mixture were withdrawn from time to time and treated as described above. At the end of eight hours the titration showed that the esterification was practically complete. The esterified mixture was cooled and decanted, and the copper sulphate residue was extracted with ether. The mixture was then fractionally distilled, the main portion coming over at 185°–190°, and on refractionating boiled at 187°–189°. This portion reacted vigorously with acetyl chloride, effervescing briskly with evolution of hydrochloric acid gas.

Weighed portions of this ester were placed in flasks and saponified with an excess of decinormal sodium hydroxide, according to the following equation :



$$\begin{array}{l} CH_2OH \\ | \\ CH_2.O.CO.CH_3 \end{array} + NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + CH_3.CO.ONa\cdot$$

The excess of sodium hydroxide was then titrated with decinormal hydrochloric acid using phenolphthalein as an indicator. From results obtained the ester was shown to be 99·38 per cent pure.

The use of anhydrous copper sulphate as a dehydrating agent† in the esterification of certain hydroxy-acids has been previously described in the literature. In the present investigation this dehydrating agent is used for the first time in the esterification of polyhydric alcohols.

Another point worthy of mention in connection with the preparation of this compound is the low boiling point given by the various investigators. Atkinson gives 182°, De Mole 180°–182°, and Lourenço 180°, as the boiling point of their

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* Loc. cit.

† Bogojawlensky and Narbut, Ber. d. d. Chem. Gesell., xxxviii, 3344, 1895. Clemmenson and Heitman, Amer. Chem. J., xlii, 319, 1909. Dean, this Journal, xxxvii, 332, 1914. Drushel, ibid., xxxix, 114–117, 1915.

respective products. Glycol diacetate boils at 186°–187° and ethylene glycol at 197°. From the molecular constitution of the monacetin of ethylene glycol we would naturally expect its boiling point to lie between those of ethylene glycol and glycol diacetate. The boiling point of the main portion of the product obtained by direct esterification was distinctly higher than that given in the literature, and lies between that of the glycol and of the diacetate.

The β-methoxy-ethyl acetate was prepared by treating the β-methoxy-ethyl alcohol with the theoretical quantity of acetyl chloride. The ester, boiling at 144°–145°, was purified by fractional distillation. This ester has been previously prepared* by treating the corresponding alcohol with acetic anhydride.

The β-methoxy-ethyl alcohol was obtained for the preparation of the β-methoxy-ethyl acetate by preparing monosodium glycollate, and treating it with the theoretical quantity of methyl iodide under suitable conditions according to the method of Palomaa.† A separation of the glycol-ether, boiling at 124°–126°, was effected by fractionation.

The β-ethoxy-ethyl acetate was prepared by treating β-ethoxy-ethyl alcohol with acetyl chloride. The excess of acetyl chloride was removed by fractional distillation, and the ester was found to boil at 157°–158°. The alcohol used in this preparation was obtained by the method of Palomaa. The monosodium glycollate was treated with ethyl iodide as described in this method. Upon fractionation the alcohol distilled over at 134°–135°, and possessed the properties given by Palomaa‡ and De Mole.§

The β-ethoxy-ethyl alcohol was also obtained by a second method which is not recorded in the literature, and appears here for the first time. In attempting to prepare β-ethoxy-ethyl acetate by refluxing equimolecular quantities of β-brom-ethyl acetate and sodium ethylate, it was found that β-ethoxy-ethyl alcohol was obtained. The materials were refluxed in a water-free alcoholic solution for half an hour on a water bath. On filtering from sodium bromide and fractionating the reaction mixture, a product was obtained which had all the physical characters of the β-ethoxy-ethyl alcohol. It also reacted with acetyl chloride giving the β-ethoxy-ethyl acetate.

The β-chlor-ethyl acetate was prepared by treating ethylene chlorhydrin with acetyl chloride‖ in slight excess of the theoretical amount. The pure ester, boiling at 143°–145°, was obtained by fractionation. The β-ethylene chlorhydrin for the preparation of this ester was obtained according to the method

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*Palomaa, Ber. d. d. Chem. Gesell., xxxv, 3300, 1902.

†Palomaa, ibid., xlii, 3873, 1909.

‡Palomaa, ibid., xlii, 3876, 1909.

§De Mole, ibid., ix, 745, 1876.

‖Henry, Ber. d. d. Chem. Gesell., vii, 70, 1874.

of Ladenburg.[*] This ester was analyzed for halogen as a further test of the purity of the substance.

Chlorine found, I. 28·40%, II. 28·18%, III. 28·34%.
Chlorine calculated, 28·94%.

The β-brom-ethyl acetate was obtained by the method of Louis Henry,[†] which is essentially the same as that described by De Mole,[‡] who treated his monacetin of ethylene glycol with hydrobromic acid to obtain this ester. Ethylene glycol diacetate was saturated with dry hydrobromic acid gas, and the resulting product was fractionated. The boiling-point and specific gravity of the purified ester corresponded to the values given in the literature. The halogen content of the ester was also determined by analysis.

Bromide found, I. 47·50%, II. 47·56%, III. 47·50%.
Bromine calculated, 47·86%.

Hydrolysis of Esters.

Esters Derived from Alpha Substituted Ethyl Alcohols.

The following esters of this class were studed:

α-chlor-ethyl acetate, $CH_3.CHCl.O.CO.CH_3$.
α-ethoxy-ethyl acetate, $CH_3.CH(OC_2H_5).O.CO.CH_3$.
α-chlor-ethyl propionate, $CH_3.CHCl.O.CO.CH_2.CH_3$.

These esters are found to be unstable compounds, which are decomposed immediately upon dissolving in decinormal hydrochloric acid. This was shown by dissolving 2·5 cm^3 of the α-chlor-ethyl acetate in 250 cm^3 of the standard decinormal hydrochloric acid. On titrating 25 cm^3 of this reaction mixture with decinormal sodium hydroxide, the initial titration required considerably over 45 cm^3, and the titration made after allowing the reaction mixture to remain in the thermostat for ten days showed an increase of only one to two cubic centimeters. This increase was accounted for by the more complete splitting out of halogen, which was shown by titrating with silver nitrate.

In the case of the α-chlor-ethyl acetate the hydrolysis products were acetaldehyde, acetic acid and hydrochloric acid, while the α-chlor-ethyl propionate gave acetaldehyde, propionic acid, and hydrochloric acid. The α-ethoxy-ethyl acetate gave a similar result yielding acetaldehyde, ethyl alcohol and acetic acid. The presence of the aldehyde was shown in each case by treating a portion of Schiff's reagent with a few drops of the solution of the hydrolyzed ester, which at once imparted a deep reddish violet color to the solution.

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[*] Ladenburg, ibid., xvi, 1407–1408, 1883. Jahresb. 1883, 591.

[†] Henry, Rec. d. trav. chim. d. Pays-Bas, xxi, 243–254, 1901. Bull. Acad. Roy. Belg. cl. sci. (3), xxxvii, 236–248, 1901.

[‡] De Mole, Ann. d. Chem., clxxii, 121, 1874.

In alkaline solution the reaction was similar to that described above, and the presence of the aldehyde was shown by warming the solution of hydrolysis products on the steam bath, when there was formed the characteristic aldehyde resin of acetaldehyde.

Esters Derived from Beta Substituted Ethyl Alcohols.

The following esters of this class were studied:

β-hydroxy-ethyl acetate, $CH_2(OH)CH_2.O.CO.CH_3$,
β-methoxy-ethyl acetate, $CH_2(OCH_3).CH_2.O.CO.CH_3$,
β-ethoxy-ethyl acetate, $CH_2(OC_2H_5).CH_2.O\ CO.CH_3$
β-chlor-ethyl acetate, $CH_2Cl.CH_2.O.CO.CH_3$,
β-brom-ethyl acetate, $CH_2Br.CH_2.O.CO.CH_3$.

These esters were hydrolyzed in decinormal hydrochloric acid at 25°, 35°, and 45°, and measurements made from which the velocity constants were calculated. The hydrochloric acid used as a catalyzing agent was standardized by precipitation with silver nitrate. The titrations were made with decinormal sodium hydroxide, free from carbon dioxide, using phenolphthalein as an indicator.

The hydroxy-, methoxy-, and ethoxy-ethyl acetates were found to be very soluble in water. The introduction of halogen in the β-position of the ethyl radical of the alcohol gives to the derived ester a much greater insolubility. Only eight cubic centimeters of the β-brom-ethyl acetate could be dissolved in a liter of water. The β-chlor-ethyl acetate was found to be slightly more soluble.

In the case of the hydroxy-, methoxy-, and ethoxy-ethyl acetates 2·5 cm^3 of each ester were dissolved in 250 cm^3 decinormal hydrochloric acid, previously warmed in the thermostat to the required temperature. As soon as the ester was completely dissolved a 25 cm^3 portion of the reaction mixture was withdrawn by means of a pipette, and run into about one hundred cubic centimeters of cold distilled water in a 300 cm^3 flask. The pipette was allowed to drain thirty seconds and the time was then recorded, and the solution titrated at once with decinormal sodium hydroxide. Subsequent titrations were made at suitable time intervals, and the final measurements were taken when a sufficient time had elapsed to insure that the hydrolytic action was complete. To insure uniformity in experimental conditions a sample of ethyl acetate was hydrolyzed at the same time as the esters of this group, and the hydrolysis of each ester was made in duplicate.

On account of the greater insolubility of the beta halogen substituted esters only two cubic centimeters of each ester were dissolved in 250 cm^3 of decinormal hydrochloric acid. Measurements of the velocity of the hydrolysis of these esters were made as just described. In order to ascertain if any halogen was liberated in the form of free halogen acids derived from the esters, or the halogen substituted alcohols resulting from the hydrolysis of the esters, titrations were made with decinormal silver nitrate at the time when the equilibrium was reached in the titration of the acid with decinormal sodium hydroxide.

At 25° and 35° there was no splitting out of halogen in the case of the β-chlor-ethyl acetate, and none from the β-brom-ester at 25°. At 35° and 45°, however, the β-brom-ethyl acetate was found to decompose slightly in this way, and at 45° a slight decomposition was indicated in the case of the β-chlor-ethyl acetate, which was so small as to be negligible. The necessary correction for the formation of halogen acid was applied to the titrations made at 35° and 45° in the hydrolysis of the β-brom-ethyl acetate, where as much as 4 per cent to 4·5 per cent of the halogen was found to be set free as halogen acid.

From the titrations made as described above the velocity constants recorded in Table I were calculated by using the titration formula for monomolecular reactions:

$$K = \frac{2{\cdot}3}{t}\Big[\log(T_\infty - T_0) - \log(T_\infty - T_n)\Big],$$

where T_0 is the initial titration, T_∞ the final titration, and T_n an intermediate titration all expressed in cubic centimeters of decinormal sodium hydroxide, and t represents the time interval in minutes between the initial titration T_0 and that represented by T_n.

On referring to Table II it is seen that the substitution of chlorine, of hydroxyl, and of ethoxyl groups in the beta position produces practically the same retardation of the rate of hydrolysis in each case. The substitution of bromine in the beta position produces a retardation of the hydrolysis which is considerably less than that produced by the chlorine substitution. The ethoxyl group produces a slightly greater retardation than the methoxyl group.

The temperature coefficients are found to vary from 2·2 to 2·5 for an increase of ten degrees. The substitution of bromine in the beta position has a lowering effect upon the temperature coefficient. In the case of other esters of this series the coefficients were found to be practically constant, having the values of 2·5 for the range from 25°–35° and 2·3 to 2·4 for the increase from 35°–45°.

Summary.

1. The β-hydroxy-ethyl acetate may be prepared by refluxing equimolecular quantities of ethylene glycol and glacial acetic acid for eight hours over twice the theoretical quantity of anhydrous copper sulphate.

2. By heating equimolecular quantities of ethylene dibromide and freshly fused potassium acetate on a water bath for

TABLE I.

Hydrolysis at 25° in decinormal hydrochloric acid.

Ester	β-hydroxy-ethyl acetate	β-methoxy-ethyl acetate	β-ethoxy-ethyl acetate	β-chlor-ethyl acetate	β-brom-ethyl acetate
Time	2830	----	3300	2943	2835
$K \times 10^5$	46·2		46·8	47·4	53·3
	47·4		47·1	46·5	54·2
	47·1		46·6	46·3	54·0
	46·9		46·2	46·0	55·4
	47·3		46·1	46·0	55·8
	47·2		46·5	47·4	56·0
	47·6		45·5	46·1	56·9
Averages	47·1		46·4	46·5	55·1
Averages (duplicate)	47·2		46·6	47·2	56·5
Hydrolysis at 35° in decinormal hydrochloric acid.					
Time	660	840	870	660	660
$K \times 10^5$	(111·8)	122·8	117·8	115·5	
	115·6	121·2	117·3	117·5	(109·3)
	117·8	119·6	117·0	118·4	124·2
	117·6	122·3	118·2	118·2	132·2
	117·9	122·6	117·2	117·4	135·5
	117·2	123·4	117·5	117·6	139·7
	118·6	123·7	118·5	118·6	140·7
Averages	117·4	122·2	117·6	117·6	134·5
Averages (duplicate)	117·2	122·8	117·7	117·6	134·8
Hydrolysis at 45° in decinormal hydrochloric acid.					
Time	210	212	213	210	210
$K \times 10^5$	(252)	(259)	(277)	(252)	
	280	281	279	271	(226)
	278	281	279	272	288
	278	280	278	273	297
	278	283	279	278	298
	279	283	280	277	306
	280	282	280	278	300
Averages	279	282	279	275	298
Averages (duplicate)	279	281	280	275	297

TABLE II—SUMMARY.

Temperature	K × 10^5 25°	K × 10^5 35°	K × 10^5 45°	Temp. Coeff. 25°-35°	Temp. Coeff. 35°-45°
Ethyl acetate	64·7	162·1	379·	2·5	2·3
	64·8	161·9	376·		
β-hydroxy-ethyl acetate	47·1	117·4	279·	2·5	2·4
	47·2	117·2	279·		
β-methoxy-ethyl acetate	--	122·2	282·	--	2·3
	--	122·8	281·		
β-ethoxy-ethyl acetate	46·6	117·6	279·	2·5	2·4
	46·4	117·7	280·		
β-chlor-ethyl acetate	55·1	134·5	298·	2·4	2·2
	56·5	134·8	298·		

eighteen hours, the product obtained is glycol diacetate and not the β-hydroxy-ethyl acetate.

3. β-ethoxy-ethyl alcohol is formed by digesting equimolecular quantities of β-brom-ethyl acetate and sodium ethylate for half an hour in alcoholic solution.

4. The substitution of halogen or an alkoxyl group in the alpha position of the alkyl radical of an ester accelerates the decomposition of the ester to such an extent that the reaction velocity is not measurable. In the case of all three esters of this type that were hydrolyzed acetaldehyde formed one of the hydrolysis products.

5. The substitution of hydroxyl, alkoxyl, or halogen in the beta position of the alkyl radical produces a considerable retardation on the rate of hydrolysis. In the case of the esters derived from the beta substituted ethyl alcohols it was found that the hydroxyl and ethoxyl groups and chlorine produce practically the same degree of retardation.

6. The ethoxyl group produces a slightly greater retardation than the methoxyl group.

7. The introduction of halogen in the beta position of the alkyl radical produces a retardation of the rate of hydrolysis. In the case of the β-brom-ethyl acetate this retardation is less than in the case of the β-chlor-ethyl acetate.

8. The temperature coefficients in the case of the esters derived from the beta substituted alcohols are found to vary from 2·2 to 2·5 for an increase of ten degrees. The substitution of bromine in the beta position has a lowering effect upon the temperature coefficient.

Art. XXXIII.—*The Perchlorate Method for the Determination of the Alkali Metals;* by F. A. Gooch and G. R. Blake.

[Contribution from the Kent Chemical Laboratory of Yale Univ.—ccxciv.]

In the work of which an account is here given, the object at the outset was the examination of the perchlorate precipitation of rubidium and cæsium, as proposed by Montemartini and Matucci,[*] for the estimation of those elements; but the recent paper of Baxter and Kobayashi, which appeared while this work was in progress, upon the perchlorate determination of potassium, suggested the desirability of including that element also within the scope of the investigation. In the work of Baxter and Kobayashi[†] careful attention is paid to the relations of solubility of potassium perchlorate in the washing media, the use of alcohol containing about 0·1 per cent of perchloric acid (as first proposed by Wense[‡]) and saturated with potassium perchlorate (as suggested by Davis and advocated by Thin and Cumming[§]) is adopted, and further recommendations are made that the washing alcohol be of absolute strength and of a temperature as near as possible to 0°. The authors state that there is no danger of the deposition of potassium perchlorate from the saturated alcoholic solution owing to upward change of temperature during the manipulation and make record of the observation that the addition of a large amount of sodium perchlorate failed to induce the precipitation of potassium perchlorate from the solution saturated with the latter salt. It is obvious, however, that if a condition of supersaturation in respect to potassium perchlorate were brought about by the addition of sodium perchlorate to the solution, the contact of the supersaturated solution with potassium perchlorate already precipitated might induce a further precipitation of that salt from the washing liquid; and this is a point of much importance in the application of the perchlorate method to the determination of rubidium and cæsium. We have therefore tested the matter by adding sodium perchlorate to a saturated solution of potassium perchlorate in alchohol (97 per cent), made and used at the working temperature of the laboratory, shaking the solution in contact with a weighed amount of solid potassium perchlorate, filtering and weighing upon asbestos the insoluble precipitate. In the first two experiments solid sodium perchlorate was dissolved in the saturated alcholic solution of potassium perchlorate to which a weighed amount of solid potassium perchlorate had been added. In the last two experiments the sodium

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[*] Gaz. Chem., xxxiii, 189, 1903.
[†] Jour. Am. Chem. Soc., xxxix, 249, 1917.
[‡] Zeitschr. anal. Chem., v, 691, 1891.
[§] Jour. Chem. Soc., cvii, 361, 1915.

perchlorate was dissolved to a clear solution in the alcohol previously saturated with potassium perchlorate and to this liquid mixture the weighed amount of solid potassium perchlorate was added. The mixture in each case was thoroughly shaken and filtered upon asbestos in the perforated crucible. The precipitate, transferred by the use of the filtrate and gathered in thin compact layer upon the asbestos felt, was washed with a small amount of alcohol (about 5 cm^3) applied in portions successively with intermediate drainings. The results, given in Table I, show that when a saturated solution of potassium perchlorate in alcohol is used as the washing liquid for precipitated potassium perchlorate in presence of sodium perchlorate, there is the possibility that the precipitate may be augmented by potassium perchlorate derived from the washing liquid.

TABLE I.

Treatment of the Saturated Solution of Potassium Perchlorate in Alcohol.

$KClO_4$ taken grm.	$KClO_4$ found grm.	Excess of $KClO_4$ found grm.	Volume of saturated alcohol cm^3
0·1025	0·1050	0·0025	50
0·1020	6·1036	0·0016	50
0·1029	0·1048	0·0019	50
0·1012	0·1033	0·0021	50

As regards the solubility of potassium perchlorate in alcohol carrying a small amount of perchloric acid, as recommended by Wense,* it is evident that the solvent effect may be modified, without the use of a medium saturated with the salt to be precipitated, by restricting the amount of liquid used in the digestion, transfer, and washing the precipitate. We have, therefore, tried the expedients (1) of keeping the volume of liquid low and (2) of again using the first filtrate after the digestion for transferring the precipitate to the filtering crucible, completing the washing of the crystalline precipitate with a very small amount of the washing liquid applied in successive portions. The effects of these procedures, in the perchlorate determination of potassium, rubidium, and cæsium, are shown in the following account of the experimental work.

In all the tests, the carefully prepared alkali chlorides were weighed in small beakers, dissolved in water, and treated with pure perchloric acid which distilled without residue. The liquid was evaporated to the fuming point of perchloric acid. For the smaller amounts (0·1 grm.) of material a single evaporation proved to be effective in converting the chlorides to perchlorates. In the case of the larger amounts the residues

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* Loc. cit.

were redissolved in a little water and then subjected to one or two similar treatments with perchloric acid. The residues were digested with the alcoholic washing liquid (97 per cent alcohol, containing about 0·1 per cent of perchloric acid), transferred to an asbestos filter in the perforated crucible, washed, dried at about 130°, and weighed. In some cases the precipitate was redissolved and again treated after decantation of the solution before repeating the treatment with perchloric acid and transferring the precipitate to the filter. These details of treatment are indicated.

TABLE II.

The Determination of Potassium as the Perchlorate.

KCl taken grm.	NaCl taken grm.	$KClO_4$ found grm.	Theory for $KClO_4$ grm.	Error grm.	$HClO_4$ 70% cm^3	Filtrate (Approx.) cm^3
A The transfer made with the washing solution.						
* 0·1007	....	0·1862	0·1871	−0·0009	0·1	60
* 0·1009	....	0·1870	0·1875	−0·0005	0·1	60
* 0·1014	....	0·1876	0·1884	−0·0008	0·1	60
* 0·1005	....	0·1862	0·1867	−0·0005	0·1	60
B The transfer effected with the use of the filtrate.						
† 0·1000	....	0·1866	0·1858	+0·0008	3×0·1	20+5
† 0·1020	....	0·1894	0·1895	+0·0001	3×0·1	20+5
‡ 0·1005	0·1	0·1872	0·1868	+0·0004	0·1	20+5
§ 0·1033	0·1	0·1924	0·1920	+0·0004	0·1	20+5
§ 0·1016	0·1	0·1894	0·1889	+0·0005	0·1	20+5
‖ 0·3015	0·1	0·5622	0·5602	+0·0020	3×0·1	20+5
‖ 0·3012	0·1	0·5622	0·5596	+0·0026	3×0·1	20+5
¶ 0·3021	0·1	0·5615	0·5613	+0·0002	3×0·1	10+10+5
¶ 0·3002	0.1	0·5571	0·5578	−0·0007	3×0·1	10+10+5
¶ 0·3013	0·5	0·5613	0·5598	+0·0015	3×0·1	10+10+5
¶ 0·3008	0·5	0·5603	0·5589	+0·0014	3×0·1	10+10+5

* One evaporation in glass.

† Three treatments and evaporations in glass, following solution in each case in the least amount of water.

‡ One treatment in platinum.

§ One treatment in quartz.

‖ Three treatments and evaporations in platinum without decantation, following solution in each case in the least amount of water.

¶ Three treatments and evaporations in platinum; digestion of the residue with 10 cm^3 of washing solution, decantation, solution, evaporation, digestion and transfer with 10 cm^3 of washing liquid.

Table II contains results of experiments with potassium chloride. Those of section A represent results obtained by keeping the washing liquid within moderate limits. In section B are the results obtained by using the first filtrate instead of the washing liquid to effect the transfer of the precipitate to the filter.

The results and details of similar experiments with pure rubidium and cæsium chlorides are given in Tables III and IV and with mixtures of potassium, rubidium, and cæsium chlorides in Table V.

Table III.

The Determination of Rubidium as the Perchlorate.

RbCl taken grm.	$RbClO_4$ found grm.	Theory for $RbClO_4$ grm.	Error grm.	$HClO_4$ (70%) cm^3	Filtrate (Approx.) cm^3	
A						
The transfer made with the washing solution after digesting fifteen to twenty minutes.						
0·1000	0·1527	0·1529	—0·0002	0·1	60	One evaporation in glass.
0·1000	0·1528	0·1529	—0·0001	0·1	60	
0·1000	0·1529	0·1529	—0·0000	0·1	60	
0·1000	0·1527	0·1529	—0·0002	0·1	20+20	One evaporation; two decantations.
0·1000	0·1531	0·1529	+0·0002	0·1	20+20	
0·1000	0·1531	0·1529	+0·0002	5	60	One evaporation in glass.
0·1000	0·1530	0·1529	+0·0001	5	60	
0·1000	0·1526	0·1529	—0.0003	5	60	
B						
The transfer made with the washing liquid without standing to digest.						
0·1000	0·1526	0·1529	—0·0003*	5	60	One evaporation with large amount of perchloric acid.
0·1000	0·1525	0·1529	—0·0004*	5	60	
0·1000	0·1524	0·1529	—0·0005*	5	60	
0·1000	0·1521	0.1529	—0·0008*	5	60	
0·1000	0·1508	0·1529	—0·0021*	5	60	
C						
The transfer effected, after digestion, with the use of the filtrate.						
0·1000	0·1534	0·1529	+0·0004	3×0·1	20+5	Three evaporations in platinum.
0·1000	0·1526	0·1529	—0·0003	3×0·1	20+5	

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* These results are low in spite of possible contamination by silica. See Table V, A.

TABLE IV.

The Determination of Cæsium as the Perchlorate.

CsCl taken grm.	$CsClO_4$ found grm.	Theory for $CsClO_4$ grm.	Error grm.	$HClO_4$ (70%) cm^3	Filtrate (Approx.) cm^3	
A The transfer made with the washing solution.						
0·1000	0·1365	0·1380	−0·0015	0·1	60	One evaporation in glass.
0·1000	0·1368	0·1380	−0·0012	0·1	60	
0·1000	0·1378	0·1380	−0·0002	0·2	45	
0·1000	0·1372	0·1380	−0·0008	0·2	45	
0·1000	0·1376	0·1380	−0·0004	0·2	20	
B The transfer made with the use of the filtrate.						
0·1000	0·1376	0·1380	−0·0004	0·1	20+5	One evaporation in glass.
0·1000	0·1378	0·1380	−0·0002	0·1	20+5	
0·1000	0·1378	0·1380	−0·0002	0·1	20+5	
0·1000	0·1377	0·1380	−0·0003	0·1	20+5	
0·1000	0·1379	0·1380	−0·0001	3×0·1	20+5	Three evaporations in platinum.
0·1023	0·1411	0·1412	−0·0001	3×0·1	20+5	

TABLE V.

KCl taken grm.	RbCl taken grm.	CsCl taken grm.	Perchlorate found grm.	Theory for perchlorates grm.	Error grm.	$HClO_4$ (70%) cm^3	Filtrate cm^3
A One evaporation in glass; transfer with the use of filtrate.							
0·1004	0·1000	0·1004	0·4633*	0·4781	−0·0148*	0·3	20+20
0·1011	0·1000	0·1005	0·4605*	0·4795	−0·0190*	0·3	20+20
0·1014	0·1000	0·0807	0·4562†	0·4527	+0·0035†	5	20+20
0·1019	0·1000	0·0843	0·4586†	0·4558	+0·0072†	5	20+20

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* After dissolving in water and again evaporating with 0·3 cm^3 of the perchloric acid the recovered residues showed error of +0·0006 grm. and +0·0012 grm. respectively—showing the imperfect conversion of large amounts of chloride in a single evaporation with a moderate amount of perchloric acid.

† These residues, obtained by evaporating with a large amount of perchloric acid in glass, contained silica. After dissolving, filtering, and reprecipitating the errors were reduced to +0·0009 grm. and +0·0015 grm. respectively.

TABLE V (continued).

KCl taken grm.	RbCl taken grm.	CsCl taken grm.	Perchlorate found grm.	Theory for perchlorates grm.	Error grm.	$HClO_4$ (70%) cm^3	Filtrate cm^3
B							
Three evaporations with intermediate solution, in platinum: transfer by means of the filtrate.							
0·1038	0·1000	0·1025	0·4873*	0·4873	0·0000*	3×0·4	20+5
0·1010	0·1000	0·1018	0·4817*	0·4811	+0·0006*	3×0·4	20+5

The results of the experiments recorded go to show (1) that the use of an alcoholic liquid saturated with the substance to be precipitated is unnecessary to the attainment of good analytical results; (2) that it is practicable to so restrict the volume of the washing liquid (97 per cent alcohol containing 0·1 per cent of perchloric acid) that the solubility of the precipitated perchlorates is insignificant for practical purposes; (3) that a single evaporation with a moderate excess of perchloric acid (0·1 cm^3 for every 0·1 grm. of salt) is not sufficient to convert considerable masses of alkali chlorides (e. g., 0·3 grm.) completely to perchlorate, and that in such a case the residue of the first evaporation with perchloric acid should be dissolved in the least amount of water, another portion of perchloric acid added, and the evaporation repeated; (4) that in separations of the larger amounts of insoluble perchlorates (0·3 grm.) from sodium perchlorate the residue left after digestion of the nearly dry mass of perchlorates in the washing liquid and decantation should be dissolved in a small amount of water and the process of evaporation and extraction repeated; (5) that, in the case of rubidium at any rate, digestion of the residue for fifteen or twenty minutes with the washing liquid before effecting the transfer is advantageous.

It is to be noted that the evaporation of large amounts of perchloric acid in glass may result in a considerable action upon the glass and it has been found that perchloric acid which has stood a long time in glass may yield an appreciable residue on evaporation.

* Upon dissolving these residues, again precipitating, and weighing, errors found were −0·0004 grm. and +0·0004 grm. respectively.

Art. XXXIV.—*Protichnites and Climactichnites; A Critical Study of Some Cambrian Trails;** by Lancaster D. Burling.

Judging the nature of the maker of a trail by peculiarities in its composition may be difficult and the solution false—for example, the writer has watched the larvae of the common may-fly crawling along the mud on the tidal flats of the St. Lawrence and leaving a perfectly smooth sinuous trail or groove which would naturally be associated in the mind of almost anyone with the work of a worm, certainly nothing with the legs of a may-fly larva. That the Upper Cambrian sea was peopled by animals of large size is well known, but the trails upon which this inference is based have so far failed to indicate the true nature of their makers. Indeed they have been the subject of frequent and widely variant conjecture. A critical study of some of the trails in the Cambrian has yielded conclusions so substantial or so different from those in the literature that they appear to be worthy of record.

Protichnites.

The trails to which this name has been applied were referred to the agency of a tortoise by Owen[1],† who later[2] assigned them to the work of a crustacean like *Limulus*. In this view he was followed by Dawson[3] and Dana.[4] Dawson later[5] assigns them indubitably to the work of crustaceans, but lessens the weight of this reference by suggesting that *Climactichnites* may have been made by the same animal. With the exception of Chapman,[6] who suggests that both *Protichnites* and *Climactichnites* are of fucoidal origin, succeeding authors, beginning with Billings in 1870,[7] have referred them to the work of trilobites. Packard[8] thinks they could "perhaps have been made by the extremities of the feet of a small shrimp-like creature." Later[9] he questions the ability of *Paradoxides* to make the trail, a question first raised by Dawson.[10] Walcott[11] unhesitatingly states that they "were made by trilobites of the genus *Dicellocephalus*."

Let us look at the trails themselves and see whether or not their critical study may not yield results of tangible value in the identification of their makers. *Protichnites* (see fig. 1) is characterized by two rows of footprints paralleling a median groove. They have been found on Upper Cambrian sandstones in Ontario and New York. The trails give us several clues as to the animal which made them, and these facts

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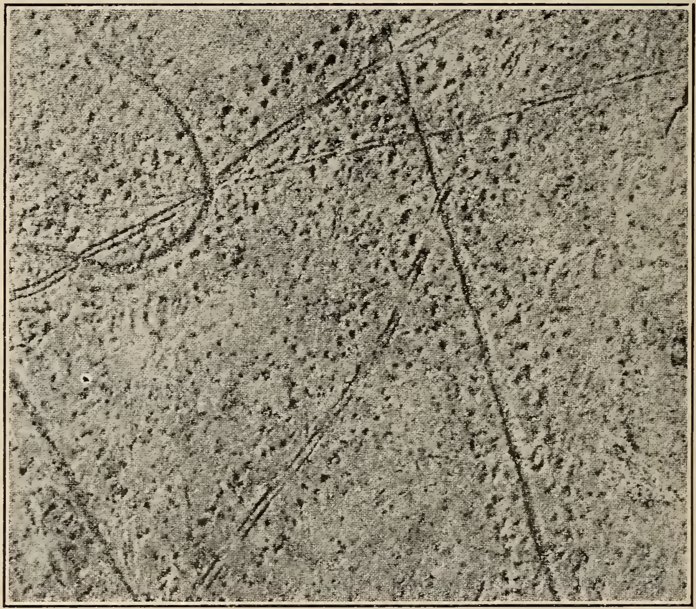
* Published by permission of the Deputy Minister of Mines.
† For references, see the literature at end of article.

and the inferences they support follow, using the same notation in each case.

Facts: (*a*) the side tracks are frequently three-toed;[12] (*b*) these trifid tracks usually toe in; (*c*) the side tracks are usually 2 or 3 inches apart[13] though trails up to 5 or 6 inches across have been observed; (*d*) the trails are not straight, and a single trail has been observed to reverse its direction entirely so that the animal moved off in a direction parallel to but opposite to that of its previous track, all in a distance of less than three times the width of its track, the sharpest curve observed having a radius but little more than half the width of its track; (*e*) some of the median grooves are double and very sharply incised, others on the same slab betray no doubling, yet the width of the single groove closely approximates the distance between the double tracks; (*f*) the median groove does not swing to the side when the trail makes a turn, even on the sharpest curves the median groove lies midway between the

Fig. 1.



Upper Cambrian Trails.

Fig. 1. *Protichnites logananus* Marsh × 1/6. (After Walcott.) Ausable Chasm, N. Y. U. S. Nat. Mus.

side leg tracks; (*g*) in one trail the median groove is only impressed at intervals, but these are regular and occur 26 times in a horizontal distance equal to 25 times the width between the tracks; (*h*) where the trail crosses a ripple marked surface all traces of ripple mark are obliterated for a distance a little wider than the extreme width of the trail, and the feet tracks are large and coarse with the median groove deeply incised; (*i*) on a surface adjacent to that showing *g* occurs a trail simulating *Protichnites*, but without the median groove and with the feet tracks small and sharply impressed; (*j*) the side rows of leg tracks are not arranged along a single straight line, but appear to be more or less double; (*k*) where the median groove is deep the side tracks are proportionately deep; (*l*) where the median groove is only marked at intervals, as in *g*, the impressions of the legs betray a tendency to be arranged in slightly curved lines concave toward the center, with the crests about as far apart as the intervals dividing the impressions of the median groove and more or less opposite to these impressions; (*m*) the number of leg impressions was counted in two places on the trail mentioned in *g*; in one where a group of 9 median groove impressions was available 65 leg impressions occurred on one side, 63 on the other; in another group of 6 the number of leg impressions was respectively 38 and 40; each of these groups was crossed by another trail, and the number of legs may be greater on this account.

Inferences: (*a*) Some of the appendages used by the animal in walking were three-toed; (*b*) the animal toed in, and toeing in is usually characteristic of heavy low-lying bodies whose feet touch the ground well toward if not beyond the sides of the body; (*c*) if the inference in *b* is correct, the animal was neither wider nor narrower than the track and individuals ranged in size from 2 to 6 inches in width; (*d*) its body was either extremely flexible or else short and more or less circular in outline; (*e*) the animal usually (see *i*) did not carry the entire weight of its body on its legs, but allowed a median portion to rest on the bottom and this portion was apparently forked in some, club-shaped in others—perhaps a sexual difference; (*f*) the part of the body which rested on the bottom was not the telson of a *Limulus*-like crustacean or trilobite, but was a process situated somewhere between or very close to the legs; (*g*) the animal was able to bear almost its whole weight (all, if *i* was made by the same animal) on its legs, but where its median portion did just graze the ground it did so once for every time it moved forward through a distance equal to its own width; this corroborates *d* in indicating the general correctness of making the animal round or oval in outline; (*h*) the animal was heavy, and its legs were comparatively short and sank deeply into the bottom; (*i*) the ends of the legs were more or less pointed and could only support the entire animal when walking on a hard bottom (*i* may have been made by a different animal); (*j*) the legs were not all of the same length; (*k*) the question of whether the median portion touched the bottom or not was apparently one of whether or not the bottom was soft enough to allow the legs to sink in, though it must be recorded that the trail described in *i* is 6 inches or more across and may have been made by a very large and perhaps strong form; (*l*) the front and back legs were respectively shorter than those in the centre; (*m*) in making this trail, *g*, the animal was apparently skipping along with the body supported in the water, and the impressions of the feet are probably not confused. If this inference is correct, and remembering that the trails are crossed by others, the number of pairs of legs was in all probability 6, though it averages nearly 7.

CLIMACTICHNITES.

Logan, the first describer of these trails, believed them[14] to be the work of molluscs, a suggestion which received support as late as 1903 when Woodworth[15] published the first illustration of the peculiar oval bodies which have been found at one end of the trails at Mooers, New York. Walcott[16] has recently figured a similar oval body from the Upper Cambrian at New Lisbon, Wisconsin. He refers them to the work of annelids, a reference which was anticipated by Gratacap in 1901.[17] Curiously enough several of the earlier writers believed *Climactichnites* and *Protichnites* to be different expressions of the trail of the same animal, an observation which received experimental confirmation at the hands of Sir William Dawson[18] who discovered that when walking on the bottom the horse-shoe crab used its legs and made a trail like *Protichnites*, but that in shallow water just covering the body it propelled itself by moving its abdominal gill plates and left a trail resembling *Climactichnites*, (*a*) "except that the oblique furrows made by the legs between the median and lateral ridges are directed in the reverse direction";[19] (*b*) "except that in the track of *Limulus* the lateral and median lines are furrows instead of ridges."[20] Jones[21] believed them to be the flattened galleries of burrowing crustaceans, and Grabau[22] in 1913 suggests that the oval bodies of Woodworth may be collapsed burrows. Dana,[23] Billings,[24] and Packard[25] believed they were to be ascribed to trilobites. Todd[26] concludes that the animal was provided with a rigid caudal shield, with bristles or slender spines, and that the ambulatory organs leaving the last impressions were very perfectly flexible and must have been in pairs, each capable of motion independent of its fellow. Hall[27] says that "the markings under consideration do not appear to have been made by an animal provided with free movable limbs, or otherwise with very short limbs, without the acute appendages belonging to *Limulus*." Patten[28] was the first to suggest an Eurypterid origin, "the abdominal gill plates making the rhythmic ridges in the sand." Grabau and Shimer[29] assign the trails to the work of "some unknown terrestrial or semi-terrestrial animal."

Authors are generally agreed that the oval bodies represent the end of the trail; thus Woodworth[30] has suggested that they represent the end of the trail, and Eastman[31] states that "the animal, if an Eurypterid, moved toward the sedentary impression and not away from it." Todd,[32] who apparently did not have the opportunity of observing the oval bodies, records his belief that the apex of the V-shaped impressions points forward, and Walcott[33] speaks of the oval bodies as terminal and (p. 284) of the forward-curving transverse furrows made by pressing the beach-sand backward in creeping."[34] The observa-

Fig. 2.

Upper Cambrian Trail.

Fig. 2. *Climactichnites youngi* (Chamberlin), 5/6 nat. size. (After Walcott.) New Lisbon, Wis. U. S. Nat. Mus.
(The front end of the trail is toward the bottom of the page.)

tions of Kishinouye[35] indicate that the apex of the V-shaped impressions in the somewhat similar track of *Limulus* points forward. As already mentioned, however, Packard records[36] the fact that the oblique furrows of *Limulus* are directed in a direction reverse to that of the ridges of *Climactichnites*, and Patten,[37] in comparing the tracks with those of *Limulus*, states that the tracks showed a beginning in a hollow in the sand, and thus corresponded to those of *Limulus* "which remains buried on recession of the tide and upon its first return crawls and then swims away."

Grabau[37a] mentions *Climactichnites*-like trails in the Silurian, which may have been produced by eurypterids with bilobed telsons, myriopodus types, or insecta.

Climactichnites may be characterized as consisting of a series of more or less transverse subparallel ridges bounded on either side by a lateral ridge. They have been found on Upper Cambrian sandstones in Ontario, New York, and Wisconsin. Let us examine the trails critically to see whether or not they speak for themselves, dividing fact from inference as we did in discussing *Protichnites*.

Facts: (*a*) the lateral ridges may be almost absent or may be very coarse, in which case they are regularly swollen at intervals equal to the distance between the transverse ridges, and each swollen portion appears to merge at one end into an adjacent cross ridge; (*b*) the lateral ridges vary from 1¼ to 4½ inches apart in specimens from Wisconsin, but average 4 to 6 inches apart in specimens from New York and Canada; (*c*) the transverse ridges are usually arched or V-shaped but they are frequently very irregular, even sinuous or double bow-shaped, and the angle of the V varies within wide limits; the apex of the V is not always symmetrically spaced, betraying a general tendency to swerve to the outside on curves, but being irregularly disposed even on tangents; (*d*) there is more or less interruption of each ridge at the apex of the V, so much so that the line connecting the apices sometimes forms a slightly marked ridge; (*e*) the transverse ridges are usually equally spaced, but this again varies greatly and the ridges may be small and irregularly spaced; (*f*) lying upon the ridged trail in the specimen from New Lisbon, Wisconsin (see fig. 2), is a series of very closely spaced almost semicircular raised lines which cross the transverse ridges without interruption or deflection; (*g*) the convexity of the lines mentioned in *f* is directed in the same direction as the apex of the V-shaped arch in the transverse ridges; (*h*) Todd[38] mentions longitudinal lines which are sometimes wavy; (*i*) the trail completely reverses its direction in a distance almost equal to 5 times its width, the sharpest curve observed being one with a radius of little more than one-half

Fig. 3.

Upper Cambrian Trail, New Lisbon, Wisconsin.

Fig. 3. *Climactichnites youngi* (Chamberlin), 3/4 nat. size. (After Walcott.) U. S. Nat. Mus.

(As now interpreted the animal moved toward the bottom of the page.)

the width of the track; (*j*) at one end of several of the trails convex oval bodies as wide as, or slightly wider than, the trail and little more than 2½ times as long are present (see figs. 3 and 4). Woodworth[39] figures these as symmetrically rounded at both ends, Walcott's specimen[40] shows the outline at only one end, but the slab in the Museum at Albany,[41] of which there is a partial replica in the Brooklyn Museum (see figure 5), shows specimens with one end rounded, the other (the end toward the trails) unsymmetrically arched outward, symmetrically

Fig. 4.

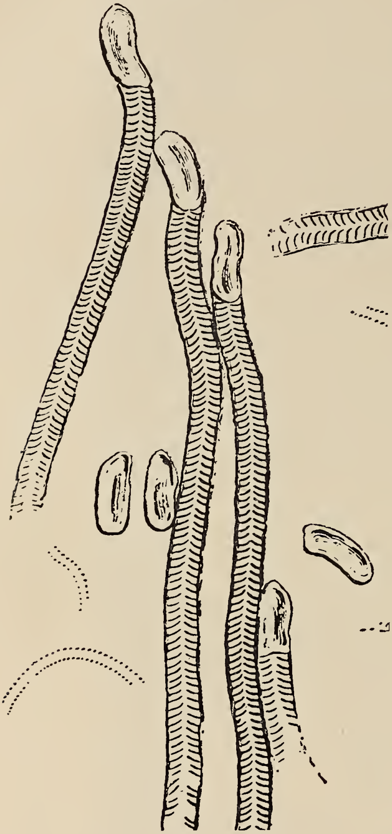
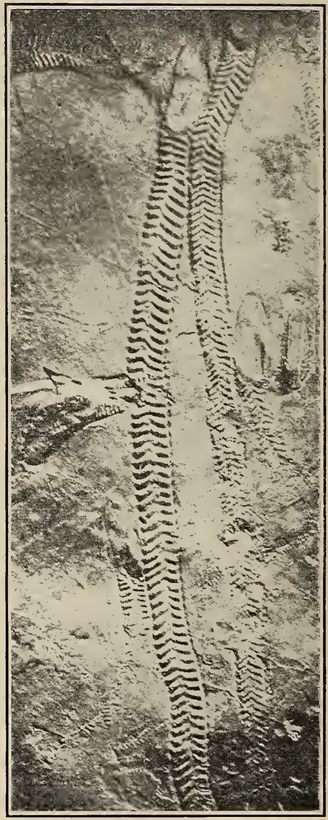


Fig. 5.



Upper Cambrian Trails, Mooers, N. Y.

Fig. 4. *Climactichnites wilsoni* (Logan), × 1/25. (After Clarke.) State Museum, Albany, N. Y.

Fig. 5. From a photograph of a cast of the slab shown in fig. 1, in the Brooklyn Museum. The animal that made the trail is now believed to have moved away from the oval body end.

V-shaped outward, abruptly truncated at right angles to the longer diameter, and even arched inward; (*k*) the "oval bodies" are themselves frequently curved, even broadly S-shaped; (*l*) the apex of the V-shaped transverse ridges always points toward the "oval bodies"; (*m*) the V-shaped transverse ridges may often be seen to extend nearly half way beneath the oval-body; (*n*) the trails are nearly always faint and disappear at the end opposite to the one bearing the "oval body."

Inferences: (*a*) the side ridges were apparently made in the same push that made the transverse ridges, and that both are ridges instead of furrows indicates that the apex of the V-shaped ridges points backward with reference to the line of progress, for this is the only direction in which material could be shoved outward and heaped up along the edges of the trail; (*b*) in all probability these figures represent the entire width of the animal; (*c*, *d*, and *e*) the portion of the animal making the transverse ridges was very flexible and capable of making movements differing in amplitude, direction, and form; the interruptions in the center (*d*) are to be expected, and do not require a division of the ridge-forming portion, a view which is corroborated by the wide lateral shifting exhibited by this median ridge; (*f*) these semicircular raised lines must have been made last or they would have been obliterated or marred, and must indicate the conformation of the back end of the animal; their close spacing would indicate slowness of forward movement or creep; (*g*) the apex of the V-shaped ridges therefore points also toward the rear; (*h*) probably made, as Todd suggests, by bristles or other portions of the under surface as the animal moved along,—I have not observed them; (*i*) the animal, or its ambulatory organ, was very flexible, or else short and more or less elliptical in outline; (*j*) the evidence seems to warrant us in disagreeing with the concensus of previous opinion (see p. 391), and in supposing these oval bodies to represent the initial resting place of the animal that made the trails, the round ends, as indicated in *a* and *f*, being the rear and the V-shaped end the front. This front end was capable of being moved from V-shape forward (its position in repose) to V-shape backward, and this movement carried the animal along. The convexity of these oval bodies may be explained as follows: If an animal with a very flexible under surface or foot were stranded on the retreat of the tide, scour would obliterate the previous tracks and would reduce the general level of the beach wherever it was not protected from erosion by the disk-like foot, and the edges of this organ would naturally be depressed in an endeavor to prevent being washed away. The lens of sand thus enclosed would be left upon the departure of the animal at the approach of the next tide, its preservation, and that of the tracks made in moving away, being due to fortuitous circumstances; (*k*) corroborates *i* in proving the animal or its foot to be extremely flexible; (*l*) therefore, if we are right in *a*, *f*, and *j*, the apex of the V always points in the direction from which the animal has been moving, not forward as nearly everyone has supposed, Patten[42] being the only one to suggest a possible difference; (*m*) unless the ambulatory organ or organs occupied nearly half of the under surface this fact alone would prove that the animal moved away from the oval-body end. The preservation of these marks in the portion of the trail where the body must have rested seems to the writer to be explained by supposing the edges of the disk-like foot to be sufficiently extended in repose to protect the last marks made by the animal previous to its rest—the oval body is frequently about one fifth wider than the immediately adjacent trail; (*n*) the progressive faintness and disappearance of the trails at the end opposite to that bearing the oval bodies is characteristic of nearly all of the trails; all of those, for example, which exhibit both ends in the specimen at Albany.[43] They certainly seem to corroborate *a*, *f*, *j*, and *m*, in indicating that the animal started from the oval-body end and rose into the water at the other end, as pointed out by Patten,[44] and that they could swim.

In some trails, notably the one running down the center of the slab in the museum at Albany, the disposition of the ridges is such as to suggest that the animal did move toward the oval body end of the trail. The impressions of the curved margin described under *f* on a previous page were unknown to geologists until the specimen from New Lisbon, Wisconsin, was figured by Walcott in 1912, and while Walcott adheres to the belief that the New Lisbon animal also moved toward the oval-body end we have endeavored to show that this specimen proves the oval body end to be the initial portion of the trail. The V-shaped ridges in both the Albany and New London specimens point toward the oval-body end, and it is somewhat improbable that the animal should have moved *toward* that end in the one case and *away* from it in the other. However, there are certain differences in the trails, and these may be due either to causes dependent on the physical conditions at the time the trails were made or to differences in the animals themselves. The New Lisbon specimen certainly started from the oval body end to crawl away; those in the Albany slab may have come to rest in the manner described by the early observers. Naturally, however, the conclusion that the oval-body end was made last has called forth attempts to explain the disappearance of the animal.

Conclusions.—The animals that inhabited the sea some thirty million years ago are known to us with a perfection that is a continual source of wonder, and the discoveries of the past few years in these ancient rocks are little short of marvellous, but that the Cambrian seas were peopled by a host of forms of which we know little or nothing is no less certain than that the waters of pre-Cambrian time were full of life. While certain of these unknown forms offer us nothing more substantial than the record of their reptant efforts, the desire to know is responsible for attempts at their deciphering. The facts are daily becoming more numerous and the inferences surer. That *Protichnites* was made by a short, low-lying, and more or less heavy set, approximately 12-legged crab-like animal, and that *Climactichnites* was made by the snail-like creep of a flexible slug-like animal which was frequently stranded at low tide, but was able to swim in the waters of the full tide, have passed the stage of guess-work and border on the real.

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34. It should be noted that these "forward-curving transverse furrows" are more or less sinuous and bend sharply backward (using the same terminology) at their union with the sides of the trail, which they join at a tangent. Consideration of this one trail alone (pl. 39, fig 2 of Walcott) seems sufficient to prove that the animal must have progressed in a direction exactly opposite to that assumed by Walcott. Under the new interpretation the transverse furrows bend sharply forward at the sides and are bent backward in the center, and are closely covered by the series of curved raised lines left by the posterior margin of the animal (see *g* of text).
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41. See Bull. New York State Mus., No. 80. 1905, pl. 3.
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SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *A New Method for the Recovery of Salts of Potassium and Aluminium from Mineral Silicates.*—Many efforts have been made to devise methods for extracting potassium from orthoclase feldspar which occurs in such quantity and purity as to make it a possible source of supply for salts of this element, and the desirability of such a process has greatly increased since the time that the supply of German potash salts has been cut off. The methods heretofore proposed for this purpose do not appear to have been successful on the large scale. J. C. W. Frazer, W. W. Holland and E. Miller, of Johns Hopkins University, have now proposed for the purpose a method which appears unusually promising, since comparatively low temperatures are required for the operation, and since, besides the potassium, the aluminium of the mineral may be extracted in the process. The finely ground feldspar is mixed with about 0.8 parts of potassium hydroxide (or an equivalent amount of the sodium compound) and heated for about an hour at a temperature of 275 to 300° C. A reaction takes place whereby practically one-third of the silica of the feldspar is converted into potassium silicate, soluble in water, while the residue corresponds in composition to the mineral leucite:

$$KAlSi_3O_8 + 2KOH = KAlSi_2O_6 + K_2SiO_3 + H_2O$$

Upon treating the mass with water the alkali used in the process goes into solution, largely as silicate. It is then causticized with lime, and, after filtering off the resulting calcium silicate, the liquid is evaporated and the alkali is used again for the treatment of feldspar, with a total loss of only about 1%, according to the experiments of the authors, working on a small scale.

The residual artificial leucite gives up its potassium very readily to dilute acids, so that the point where the potassium is extracted can be detected by an indicator, such as methyl orange. It is possible, therefore, to extract the potassium as chloride, sulphate or nitrate by the use of the corresponding acids without attacking the aluminium in the compound. The residue, now filtered from the potassium salt solution, resembles kaolinite somewhat in composition, but it is readily decomposed by sulphuric acid with the formation of aluminium sulphate and gelatinous silica. After dehydrating the silica by drying, the two things may be separated by treatment with water and filtration.—*Jour. Indust. Eng. Chem.*, ix, 935.

H. L. W.

2. *Electrochemical Equivalents;* by Carl Hering and Frederick H. Getman. 12mo, pp. 130. New York, 1917 (D. Van Nostrand Company).—This little book gives an excellent table of electrochemical equivalents for practically all of the known elements. The international atomic weights of 1917 are used as the basis, and the equivalents are calculated for all the possible valences or changes of valence in each case. The values given are in terms of milligrams per coulomb, coulombs per milligram, grams per ampere-hour, ampere-hours per gram, pounds per 1000 ampere-hours, and ampere-hours per pound. The data just mentioned are given in the principal table, but there are several other tables containing useful information. While the book does not profess to be a treatise on electrochemistry, sufficient explanatory text is given to permit the use of the data without need of reference to other works. There are discussions of fundamental laws and data, the methods of calculation are clearly explained and illustrated by numerous examples, the principles of electrolysis and the electronic theory are well presented, while in the appendix the subject of valence and chemical calculations are taken up. The book appears to be a very useful one, not only for the purposes of practical electro-chemical calculations, but also as a reliable and concise source of theoretical information in the field where chemical and electrical sciences are connected. H. L. W.

3. *A Laboratory Manual of General Chemistry;* by William J. Hale. 12mo, pp. 474. New York, 1917 (The Macmillan Company).—This book presents an unusually extensive and advanced course of laboratory work. The experiments are not only very numerous, but there are some rather elaborate quanti-

tative experiments, particularly near the beginning of the course, and there is also a good deal of work in the direction of the qualitative grouping of elements and radicals. The course of work evidently deserves high praise in regard to its fullness, its instructiveness, and its clear presentation of the operations. It appears, however, that the course as a whole is too extensive for the time that is usually available for such courses, and that the somewhat complicated quantitative work is introduced at such an early stage that the average beginner would very probably lack the manipulative ability and the knowledge to carry them out properly and to comprehend them satisfactorily. However, it may be said that it is easier to omit portions of a too extensive book than to add material to one that is too short or too elementary. While practically one-half of the pages of this book are left for the student's notes, these pages are supplied with printed numbers corresponding to numbers placed in the text of the opposite pages, so that the student may know where to record his observations and answers to questions. This arrangement will facilitate the proper taking of notes, and it will be an aid to the instructor who examines them. H. L. W.

4. *A Short Manual of Analytical Chemistry;* by JOHN MUTER. 6th American Edition, Edited by J. THOMAS. 8vo, pp. 237. Philadelphia, 1917 (P. Blakiston's Son & Co.).—This book, which is intended for the use of students of pharmacy, deals with qualitative and quantitative, inorganic and organic analysis. In spite of its moderate size and the wide field that it covers, it gives a surprisingly comprehensive amount of information. It is a well-known work which has passed through 10 English and 6 American editions. The latter are by no means mere copies of the former, since the American editions are made to correspond with the legal requirements for drugs as fixed by the United States Pharmacopœia. The book contains so much information about analytical methods that it should be useful as a reference book to all kinds of analytical chemists. H. L. W.

5. *Allen's Commercial Organic Analysis.* Edited by W. A. DAVIS. Fourth Edition. Vol. IX. 8vo, pp. 836. Philadelphia, 1917 (P. Blakiston's Son & Co. Price $5 net).—This volume of the entirely rewritten fourth edition of this monumental work has been issued in order to bring up to date the matter of the preceding eight volumes, especially the earlier ones, since the work of revision was begun in 1907. The articles included are very numerous and naturally vary in length and importance. In many cases the original contributors have furnished the revisions, but in some cases others have done the work. An important feature of the volume is a complete general index to the whole series of nine volumes. This will greatly facilitate reference to the work. H. L. W.

6. *The Ionizing Potential of Sodium Vapor.*—Several experimenters have shown that, when the vapors of cadmium, magnesium, mercury, and zinc *in vacuo* are bombarded by electrons from a hot cathode, a single-line spectrum is emitted, provided the kinetic energy of the electrons does not exceed a certain critical value. The line appeared when the potential difference involved attained the value required by the quantum relation and the frequency of the radiation; for example, 4.9 volts for the wave-length 2536.7 in the spectrum of mercury.

An extended series of experiments on the vapor of *sodium* has been carried out recently by R. W. Wood and S. Okano. Since they used three or four different forms of apparatus and varied the experimental conditions in many ingenious ways, in order to eliminate the hypothetical sources of error as far as possible, it will not be feasible, for lack of space, to do justice to the experimental details of the investigation. By making visual observations with a very efficient Schmidt and Haensch pocket spectroscope, it was found that the red and green lines of the subordinate series faded gradually as the voltage was decreased and finally disappeared at 2.3 volts. The quantum relation leads to the expectation that the D-lines would vanish at about 2.1 volts. As a matter of fact the yellow radiation could be detected until the potential difference had dropped as low as 0.5 volt. The lack of agreement between the predicted and observed values may be due to the presence in the cathode stream of a relatively small number of electrons having a much higher speed than the mean value corresponding to 2.1 volts. The authors suggest that this possibility may be tested by separating the electrons magnetically into beams each of which is composed of corpuscles moving with sensibly equal speeds.—*Phil. Mag.*, xxxiv, p. 177, September, 1917. H. S. U.

7. *Penetrating Power of X-Rays from a Coolidge Tube.*—The paper under consideration was written by Rutherford and it contains an account of some experiments made to determine the maximum penetrating power of the X-rays excited by high voltages in a Coolidge tube, lead being used as the absorbing material.

The radiation was excited by a large induction-coil, actuated by a mercury motor-break in an atmosphere of coal-gas, and capable of giving 20 inch sparks. The heating current through the tungsten spiral of the tube was adjusted to give a radiation of maximum intensity at the voltage required. This voltage was fixed by an alternative spark-gap between points. The radiation was found to be most constant when a fairly rapid stream of sparks passed between the points. The voltage corresponding to the alternative spark-gap was determined by comparison with the sparking potential between two brass spheres 20 cm. in diameter. The ionization current was measured by means of cubical electroscopes of the type usually employed in gamma-ray work. For determining the initial absorption, the lead front of the electroscope was cut away and replaced by thin aluminum foil. In cases where greater thicknesses of absorber were necessary, lead electroscopes having sides respectively 3 mm. and 8 mm. thick were employed. The absorbing lead screens were of much larger area than the face of the electroscope and, since they were placed close to the front of this instrument, the greater part of the radiation scattered in a forward direction by the absorber entered the electroscope.

The experimental data are tabulated in four columns which give respectively, the maximum voltage (79,000 to 196,000 volts), the range of thickness in lead (0.7 mm. to 10.0 mm.), the absorption coefficient μ (27 to 8.5 cm.$^{-1}$), and the mass absorption coefficient μ/ρ (2.37 to 0.75). The following facts are brought out by this table. In the first place, the thickness of lead through which the radiation was measurable increased with the voltage applied. This was due not only to the increase in the penetrating power of the radiation but also to the large increase with voltage of the intensity of the radiation. At 196,000 volts the radiation was detected and measured after passing through 10 mm. of lead. The intensity had then fallen to less than the one-millionth part of its initial value. Again, for the end radiations, μ does not change very much between 79,000 ($\mu = 26$) and 144,000 volts ($\mu = 22$), and between 105,000 and 144,000 volts μ remains constant. Within the latter range of voltages the radiation is absorbed nearly exponentially with a value of μ equal to 22 cm.$^{-1}$ Above 144,000 volts the absorption is no longer exponential, but the value of μ decreases progressively with increase of thickness of absorbing layer. For example, at 183,000 volts μ decreases from 26 to 12 as the thickness of the absorber is increased from 0.7 mm. to 7.0 mm. These apparently peculiar results are readily explained by taking into account the characteristic absorption band of lead. By assuming that the portion of the graph ($x = \log \mu/\rho$, $y = \log \lambda$; $\lambda =$ wave-length) corresponding to wave-lengths less than those of the absorption band is an approximately straight line parallel to the segment of the locus on the longer wave-length side of the band, the author extrapolates to the value $\mu = 5$, for the minimum value associated with 196,000 volts. The experimental value was found to be 8.5. Since this last number is known to be too large and as the value 5 was obtained from the data of other observers, the author concludes that his results are not inconsistent with the quantum relation $e\,V = h/\lambda_{\min}$ This equation has been shown by Hull and Rice to hold up to 100,000 volts and probably as far as 150,000 volts. Rutherford's investigation therefore confirms their work and extends the range of validity of the quantum equation. A few data are also given for the absorption by aluminum of the end radiation after passing through iron.

The observations on the absorption of X-rays in aluminum and lead throw important light on the difficult question of the probable wave-lengths of the penetrating gamma rays from radioactive substances. The line of argument may be suggested by the following brief account. The numerical data for X-rays obtained by Rutherford and by Hull and Rice are collected in the first six horizontal lines of a table. The first and second columns contain respectively the voltages (84,000 to 196,000) and the corresponding shortest wave-lengths (0.147 Å to 0.063 Å), conformably to the equation $E = h\nu$. The values of the mass-absorption coefficient (μ/ρ) for aluminum and lead are entered in the third and fourth columns. The seventh line pertains to the penetrating gamma rays from radium C. In this line the first and second spaces are to be filled in, while the third and fourth contain the values of μ/ρ given by Ishino. A discussion of all the data in the last two columns leads, by extrapolation, to a general estimate of the voltage required to excite the gamma rays, and from this datum together with $E = h\nu$ the order of magnitude of the wave-length of these rays is obtained. The following quotation contains in concise form the final conclusions.

"In our present ignorance of the law of variation of μ/ρ with frequency in this region of the spectrum, it is only possible to estimate the actual wave-length of the most penetrating gamma rays. It is clear, however, that the waves are at least three times and may be ten times shorter than those which correspond to 200,000 volts, *i. e.*, they correspond to waves generated by voltages between 600,000 and 2,000,000 volts, and thus lie between .02 and .007 Å.U. It is thus clear that the gamma rays from radium C consist mainly of waves of about $\frac{1}{100}$ the wave-length of the soft gamma rays from radium B, and are of considerably shorter wave-length than any so far observed in an X-ray tube, with the highest voltages at our disposal."

The last part of the paper deals with the β rays from radium B and radium C and their probable relation to the associated γ rays. "The results as a whole suggest that the groups of β rays are due to the transformation of the gamma rays in *single* and not *multiple* quanta, according to the relation $E = h\nu$." "If the single quantum relation should prove to hold generally for the conversion of γ rays into β rays, the magnetic spectrum of β rays should afford a reliable method of extending the investigation of X-ray spectra into the region of very short waves where the crystal method either breaks down or is practically ineffective, and thus places in our hands a new and powerful method of analysing waves of the highest obtainable frequency."—*Phil. Mag.*, xxxiv, p. 153, September, 1917. H. S. U.

8. *Problems in General Physics;* by MORTON MASIUS. Pp. vi, 90. Philadelphia, 1917 (P. Blakiston's Son and Co.).—This little book contains 1000 problems and it covers the entire field usually taught in engineering colleges. The topics that are more important or lend themselves more readily to treatment by problems have received greater attention than the relatively less important ones; for example, certain parts of mechanics and electricity have more space devoted to them than optics. The problems under each heading (equilibrium, calorimetry, etc.) are divided into four groups of equal average degree of difficulty. It is, therefore, possible to select four different sets of about 250 problems each, for use in four consecutive years, or with four divisions of the same class in one year. Since the problems in each group increase in difficulty from the first to the last, an easy course can be made out from the first problems in all four sets, and a more advanced course can be based on the last exercises in the groups. Physical constants required for the solution of the problems have been omitted whenever they are given in the tables in A. W. Duff's "A Textbook of Physics." Answers to the problems have not been incorporated in the volume. As far as one can judge, without testing the book with students, the problems seem to have been carefully selected and arranged. The only obvious drawback to the book consists in the unnecessarily small type used in the printing. H. S. U.

II. GEOLOGY.

1. *A monograph of Japanese Ophiuroidea, arranged according to a new classification;* by HIKOSHICHIRO MATSUMOTO. Jour. College of Science, Imperial University of Tokyo, xxxviii, Art. 2, 408 pp., 7 pls., 100 text figs., 1917.—In this excellent work are noted or described the known living species of ophiurians, numbering 232 species, here grouped into 88 genera. They have been studied from all angles, and on pages 352–365 is also given their geographical distribution.

Of especial interest to paleontologists working with Paleozoic forms are the following definitions:

"Subclass I. Œgophiuroida Matsumoto. Ophiuroidea with external ambulacral grooves and without ventral arm plates. Radial shields, genital plates and scales, oral shields, peristomial plates and dorsal arm plates also absent. Ambulacral plates alternate or opposite; in the latter case, they may often be soldered in pairs to form the vertebræ. Adambulacral plates, i. e., lateral arm plates, subventral in position. Madreporite either dorsal or ventral, often large and similar in shape to that of an asteroid.

"This subclass mostly consists of Palæozoic forms, and lacks all the fundamental characters by which the recent ophiurans are clearly distinguished from the asteroids. Indeed, the distinction of the present subclass from the asteroids depends merely upon the different development of certain common structures.

"Subclass II. Myophiuroida Matsumoto. Ophiuroidea without external ambulacral grooves, and with ventral arm plates. Radial shields, genital plates and scales, oral shields, peristomial plates and dorsal arm plates usually present; but sometimes, some or all of them may be rudimentary or absent. Ambulacral plates opposite, usually completely soldered in pairs to form the vertebræ. Madreporite represented by one, or sometimes all, of the oral shields.

"This subclass includes certain Palæozoic forms and all the ophiurans from the Mesozoic downwards.

"The Palæozoic Myophiuroida appear to me to represent a distinct order by themselves." (pp. 5–6.)

"Though it is my purpose to discuss the results of a study of Palæozoic ophiurans in a future paper, I will here enumerate some of the more important structures of Palæozoic Myophiuroida, as bearing on the question before us.

"1. Disk covered with delicate scales or by a naked skin, without distinct primaries.

"2. Radial shields absent.

"3. Genital plates and scales absent.

"4. Oral shields absent.

"5. Adoral shields not very distinctly specialized from the lateral arm plates.

"6. Oral plates and frames long and slender.

"7. Distinct creases probably present between the interbrachial ventral surfaces and arm bases.

"8. Dorsal arm plates entirely absent, or present only in a few basal joints; the dorsal side of the arms therefore largely unprotected.

"9. Lateral arm plates with prominent spine ridges, which extend to the ventral side of the arm; those of the two sides not meeting above or below, except in the very distal arm joints.

"10. Ventral arm plates higher in position than the lower borders of the lateral arm plates, so that the arm is longitudinally grooved ventrally.

"I believe that the Palæozoic Myophiuroida are the stock from which the recent ophiurans have been directly derived, because they show no trace of peculiar specialization and are fairly intermediate in their organisation as a whole between the Œgophiuroida and recent ophiurans. If this view be right, then the most archetypal group of recent ophiurans must be looked for among those forms which have the strongest resemblances to the Palæozoic Myophiuroida." (pp. 367–369.) C. S.

2. *Publications of the United States Geological Survey;* George Otis Smith, Director.—Recent publications of the Survey are noted below. See earlier May, 1917, pp. 418, 419; June, 1917, pp. 489, 490.

Geologic Folios.—No. 205. Detroit, Michigan (Wayne, Detroit, Grosse Pointe, Romulus, and Wyandotte Quadrangles); by W. H. Sherzer. Pp. 22, 12 maps, 12 pls., 20 figs.

No. 206. Leavenworth-Smithville, Missouri-Kansas; by Henry Hinds and F. C. Greene. Pp. 13, 4 maps, 10 pls., 10 figs.

No. 207. Deming, New Mexico; by N. H. Darton. Pp. 15, 3 maps, 1 structure-section sheet, 9 pls., 11 figs.

Professional Papers.—No. 94. Economic Geology of Gilpin County and adjacent parts of Clear Creek and Boulder Counties, Colorado; by E. S. Bastin and J. M. Hill. Pp. 379, 23 pls., 79 figs.

No. 97. Geology and Ore Deposits of the Mackay Region, Idaho; by J. B. Umpleby. Pp. 129, 21 pls., 14 figs.

No. 100-A. The Coal Fields of the United States: General Introduction; by M. R. Campbell. Pp. 36, 1 pl., 3 figs.

No. 108. Shorter Contributions to General Geology, 1917. C, D, E. F.

Mineral Resources of the United States for 1916. Numerous advance chapters.

Bulletins.—No. 625. The Enrichment of Ore Deposits, by W. H. Emmons. Pp. 530, 7 pls., 29 figs.

No. 647. The Bull Mountain Coal Field, Musselshell and Yellowstone Counties, Montana; by L. H. Woolsey, R. W. Richards, and C. T. Lupton; compiled and edited by E. R. Lloyd. Pp. 218, 36 pls., 2 figs.

No. 652. Tungsten Minerals and Deposits, by F. L. Hess. Pp. 85, 25 pls., 4 figs.

No. 653. Chemical Relations of the Oil-Field Waters in San Joaquin Valley, California (Preliminary Report); by G. S. Rogers. Pp. 119, 7 figs.

No. 657. The Use of the Panoramic Camera in Topographic Surveying, with notes on the application of Photogrammetry to Aerial Surveys; by J. W. Bagley. Pp. 88, 15 pls., 22 figs.

No. 660. Contributions to Economic Geology, 1917, Part I. A. B.

No. 661. Contributions to Economic Geology, 1917, Part II. A, B, C, E.

No. 666. Our Mineral Supplies. Several advance chapters.

Water Supply Papers.—Nos. 362, 386, 391, 401, 403, 405. Surface Water Supply of the United States; Nathan C. Grover, Chief Hydraulic Engineer. 1913. No. 362. Part XII. North Pacific Drainage Basins. Pp. 775, 2 pls.

1914. No. 386. Part VI. Missouri River Basin. Pp. 261, 3 pls. No. 391. Part XI. Pacific Slope Basins in California. Pp. 370, 2 pls.—No. 394. Part XII. North Pacific Drainage Basins. Pp. 180, 2 pls.

1915. No. 401. Part I. North Atlantic Slope Drainage Basins. Pp. 186, 2 pls. No. 403. Part III. Ohio River Basin. Pp.

209, 2 pls. No. 405. Part V. Hudson Bay and Upper Mississippi River Basins. Pp. 245, 4 pls.

No. 423. Geology and Water Resources of Big Smoky, Clayton, and Alkali Spring Valleys, Nevada; by O. E. MEINZER. Pp. 167, 17 pls., 10 figs.

No. 425-A. Ground Water in San Simon Valley, Arizona and New Mexico; by A. T. SCHWENNESEN, with a section on agriculture, by R. H. FORBES. Pp. 39, 3 pls. 2 figs.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Eleventh Annual Report of the President,* HENRY S. PRITCHETT, *and Treasurer,* ROBERT A. FRANKS, *of The Carnegie Foundation for the Advancement of Teaching.* Pp. 172. New York City (576 Fifth Avenue).—This report, for the year ending September 30, 1916, shows a total endowment of $14,250,000, an accumulated surplus of $1,327,000, and an annual expenditure of $779,000. Of this $39,000 was spent in administration, $47,000 in educational enquiry, and $687,000 in retiring allowances and pensions. During the year 30 retiring allowances and 16 widows' pensions were granted, the average grant being $1703. The total number of allowances now in force is 331, the total number of widows' pensions 127, the general average being $1553. The total number of allowances granted since the beginning of the Foundation is 685, the total expenditure for this purpose having been $4,910,000.

Part II discusses the general subject of insurance and annuities, to which the President has made important contributions in earlier volumes. The report includes official replies from 52 of the institutions associated with the Foundation concerning the new contributory plan of insurance and annuities proposed by the Foundation, and presents the fundamental principles of a pension system which have been approved by the trustees of the Foundation and a joint commission representing the American Association of University Professors, the Association of American Universities, the National Association of State Universities, and the Association of American Colleges. Details are given concerning the new Teachers Insurance and Annuity Association which is to be established, together with an estimate of its prospective service to the teaching profession.

In addition to its annual reports, the Foundation has published nine bulletins on special subjects. Bulletin No. 10, now issued (pp. 127), is by I. L. KANDEL, and has as its subject "A Study of Federal Aid for Vocational Education." It traces the legislative history of Federal grants for education and reaches the conclusion that these grants have always been made for political purposes and without any well-considered educational reasons.

2. *Publications of the Carnegie Institution of Washington.*—Recent publications of the Carnegie Institution are noted in the following list (continued from April, 1917, vol. xliii, pp. 341, 342):

No. 159. *The Mosquitoes of North and Central America and the West Indies;* by LELAND O. HOWARD, HARRISON G. DYAR, and FREDERICK KNAB. Volume IV. Systematic Description in two parts. Part II. Pp. 1064.

No. 175 (Vol. 3). Ocean Magnetic Observations 1915-1916 and Reports on Special Researches; by L. A. BAUER, with the collaboration of W. J. PETERS and others. Pp. vii, 445; with 25 plates and 35 text figures.

No. 208. A Concordance to the Poems of John Keats; by DANE LEWIS BALDWIN and others. 4to. Pp. xxi, 437; with portrait (frontispiece).

No. 215. History of Transportation in the United States before 1860; by CAROLINE E .MACGILL and a staff of collaborators, under the direction of B. H. MEYER. Pp. xi, 670.

No. 226. Contributions to Embryology. 4to. Vol. VI. Nos. 15-19. Pp. 1-168, 21 pls., 24 text figs. Papers here included are the following: by F. P. MALL on cyclopia in the human embryo; by MADGE DEG. THURLOW on mitochondria in nerve cells; by MARGARET R. LEWIS on chick embryos; by FLORENCE R. SABIN on origin and development of primitive vessels of the chick and pig; by F. P. JOHNSON on a human embryo of twenty-four pair of somites.

No. 250. Ulugh Beg's Catalogue of Stars, Revised from all Persian Manuscripts existing in Great Britain; with a vocabulary of Persian and Arabic Words; by EDWARD BALL KNOBEL. 4to. Pp. 109.

No. 251. Papers from the Department of Marine Biology; ALFRED G. MAYER, director. Vol. XI. Pp. v, 360. Fourteen articles are here included, illustrated by numerous plates and text figures.

3. *Publications of the British Museum of Natural History.*—The following publications have been recently received: Economic Series, No. 4; Mosquitoes and their relation to Disease; their life-history, habits and control; by F. W. EDWARDS. Pp. 20. No. 5. The Bed-Bug—Its habits and life-history and how to deal with it; by BRUCE F. CUMMINGS. Pp. 20. No. 6, Species of Arachnida and Myriopoda (scorpions, spiders, mites, ticks and centipedes) injurious to Man; by STANLEY HIRST. Pp. 60; with 26 text-figures and 3 plates.

Instructions for Collectors: No. 1A.—Mammals. Part II, Skeletons, with special notes on the collection of specimens of Cetacea; by S. F. HARMER. Pp. 8. No. 13.—Alcohol and Alcoholometers; by S. F. HARMER. Pp. 8.

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[FOURTH SERIES.]

Art. XXXV.—*Origin of the Chert in the Burlington Limestone*; by W. A. Tarr.

Table of Contents.

INTRODUCTION.

MANY explanations have been advanced to account for the occurrence and distribution of chert in limestone and dolomite. Since chert is found in these rocks in all parts of the world, geologists have had many opportunities to study its occurrence and to accumulate enough facts to give an adequate explanation of its origin. This has not been done, however, for careful descriptions of chert, its mode of occurrence, physical characteristics, and composition are lacking in most references to it. There are a few good descriptions but these are mainly old; very few of the articles dealing with chert, even in a general way, are later than 1900, and these, as a rule, do not present new evidence but cite the earlier views as to origin and conclude that they are adequate. In studying the chert of the Burlington limestone in the vicinity of Columbia, Mo., the writer observed many facts which do not accord with the prevalent view that chert is due to the segregation of silica in limestone into the characteristic chert nodules. The following paper presents the evidence which has been collected and its interpretation as the writer sees it.

I. THEORIES AS TO ORIGIN.

There have been many different views advanced to explain the origin of chert, but the majority can be classed under two heads: (1) theories that seek to explain the origin through segregation by organic means; and (2) theories maintaining that the material of the chert was a direct chemical precipitate. There are, however, other theories, as the following complete table shows:

1. Chert is the result of direct chemical precipitation.
2. Chert is the result of the secretion of silica by organisms.
3. It is the result of the replacement of calcareous material.
4. It is of organic origin, but not through replacement.
5. It is a spring deposit.
6. It is a mechanical sediment.
7. It is regarded as being due to weathering.

It would be entirely out of place to present the various theories in full in this paper, but a brief statement of the essential point in each one may be made, and the bibliography at the end of the paper furnishes many excellent summaries and further citations to the literature.

The theory that chert originated through the precipitation of silica in the colloidal form upon the sea bottom was advanced by Prestwich in 1888. The silica was thought to have accumulated about the siliceous spicules of sponges, which acted as nuclei, or in the absence of such material, decaying organic matter might also have acted in the same capacity. Once started, the aggregate would, according to the theory, continue to attract silica to itself from the surrounding muds as long as material was available. Hull and Hardman, M. A. Renard, C. A. White, E. O. Hovey, C. R. Van Hise and R. D. Irving, and N. H. and H. W. Winchell have all advocated the same view, although the first two men thought that the silica so precipitated had later replaced calcareous material. Hovey based his theory upon a study of chert from the Burlington and the Cambro-Ordovician formations of Missouri, which makes his conclusions especially interesting by way of comparison, since this paper also is based upon a study of the chert of the Burlington and the Cambro-Ordovician formations. He states:

> "Regarding the Lower Magnesian and Lower Carboniferous cherts from southern and southwestern Missouri, the present writer's conclusion is, that they are due to chemical precipitation, probably at the time of the deposition of the strata in which they occur or before their consolidation."

The advocates of the theory that the silica was first segregated by some organism have presented much evidence in its support. Their main evidence is the finding of the remains of sponges and diatoms scattered throughout the chert. This theory was early advanced in England by Bowerman and was ably supported by the researches of Sollas, Hinde, Jukes-Brown and Hill, and Sorby. It is largely accepted by American geologists as is shown by the statements made in all our latest text-books. Had these early investigations been made on material collected in Missouri, very likely a different theory would have resulted, because Missouri chert shows no remains of siliceous organisms.

The advocates of the theory that the chert and flint nodules and beds are the result of the replacement of calcareous material of the limestone early called attention to the fact that fossils known to be originally calcareous were often found silicified undoubtedly through replacement. A. H. Church was able to replace with silica the calcium carbonate of a fragment of coral by allowing a weak solution of colloidal silica to percolate over it.* On account of the finding of fossils on the interior of the chert and flint nodules which were originally calcareous, the conclusion was drawn that the silica had replaced the fossil and that the nodule had grown by further additions on the outside, each particle of silica replacing an equivalent amount of calcareous material. The presence of siliceous spicules of sponges in chert and flint suggested a possible source for the silica in the nodules, and since the silica in

* F. W. Clarke, Bull., U. S. G. S., 616, pp. 515, 543.

the spicules is in a form regarded as being soluble in ground water, it was thought to have been taken into solution and deposited about other sponge spicules which acted as nuclei. Other silica-secreting organisms, such as radiolaria, have been suggested as possible sources of the silica. In this and the preceding theory the organisms were thought to have obtained their silica either from the sea water in which it was held in solution or by decomposing silicates occurring in the muds upon the bottom. There seems to be room for doubting that the latter method is an important mode for obtaining the silica, for the silicates which accumulate in the muds have already withstood the attacks of solutions upon the earth's surface and are very stable. Most of the men who held the view given above believe that the segregation of silica by organisms was followed by its solution, removal, and deposition elsewhere, so that these two theories are really no more than one.

That the chert layers and nodules may have been due to the accumulation of abundant organic remains upon the sea bottom was an idea advanced by Wallich and has been favored by others. The possibility that a part of the silica was a chemical precipitate derived from soluble sponge spicules was also included in this theory, but the method of precipitation was not explained.

Lawson has suggested the theory that the chert of the Franciscan series in California is due to the precipitation of colloidal silica brought to the sea water by thermal springs. The chert contains sponge spicules, and Lawson states that these probably fell into the soft colloidal silica on the sea bottom and were preserved.

An unusual mode of origin was suggested by Penrose and Buckley, who thought that the silica might be transported to its present position as a fine siliceous mud. Penrose applies his theory to the Boone chert in northern Arkansas and Buckley, to the dark-colored, secondary chert in the Joplin district of southwestern Missouri. It is difficult to explain the source of such a siliceous mud.

Another theory that has been suggested to explain the origin of chert is that the aggregation of the silica is due to the ordinary processes of weathering. It is thought by Ulrich, who suggested this view, that the silica, being insoluble, is concentrated near the surface as the associated calcareous material is removed by subaerial erosion. This view is held by some others, but the finding of chert in the lower formations in some of the deepest wells that have been drilled in Missouri is strong evidence against it. Further, a careful study of the occurrence of the chert in the area described by Ulrich shows that it does not have unequal distribution, though Ulrich reported that it did and interpreted the condition as indicating superficial concentration by weathering.

It is evident from the above brief statements that while there are several views as to the origin of chert, the important ones are the first three given, which should really be regarded as two. The theory which seems to be prevalent at the present time, judging by the recent text books of geology, is that the silica was originally secreted by organisms and then aggregated into the nodular or bedded form through replacement of the limestone by circulating ground waters, either before or after the consolidation of the limestone. The supporters of the theory that chert is due to chemical precipitation assume that the silica was in the sea water, and that it has been precipitated by some means or other, which they fail to suggest.

II. The Chert in the Burlington Formation.

A. DEFINITION OF CHERT.

In this paper the term chert will include those cryptocrystalline varieties of quartz which are white, gray, or blue-gray in color. Dark gray to black varieties will be called flint, while those which owe their color to iron oxides will be referred to as jasper.

Chert is defined in our latest text books and mineralogies as an impure flint. The writer wishes to express the view that this much quoted statement is wrong and that flint is an impure chert. It is the excessive amount of organic matter in the flint which gives it its black color, and this foreign matter is absent in the chert. Since all these materials are supposed to be pure quartz it would seem that chert is the purest because of the absence of this coloring matter.

As to composition chert is practically pure silica, as the analyses given below show. The other constituents which are usually present are calcium carbonate, alumina, iron oxides, and a small amount of water, the latter being probably contained in the opaline silica present in the chert.

B. MEGASCOPIC DESCRIPTION.

Megascopically the chert is dominantly white although some of it is gray or mottled. The mottled appearance is a common feature of the chert and is due to the aggregation of organic matter into small areas and to small aggregates of disseminated pyrite.

Fossiliferous and non-fossiliferous chert occur. The fossils are still composed of calcite, but in some cases they are entirely of silica. While the greater part of the chert is massive and

Analyses of Missouri and Other Similar Cherts

	1	*2*	*3*	*4*	*5*	*6*	*7*
Silica (SiO_2)	98·23	98·17	98·92	98·71	99·46	99·23	98·60
Alumina (Al_2O_3)	2·18	·85	·48	·43	·29	·22	·52
Iron oxides (Fe_2O_3)							
Calcium carbonate ($CaCO_3$)							
Magnesium carbonate ($MgCO_3$)							
Magnesia (MgO)		·01	·02	·02	Trace	Trace	Trace
Lime (CaO)		·05	·03	·03	·04	·02	·10
Alkalies							
(Ignition)		·78	·42	·50	·34	·50	·40
	100·41	99·84	99·87	99·69	100·13	99·97	99·62

	8	*9*	*10*	*11*	*12*	*13*	*14*	*15*
Silica (SiO_2)	99·13	95·81	91·54	96·88	71·29	94 91	63·67	98·23
Alumina (Al_2O_3)	·16	1·27	4·52	2·48	2·43	2·85	2·20	·29
Iron oxides (Fe_2O_3)		2·20	·84					
Calcium carbonate ($CaCO_3$)		1·43	1·70	1·11	26·24	·75	32·12	1·00
Magnesium carbonate ($MgCO_3$)		Trace	·17	Trace	Trace	Trace	·57	
Lime (CaO)	Trace							
Magnesia (MgO)	·01							
Alkalies			·15					
(Ignition)	·20	·28	1·64					·12
	99·50	100·19	100·41	100·47	99·96	98·51	99·56	99·64

1. Fresh chert, Mississippian, Henderson Mine, Barry County, Mo.
2. Fresh chert, East Hollow, Belleville, Jasper County, Mo. (591).
3. Partly altered, same locality.
4. Altered to "cotton rock," same locality.
5. Fresh chert, Surprise Mine, Joplin, Mo. (591).
6. Blue chert, fresh, Bonanza shaft, Galena, Kan. (591).
7. Same locality, fresh (591).
8. Altered chert, same locality (591).
9. Fresh chert, Jonesboro, Montgomery County, Mo., Mo. Geol. Surv.
10. Altered chert, same locality.
11. Fresh chert, Lebanon, Laclede County, Mo., Mo. Geol. Surv.
12. Fresh chert with crinoid stems of calcite, Sulphur Springs, Ark.
13. Slightly altered Miss. chert, Roaring Springs, Newton County, Mo.
14. Fossiliferous, calcareous chert, Miss., Grand Falls, Newton County, Mo.
15. Fresh chert, Burlington formation, Columbia, Mo.

Analyses 1, 9-14, E. O. Hovey, Mo. Geol. Surv., vol. vii, pp. 727-739, 1894.

Analyses 2-8, Bull. 591, U. S. G. S., p. 222.

Analysis 15, Mrs. W. A. Tarr.

without bands of any kind, some nodules show bands, which are usually horizontal and but rarely concentric.

The nodules frequently contain cavities which are almost always lined with quartz crystals. Fossils in the chert, especially brachiopods, blastoids and horn corals, are often lined with such crystals. The spiralia of brachiopods are often preserved and covered with quartz crystals. The major part of the nodule is made up of the massive white or mottled chert but small masses of crystals may be included in the interior and very rarely there are concentric bands for a few inches around these masses. Some nodules consist of fragments of chert with more or less concentric banding. These have the appearance of having been formed, then broken up and recemented with silica.

The exterior is often bleached, soft, and porous, due to alteration. This shell, often an inch or more in thickness, is similar to the tripoli of southwestern Missouri. Such leached zones are generally lacking in the chert of the Ordovician and Cambrian formations in Missouri.

C. MICROSCOPIC DESCRIPTION.

The microscope shows the chert to be composed of opaline or amorphous silica, chalcedony, and quartz. The amount of amorphous silica in the Burlington chert is small. The chert consists mainly of a granular mosaic of chalcedony and quartz (see figs. 1, 2, and 4). Scattered throughout the slide are circular areas, from ·013 to ·026^{mm} in diameter, of very fine-grained chalcedony and quartz, the grains ranging from ·0006 to ·0013^{mm} in diameter. These circular areas may possibly be interpreted as representing the original form of the colloidal silica. Such globular forms have been described by many other authors (see especially, Jukes-Brown and Hill, W. Hinde and J. A. Howe), but have usually been regarded as the tests of foraminifera, although in some instances writers say that they are uncertain that such is the case. It would seem that these globules, which in some instances are amorphous silica, might show the structure of the original precipitate.

Spherulites are rare in the chert and those present are not perfect. They appear to occupy the areas between the fossils. The dark cross is very indistinct and the spherulites are small.

Both non-fossiliferous and fossiliferous chert were studied. They were examined especially for remains of originally siliceous fossils, but none were found. In the fossiliferous specimens studied, crinoid stems, fragments of brachiopods, and bryozoans were fairly abundant. Some of the fossils were practically replaced by silica, others were only partially replaced, and still others were unaltered. In all instances of alteration the calcite was replaced by quartz. The most coarsely crystalline areas and the largest grains of quartz are in the silicified fossils. Scattered through the grains of quartz there are many very small grains of calcite, these grains being the unreplaced residue of the original fossil. These calcite grains are so minute that they do not show any cleavage planes or other crystalline characteristics, except the interference tints.

FIG. 1.

FIG. 2.

FIG. 1 (x 40). Fresh chert, Burlington limestone, Columbia, Mo. Shows fine mosaic of quartz and chalcedony ; the larger areas of the latter show the interference cross.

FIG. 2 (x 40). Altered chert, Burlington limestone. Shows fine mosaic of chalcedony in the altered outer portion of a chert nodule.

When a fossil is only partially replaced the quartz crystals form a border around the calcite. This border may occupy fully one-fourth of the area of the fossil.

The dense white chert consists almost entirely of a mosaic of chalcedony and quartz. The grains which compose this mosaic are very minute. Probably not more than one per cent of the chert is amorphous silica. The amorphous silica remains dark during a complete rotation of the stage of the microscope between crossed nicols. Since it may show an interference cross at times, it may be more abundant than is stated. By reflected light it has a pale milky-white luster.

Much of the chert in the Burlington has an outer zone which is usually white and which is a weathered portion of the chert. This zone varies in thickness but is usually about an inch thick. Slides were made of the fresh and the altered portions of the same nodule in order to determine if possible what changes had taken place in the formation of this outer zone. The only difference observed was in the granularity of the chalcedony. The entire weathered zone was a mass of granular chalcedony (see fig. 2). The various fossils were readily seen and many grains of calcite were scattered through the zone, showing that calcium carbonate has probably been removed by leaching. The grains are very small, ranging from ·006 to ·0013^{mm} in diameter.

FIG. 3.

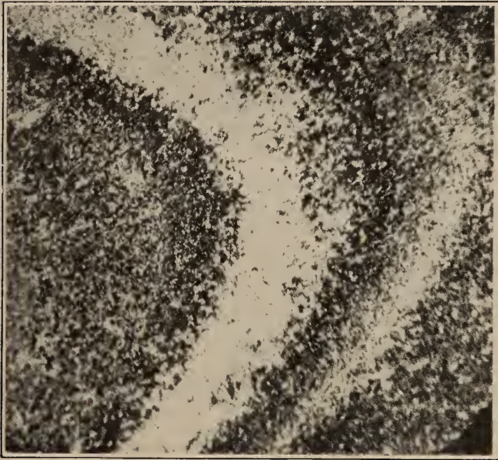

FIG. 4.

FIG. 3 (x 40). Banded chert, Burlington limestone. A mosaic of quartz and chalcedony. Dark bands due to carbonaceous material.

FIG. 4 (x 40). Fresh chert, Burlington limestone. Coarsely crystalline quartz and chalcedony. Large black and white areas are quartz, radial areas chalcedony.

Some of the slides show the banding which is a megascopic feature of the chert nodules (see fig. 3). The bands were found to be due to minute black specks of what appeared to be organic matter but which may be pyrite in part. The black specks were also seen in the lighter colored portions of the chert but were not so numerous as in the darker bands.

Other materials observed in the chert were grains of pyrite, usually small and never exhibiting crystal faces; a few grains of glauconite; and a small amount of a yellowish, dust-like material, which is probably clay.

D. MODE OF OCCURRENCE OF THE CHERT.

The Burlington limestone, of lower Mississippian age, is in this region from 100 to 175 feet in thickness. It is a heavy, irregularly bedded, coarsely crystalline limestone, mainly of a light bluish-gray color. The upper portion in some parts of Missouri is fine-grained and the lower is coarse-grained. The beds are not well defined, due evidently to a lack of silts, etc., in the waters and to rapid variation in the sizes of the calcareous materials. The beds are rather thick, but range from a few inches to several feet. The formation consists dominantly of the remains of crinoids, in fact crinoids are so abundant that the formation was formerly known as the "Encrinal limestone." The chert occurs throughout the formation but is especially abundant in the lower half near the top. The following sections of the Burlington at different localities in Missouri will show the distribution of the chert:

Section of Burlington limestone one half mile south of Columbia, Missouri.

Limestone: medium to coarse-grained; gray; contains stylolites and a few chert nodules	3 ft. 6 in.
Limestone: medium to fine-grained; gray. This is a very cherty zone; contains large masses of chert and considerable pyrite in small nodules; the large chert masses occur along planes	13 ft. 6 in.
Limestone: coarse, medium, and fine-grained; usually some shade of gray, bluish tints predominating; fossiliferous in places; stylolites rather common	13 ft.
Limestone: coarse-grained; fossiliferous; blue gray; contains stylolites, and chert nodules along a plane	4 ft.
Limestone: fine-grained, gray, stylolitic	2 ft.
Limestone: coarse-grained, grading upwards into fine-grained; blue gray to buff; contains chert in large nodules and is stylolitic	2 ft.
Limestone: fine-grained and medium to coarse-grained; blue gray; contains stylolites and chert	2 ft.
Chert: many large nodules along this plane	2 ft.
Limestone: medium to fine-grained, the texture varying rapidly both vertically and laterally; gray to blue gray; fossiliferous; contains stylolites and scattered nodules of chert	6 ft. 6 in.
Limestone: coarse-grained; light to very dark gray; stylolitic	1 ft. 6 in.
Limestone: medium to fine-grained; gray; has numerous stylolites	2 ft.

Section of Burlington limestone, Greene Co., Missouri.

E. M. Shepard, Geol. Sur. Mo., vol. xii, pp. 100–123, 1898.

Upper Burlington	
Shaly limestone: thin-bedded, compact, rarely oölitic, interbedded with layers of chert which are usually fossiliferous. The limestone is very fossiliferous, coarse-grained and varies from white to gray in color. Middle beds are coarse-grained, crystalline, soft, gray to white in color, have many nodules of chert, are stylolitic, and pass downward into a shaly, coarsed-grained limestone	200 ft.
Lower Burlington	
Limestone and chert: consists mainly of brownish yellow, blue, or slate-colored beds; fine to medium-grained; contains some fossiliferous bands; middle portion thin-bedded; top is mainly yellowish-white chert; much nodular chert and many lenticular layers of chert in the lower part	70 ft.

Section of the Burlington limestone, Calhoun Co., Missouri.

C. F. Marbut, Geol. Sur. Mo., vol. xii, p. 161, 1898.

Upper Burlington	
Gray or white, coarse-grained encrinital limestones in rather massive beds, with chert nodules scattered throughout; very fossiliferous	80 ft.
Lower Burlington	
Limestone: rather fine-grained; drab; somewhat earthy; has many crinoid stems and much chert, the latter occurring as masses throughout the limestone and as thin layers alternating with thin layers of limestone	30 ft.

Section of the Burlington formation in Pike Co., Missouri.

R. R. Rowley, Geol. Sur. Mo., vol. viii, p. 36, 1917.

Upper Burlington		
Thin bands of brown and yellow limestone and chert		20 ft.
Lower Burlington		
Blue limestone	4 ft.	
White limestone with very little chert	10–14 ft.	
White and brown layers of limestone with considerable chert in some beds	15–30 ft.	
Limestone	5– 8 ft.	50 ft.

The chert occurs chiefly in the form of rounded, elliptical, or lenticular nodules (see fig. 5). The nodules are found always with their longer axes parallel to the bedding planes but they are not necessarily along them, although such is a common occurrence. Rarely the lenticular masses merge so that the chert becomes essentially a bed. This is not a very common feature in the Burlington in this vicinity but in other localities it becomes a very important mode of occurrence, especially in the lower Paleozoic formation, where thick beds occur. Along a given plane the nodules are of a remarkably uniform size, but there are marked variations in size along the different planes. The rounded nodules are rarely more than six inches in diameter with a range of from three to six inches. The elliptical forms are from three to fifteen inches in thickness and from five to twenty-five inches in length. In ground plan the nodules are very irregular, but the dominant tendency is towards a lobed circularity. The lenticular nodules may vary from two to fifteen inches in thickness and some reach a length of several feet, as can be seen in figures 5, 6, and 7. Elliptical and lenticular forms are dominant.

FIG. 5.

FIG. 5. Banded chert nodules in Burlington limestone, Columbia, Mo. The notebook is 5½ inches long. Stylolite at (a).

The layers of chert nodules may occur along such bedding planes as the limestone shows, or they may occur at various intervals along planes in the beds (see fig. 7). This lack of a definite relationship to the bedding planes should be noted. A layer of nodules may occur in the central part of a thick massive bed of limestone which shows no evidence of a bedding plane along the plane of the chert even after weathering. The vertical interval between the planes of chert varies considerably; it may be from a few inches to many feet; but, whatever the distance, the planes of chert are always parallel to each other and to the bedding planes. The horizontal interval between the different nodules appears to be more uniform, as there seems to be a rather definite spacing of the nodules. This spacing of the planes of chert without reference to the bedding planes of the limestone and yet always parallel to them has a very important bearing upon the origin of the chert.

Fig. 6.

Fig. 6. Chert nodules, Burlington limestone, Columbia, Mo.

The shape of the chert nodules appears to be the result of flattening. The elliptical and the lenticular shapes are suggestive of this, as though the elliptical shape might be due to the spreading of the soft, globular masses of gel under their own weight. The bands frequently seen in the chert are further evidence of flattening. The great majority of these bands are horizontal and approximately parallel to the bedding planes. Those which have the same general shape as the exterior of the nodule always have the bands broadened at the ends of the nodules (see fig. 3). This is a feature which would have developed in a band if the material in which it is found had undergone a certain amount of movement laterally. Since these broadened parts of the bands are always found in those portions of the nodules which must have moved laterally if the nodule has been flattened, it is believed that they were caused by such a movement. The widened portions of the bands are usually of a lighter color than the narrower ones, showing that in the former the same amount of coloring matter has been distributed over a wider zone. When circular nodules contain bands, the bands do not show this widening.

FIG. 7.

FIG. 7. Shows chert nodules along a plane in Burlington limestone, Columbia, Mo.

The majority of the nodules show upon their surfaces many cracks (see figs. 8, 9, and 10) which may be three inches in depth and one-half inch in width at the surface of the nodule. They gradually die out in the chert. These cracks are usually filled with limestone which is always continuous with the limestone surrounding the nodules (see fig. 11). Many examples of reopened cracks are found. This reopening occurred after the complete consolidation of the beds and the chert. A coarsely crystalline, yellow or white calcite was deposited in these reopened joints. It may occur on one side or on both sides of the limestone in the original crack but is usually on one side only. The limestone which fills cracks may contain fossils just the same as the other limestone does. The cracks run in all directions through the nodules. Usually they are found on the upper surface but they may occur also on the lower. They are most abundant in the thicker portions of the nodules. The interesting structural feature, stylolite, is wonderfully well developed in the Burlington limestone. Very frequently the plane of the stylolites may follow a plane of chert nodules (see fig. 5, *a*). When such is the case the outside of the nodules shows the striated faces which are produced by the stylolites. Planes of stylolites have been observed passing through the limestone immediately over the cracks in the chert nodules and showing no evidence of deviation from a plane. This indicates that the cracks in the nodule were filled before the development of the stylolites. It is not thought, however, that the development of these cracks was due entirely to the flattening process, but that they were partly developed during the changes which the silica underwent in the early stages of the development of the nodule, especially during the change due to the loss of water.

Fig. 8.

Fig. 8. Chert nodule containing cracks filled with limestone. About one-third size.

E. AGE OF THE CHERT.

The question as to the time of the formation of the chert is a very important one in considering its origin, since the majority of the theories, and especially the commonly accepted one, appeal to the action of circulating ground water in accounting for the chert. If it can be shown that the chert is of a certain age, the time necessary for its formation can be estimated. This period of formation would be the time extending from the deposition of the limestone to the present, if the chert was formed by circulating ground waters. That the chert is pre-Pennsylvanian in age is shown by the following facts. It is a very abundant constituent of the Turkey Creek conglomerate at the base of the Pennsylvanian in Callaway County, Missouri. This chert contains an abundance of Burlington fossils, and, therefore, it must have been formed previous to the erosion of the Burlington in pre-Pennsylvanian times. Similar conglomerates are reported by Ball and Smith in their report on the geology of Miller County, Missouri, and by Buckley in his report on the Granby district in the Joplin zinc region.

FIG. 9.

FIG. 10.

FIG. 9. Cracks in chert filled with limestone.

FIG. 10. Limestone from above a chert nodule, showing ridges which once partly filled the cracks in the chert nodule (see fig. 11).

In the vicinity of Columbia, Missouri, there are numerous solution cavities in the Burlington limestone which are filled with chert fragments imbedded in Pennsylvanian shales and muds that had been washed into the cavities. Both of the foregoing facts indicate that the chert in the Burlington limestone was formed in pre-Pennsylvanian times, and that it antedates the erosional interval between the Mississippian and Pennsylvanian periods. It is not possible to fix the age any closer than this. That the chert is older than the stylolites is evident from the fact that the stylolites pass around the chert nodules. Though it does not indicate anything as to the age of the Burlington chert, it is important to note that at the base of some of the lower Paleozoic formations there is occasionally a conglomerate which contains sharply angular fragments of fresh chert derived from formations below. An example of this is the Joachim formation just over the Jefferson City formation (Ordovician) in Boone County, Missouri.

Fig. 11.

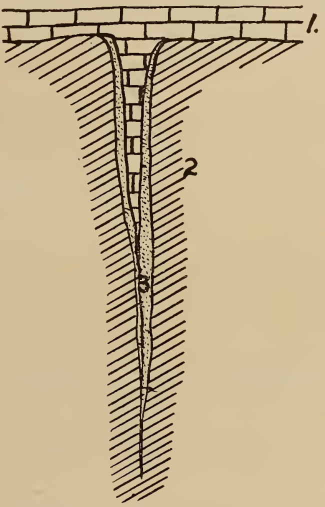

Fig. 11 (nearly natural size). Sketch of a crack in the chert (2) filled with limestone (1) and later after partial opening, with calcite (3). Such cracks always die out downward.

Another proof that the age of the chert is greater than that of the formation above it is found in the cave deposits in the Potosi dolomite (Upper Cambrian) in Washington County, Missouri. The materials in the cave deposits are quartz and chert. The latter is in angular fragments sometimes as large as one inch in length. These fragments were derived from the adjacent rocks and hence are of Cambrian age. During all the time since then, they have not been altered.

These various occurrences indicate that the period during which the chert was formed was very short in all formations, as it must have been formed before the erosion which produced the unconformity between the beds.

Further, the chert found in these conglomerates and solution cavities exhibits every feature seen in the chert embedded in the limestone around the cavities or under the conglomerates. It is no more altered and shows no evidence of having increased in size since the erosion interval between the Pennsylvanian and the Mississippian, or since Cambrian or Ordovician times in the older occurrences. Specimens from the conglomerate could not be distinguished from those taken from the fresh limestone.

It will thus be seen that the fixing of the time of formation of the chert in the Mississippian period greatly shortens the time available for ground waters to produce the chert nodules, since all the aggregation of the silica must have occurred previous to the erosion in pre-Pennsylvanian times. But what is also very strong evidence against the theory of origin by ground waters is the fact *that since Mississippian times there has been no growth or addition of material to the chert nodules*, as is shown by the absolute similarity of the chert found in the limestone, the conglomerates, and the solution cavities. Certainly ground waters have had ample opportunity to do more work of this character in the long interval of time since the Pennsylvanian than they had during the time the Mississippian formations were accumulating. Therefore, if the chert is formed by circulating waters, why have the nodules not grown? It cannot be claimed that the ground waters were less efficient solvents of silica at that time than at the present. Accurate and acceptable statements of the character of the solutions which were able to dissolve the silica from a rock in preference to dissolving the more easily soluble calcium carbonate are not generally recognized, though under the theory of the ground water origin of chert such solutions must have existed. In part, the ground waters were doubtless what Lindgren designates as the "calcium carbonate waters in sedimentary rocks," because the dominant circulation would be in limestone and shales; and, in part, sulphate waters from the Pennsylvanian shales. The Pennsylvanian shales were deposited above the Burlington limestone and contain considerable pyrite that would make possible the liberation of the sulphate radical. The following analyses show this to be true. Two spring waters from Pennsylvanian rocks near Columbia, Missouri show a great preponderance of the sulphate radical. Two spring waters from the Burlington limestone are dominantly calcium carbonate waters.

It is not probable that there has ever been much of a change in the character of the ground waters in this region, because

Analyses of Spring Waters from the Pennsylvanian and Mississippian formations near Columbia, Missouri.

	A	B	C	D
Cl	13·52	--	26·88	74·31
SO_4	2122·97	1563·42	3·23	--
CO_3	30·47	237·20	310·13	303·89
Na	8·90	44·14	18·31	47·51
Ca	318·56	535·12	111·78	89·20
Mg	53·85	106·20	6·83	10·22
Fe	246·65	29·21	--	--
Al_2O_3	269·26	13·47	5·32	31·25
SiO_2	43·31	24·96	12·08	31·41
Parts per million	3107·49	2553·72	494·56	587·79

A. Sulphate water from Bratton Spring in Pennsylvanian formation near Stephens station, northeast of Columbia, Mo. Analysis by Paul Schweitzer.

B. Sulphate water from spring in Pennsylvanian formation on University campus, Columbia, Mo. Analysis by Paul Schweitzer.

C. Carbonate water from Rollins Spring in Burlington limestone on University farm, one mile from Columbia, Mo. Analysis by Paul Schweitzer.

D. Carbonate water from spring in Burlington limestone on John W. Harris' Farm, eight miles south of Columbia, Mo. Analysis by Paul Schweitzer.

All analyses from vol. 3, Mo. Geol. Surv., 1892.
They have been recalculated to parts per million.

they have been working on essentially the same sorts of rocks since Mississippian times. A similar conclusion was reached as to the time of the development of the chert in the conglomerates and cave deposits of the Cambrian and Ordovician formations. The length of time since then is certainly great enough for the ground waters to have changed the chert if it were possible for them to do so. Therefore, if the waters were able to dissolve the silica in the earlier periods, why not during the later? It would seem that the evidence as to the age of the chert in the Mississippian is against the probability of the aggregation of the silica being due to ground waters.

III. ORIGIN OF THE CHERT.

A. OUTLINE OF THEORY.

The writer's study of the chert in the Burlington limestone has led him to the following view concerning its origin. The silica is believed to have been derived from the land by chemical weathering and transported to the sea by the streams as colloidal silica. Areas of low-lying lands, especially peneplaned areas, where chemical denudation predominates over mechanical, would be especially favorable for furnishing increased quantities of silica. Wide areas of igneous and metamorphic rocks would also be very favorable for furnishing colloidal silica, as large amounts of silica are liberated by the decay of such rocks. Present streams are transporting large amounts of silica to the sea, and under such conditions as peneplanation, especially on areas of igneous rocks, the amount of silica would be greatly increased. The theory advanced, however, is not dependent upon a peneplaned area as the source of the silica. The main idea is that silica was precipitated directly on the sea bottom after it had been brought to the sea by the streams.

The colloidal silica is believed to have been precipitated in the sea by the action of the alkalic salts in the sea water after it had undergone considerable dispersion, and a certain amount of concentration. Since it is the tendency of all colloids to aggregate into globular masses, a tendency which is very powerful in silica, it is believed that the silica thus precipitated on the sea bottom would tend to assume more or less globular to elliptical forms. Upon burial these forms would become compressed into their elliptical or lenticular shapes by the weight of the accumulating sediments. Fossils falling into this soft colloidal mass would be perfectly preserved.

The various physical features of the chert, its form, position in the beds, and microscopic characters, are well explained by the theory outlined above.

Attention should be called to the many points of similarity of Prestwich's theory, as given in his Textbook of Geology, to the one given above, although the writer's theory was developed before seeing that of Prestwich. The points of difference lie in the mode of precipitation, methods of aggregation, and the discussion of the various features of the chert. This paper develops the discussion as to the source of the silica and its transportation.

B. EVIDENCE FOR THE THEORY.

1. *Source of the Silica.*

(*a.*) *Carried to the sea by streams.*—Though some of the silica in the sea water may have been derived from the breaking down of silicates deposited upon the sea floor, it is probable that such a source would supply only a small quantity of the silica actually present. J. Murray and R. Irvine* state

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* Clarke, F. W., Bull., U. S. G. S., 491, p. 110.

that the amount of silica present is from 1 part in 220,000 to 1 part in 460,000. They suggest that organisms may obtain a portion of the silica they contain from suspended silicates in the sea water.

It is far more probable that the true source of the silica is the land and that the small amount in the sea water is evidence of the effectiveness of its removal by precipitation. An additional means of removal would be the organisms, as they would use the easily obtained colloidal silica in preference to breaking up silicates.

As evidence that the silica is derived from land the average percentages of silica carried to the sea by streams working under various climatic conditions should be noted. Clarke in Bulletin 616, U. S. G. S., has brought together analyses of streams from all over the world, and the work of the chemists of the United States Geological Survey has given us analyses of a great many of the streams in the United States. (See especially the following Water Supply Papers of the United States Geological Survey: No. 236, by R. B. Dole, and Nos. 339 and 363, by W. Van Winkle.)

Clarke gives the following averages for river and lake waters of the five larger continents:

	Average percentage of silica
Waters of North America	8·60
Waters of South America	18·88
Waters of Europe	8·70
Waters of Asia	9·51
Waters of Africa	17·89
General weighted average of all	11·67
Sir John Murray's average of river waters	10·75

These are general averages, so it will be of value to note some specific cases of the effect of the rocks in the area drained on the silica content of the rivers. The data available are best for those of North America. The following analyses of streams in Eastern United States were taken from Dole's paper, and the geologic data from the large geologic map of the United States Geological Survey, Professional Paper 71:

	Percentage of silica
Streams draining sedimentary and glacial areas	7·8
Streams draining pre-Cambrian sedimentary and metamorphic rocks	21·8
Streams draining pre-Cambrian and igneous rocks	28·5

The climatic conditions for the regions drained by these streams are those of the United States east of the 100th Meridian, so they vary widely.

Van Winkle gives much valuable data for the streams of the Pacific coast. The following are averages of the silica content of the California streams:

	Percentage of silica
Granite areas	14·3
Igneous rocks of all kinds	17·6
Igneous and sedimentary rocks	8·0
All sedimentary rocks	6·7
Average for California streams	14·3

The following figures show that climatic factors have little to do with the silica content of the streams:

	Percentage of silica
Average of all streams with a rainfall over 15 inches	14·4
Average of all streams with a rainfall of less than 15 inches	14·2

Oregon streams drain all three types of rocks and show an average silica content of 26·82 per cent, while Washington streams on similar rocks show an average of 21·1 per cent of silica. These streams are high in silica. As a rule a high silica content goes with a low total of dissolved solids. An example of this is shown by forty-five streams of eastern United States, which average more than 10 per cent silica and have 19·2 parts of silica to an average of 102 parts per million.

These citations are sufficient to show that the amount of silica being taken to the sea annually is very large, amounting on the average to 10 or 11 per cent and for many large streams or areas as much as 25 per cent.

Taking Clarke's averages again (page 105) we get the following amounts in round numbers of silica which is being added to the sea water every year:

North America	54,300,000 tons
South America	23,300,000
Europe	35,000,000
Asia	68,600,000
Africa	41,000,000
	222,200,000 tons

Such a large amount of material added to the sea annually is exceeded by that of only one base, calcium. We talk freely of the formation of great limestone beds from the material added to the ocean by the rivers, yet if all the calcium added annually entered into the formation of limestone (which is not the case, for some of it remains in solution, though all of the silica is deposited) it would exceed the amount of silica deposited at the same time only 3·11 times. What becomes of this silica? The writer believes the evidence indicates that it is in large part deposited, the deposits being now represented by the chert and flint nodules in limestone, the silica in siliceous limestone, and the colloidal silica in clays and shales. Another part is used by those organisms of the sea which require silica for their tests and other hard parts. If all or even a considerable part of the silica were to be used by organisms, large deposits of the siliceous remains of these organisms should be more frequent in our rocks.

(b) Derived from the land through chemical denudation.—When rocks decay at the earth's surface those elements are first removed which form salts that are readily soluble in the ground-water solutions. In the case of igneous and crystalline rocks these elements are sodium, calcium, magnesium, silicon, and to a minor extent potassium. In the case of sediments the elements first removed are calcium, magnesium and sodium with some potassium and silicon. The rate of removal will depend upon the rate of disintegration and decomposition of the rocks and these in turn depend upon the physiographic position, the climate, the vegetation, the character of the rocks, etc. The conditions for the most rapid removal of the soluble salts are when mechanical erosion lags somewhat behind essentially complete rock decay.

The amount of silica derived from igneous rocks is usually much in excess of that removed from sedimentary rocks. The average silica content of the streams east of the 100th Meridian which drain areas underlain by sedimentary rocks and glacial drift is 7·8 per cent, while of those streams draining areas of igneous and crystalline rocks it is 28·5 per cent.* The first figure given is not a great deal larger than the silica content of the Mississippi River at New Orleans, which is 7·05 per cent of a total salinity of 166 parts per million. Similar evidence is shown by analyses of streams in western United States.

As illustrative of the amount of silica available through weathering the following table is useful, as it shows how much silica is freed by the decay of the feldspars:

	Original percentage of silica	Percentage lost	Percentage of kaolin
Orthoclase	64·86	43·24	46·36
Albite	68·81	45·07	49·10

Leith and Mead estimate that there is 23·17 per cent of silica freed by the alteration of the average igneous rock. Under conditions of complete chemical decomposition practi-

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* R. B. Dole, W. S. Paper 236.

cally all of this silica is removed as colloidal silicic acid. If mechanical erosion does not interfere, any quartz present in the rock will finally be removed in solution and thus augment the amount derived from the decay of silicates.

These figures are sufficient to indicate that the chemical decay of rocks furnishes a large amount of silica to the streams and ultimately to the oceans.

(c) Relationship to periods of peneplanation.—A peneplain favors chemical denudation, and the deposits made in those periods during which the lands were low-lying should contain chert, the amount depending upon the petrologic character of the lands drained. During periods of low-lying land areas deposits of limestone and dolomite usually predominate over those of the other sediments, a fact that should be correlated with chemical denudation. It is in these same limestones and dolomites also that the greatest abundance of chert is found, unless there should be considerable silt deposited along the shores, in which case much of the silica will be carried down with it.

Campbell[*] has shown that when an area is flat and yet well drained, and the solutions contain acids which can attack quartz, the ground-water becomes a very good solvent and much quartz is removed. These acids are thought to be humic acid, but their efficiency as solvents for silica is seriously questioned. C. W. Hayes[†] suggests that the azo-humic acids are the chief solvents. This also is questioned. The same thing is true of the development of lateritic soils under conditions of chemical weathering, only the very insoluble substances remaining.

Table showing Geologic and Areal Distribution of Chert in the Paleozoic System.

Pennsylvanian.—Common in Missouri, Iowa, Kansas, Oklahoma and some parts of the Rocky Mountains.
Mississippian.—Abundant in lower part of the Mississippian formation in the Mississippi valley.
Devonian.—Found in lower part of some Appalachian states and central Mississippi valley.
Silurian.—A little reported in upper Mississippi valley and in the Appalachian region.
Ordovician.—Abundant in Knox dolomite and Shenandoah limestone in lower part of Ordovician and top of Cambrian. In Mississippian valley and to the southwest in Texas, New Mexico and Arizona.
Cambrian.—Upper Cambrian in Appalachian region, Mississippi valley, and in the western part of the United States.

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[*] Campbell, M. R., "Chemical erosion at baselevel," Bull. Geol. Soc. Am., vol. viii, pp. 221–226, 1897.

[†] Hayes, C. W., "The solution of silica," Bull. Geol. Soc. Am., vol. viii, p. 218, 1897.

It is readily seen that the chert in the Cambrian-Ordovician series is related to a time when the seas were extensive and the lands low-lying. The Silurian contains very little chert, due probably to the submergence of the portions of the continent which might furnish an abundance of silica and to the land areas being eroded rapidly, as in the eastern United States.

The shallow, interior lower Devonian sea received some silica along with the calcareous salts. Some silica is found with the formations of the southern Appalachians.

In Mississippian times the Mississippi valley region was again receiving much silica, for there is an abundance of chert in the lower formations, especially in the Burlington.

With the change to clastics in the Pennsylvanian the deposition of silica in this region came to a close. This change was the result of renewed mechanical erosion, and the great quantities of shale of this period were doubtless due to long-continued chemical weathering on the low-lying lands of the continent. Some chert occurs in the Pennsylvanian of the Cordilleran region where carbonate rocks continued to be deposited.

On the whole, it appears that the abundance of chert in the formations of the various periods is more or less dependent upon the character of the adjacent lands. If these are low the chemical removal of much silica is favored and chert may result, but if they are high enough to permit mechanical erosion to remove the products of weathering, the limestone off shore will be relatively free from silica. Low-lying lands, then, such as are developed when a given region approaches a peneplain, become a probable source of silica and favor the deposition of much chert.

(d) Derived from shore work.—There is no reason to think that the decomposition of the rocks along the sea shore does not furnish silica to the sea water. Though the action of the waves is largely mechanical, the rocks, after they have been broken up, are attacked chemically by the sea water and further decomposition occurs. This alteration furnishes a certain amount of silica which is added to that already present in the water.

2. *Dispersion of Silica in Sea Water.*

The colloidal silica carried to the sea by streams is distributed by the currents in the sea water, for the rate of diffusion of colloids is low, probably less than the movement of the currents. Since the material is in solution it is readily transported as far as the silica can be carried before becoming coagulated. Dispersion is aided by the slow rate of concentration of the silica. Certain salts in solution aid in this dispersion by preventing the formation of the gel. Hydrogen sulphide may do this, and so also may some potassium salts and other compounds.

Sea water is an electrolyte, hence there is a tendency for the silica to be deposited near the shore, if sufficiently concentrated, and such disposition undoubtedly occurs.

The direction and distance of transportation will depend upon the currents. In shallow epi-continental seas, currents are probably stronger than in deeper bodies of water. The Burlington limestone shows cross-bedding and this with the lenticular character of the beds suggests a shallow sea. Evidently the currents were strong enough to produce cross-bedding. Broad, shallow interior seas of warm water would favor the development of currents.

Presumably the salinity of these seas was not greatly different from that of the present oceans, and, therefore, the wide distribution of the chert was made possible because a very high salinity would have meant rapid deposition of the silica near shore.

Another important consideration that would influence the distribution of the silica would be the character of the water near shore. It is well known that the saline water is sufficiently dilute to act as an electrolyte and has a marked influence upon the rapidity of sedimentation, the fine clays and silts being rapidly thrown down in saline waters while they remain suspended for a far longer period of time in fresh water. If the waters were receiving considerable clayey material it would be deposited relatively near shore. The colloidal silica present in the waters bringing in the clay and silts would be coagulated by the electrolyte and carried down by the sinking clays and silts, because even a very small amount of the gel would adhere to the fine silts. When the waters were relatively free from such fine silts the currents would transport the colloidal silica to a much greater distance.

3. *Deposition of the Silica.*

(*a*) *Experimental.*—In order to determine to what extent a water of the composition of the sea water would cause coagulation of the silica brought to the sea by streams, a series of experiments were made with solutions which would approximate those of the sea water and streams. As bivalent ions are relatively more effective in causing coagulation than univalent ions, solutions without bivalent ions were tried as well as those containing them. While these experiments were not exhaustive, they were in sufficient detail to show conclusively the character of the reaction in such solutions. The solutions representing the sea water contained the amount of salts in solution by weight as found in sea water, that is, 34,400 parts in 1,000,000 parts of water. Not all the ions present in the sea water were added, Mg being the only bivalent ion used, but if a solution consisting mostly or entirely of univalent ions could cause coagulation then one containing bivalent ions would be still more effective. One of the solutions used contained NaCl, K_2SO_4, and $MgSO_4$, and the other one contained only NaCl.

Preliminary experiments with dilute solutions of salt and silicic acid of unknown strength showed that the silicic acid would be coagulated at once. Then solutions like those described above were used in conjunction with a dilute solution of water glass, hydrous sodium silicate, the amount of silica added being from 13 to 27 parts per 1,000,000. This represents about the range of the silica content of a great many of the present rivers. Many rivers in the United States are carrying more than 30 parts per 1,000,000 of silica. Some of these are draining areas where the rate of mechanical erosion is low. That the method of precipitation is effective for a low silica content is shown by experiment three.

Experiment 1.—A solution representing sea water was made, containing 34,400 parts of solid matter per million, which is the average strength of sea water. The salts used in making the solution were NaCl, $MgSO_4$, and K_2SO_4, the relative amounts of each taken being those found in actual sea water. Silica in the form of water glass was then added to the solution. The amount of silica added was at the rate of 27·07 parts per million. The result of the experiment was an immediate and heavy precipitate of gelatinous silica. No subsequent change occurred in it.

Experiment 2.—In this experiment the solution of sea water used was prepared by adding only NaCl, but at the normal strength of 34,400 parts per million. Then the same amount of silica was added as in the first experiment, i. e., at the rate of 27·07 parts per million. The result was an immediate precipitation of silica gel, but a much less heavy one than in the first experiment. At the end of two hours it had coagulated into small globules on the bottom of the container, but after that no further change took place.

Experiment 3.—In the third experiment sea water as described in experiment 1 was again used and a smaller amount of silica was added. The amount added was at the rate of 13·53 parts per million or just half the amount that was used in the first experiment. An immediate and heavy precipitate occurred. No change occurred in it upon standing.

Experiment 4.—In experiment 4, experiment 2 was repeated except that twice the amount of silica was used, i. e., 54·14 parts per million. The precipitate was immediate but not heavy. No subsequent change took place upon standing.

Experiment 5.—In the fifth experiment half of the solution obtained in experiment 4 was taken and to it was added the usual amount of $MgSO_4$ found in sea water. The result was an immediate and large increase in the coagulated material, so that it resembled in amount and appearance the precipitate formed when $MgSO_4$ had been among the original constituents of the water used, thus showing that a bivalent element has a marked effect in causing an increase in the amount of gel thrown down.

These experiments are sufficient to show that quantitatively and qualitatively the sea water is able to throw down the silica added to it by the rivers. The silica is probably not precipitated immediately but accumulates in the form of the colloid until it is of sufficiently high concentration to be coagulated. This explains the occurrence of the silica in layers at varying intervals in the limestone.

(*b*) *Cause of precipitation.*—The precipitation of the colloidal silica is believed to have been due to the coagulating effect of the saline water of the sea, which can be regarded as essentially an electrolyte. The colloidal silica carrying a negative charge prevented the aggregation of the suspended colloidal particles, as they mutually repelled each other. The alkalies and alkaline earths in the sea water carry positive charges, so when the negatively charged ions of the colloidal silica came in contact with these positively charged ions, the negative charge was removed and the colloidal particles of silica were able to unite into larger aggregates or to coagulate, as it is generally called. With the removal of this electrical charge the strong surface tension of the silica became an important aid in bringing about a union of the dispersed particles.

The ions of solutions of sodium, potassium, calcium, and magnesium salts, all of which carry positive electrical charges, are especially effective in bringing about the removal of the negative charge from the colloidal silica ion. This is especially true of ions with two charges, like calcium and magnesium. Recent work by Cox, Dean, and Gottschalk* has shown that calcium bicarbonate is an important precipitant, a fact which probably has an important bearing on the common occurrence of chert and flint with limestones and dolomites.

It is supposed that the coagulated particles assumed a spherical shape as they united to form molecules† and that these molecules were further aggregated to form spherical masses.

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* Cox, G. H., Dean, G. S., and Gottschalk, V. H., Mining Experiment Station, Mo. School of Mines, Bull. 2. vol. iii, pp. 9–15.

† It is estimated‡ that the molecules of colloidal silica have a molecular weight of 30,000, which indicates something as to their large size.

‡ Tolman, C. F., Jr., and Clark, J. D., Econ. Geol., vol. ix, p. 561, 1914.

As consolidation proceeded the colloidal silica crystallized in part as chalcedony, and in smaller part as quartz, leaving a very small amount of residual colloidal silica as opal.

When the waters contained much silt and clay, whose ions, like those of the silica, carried negative charges and were thus precipitated through neutralization, the silt and clay were carried down along with the coagulating colloid. The colloid had a marked tendency to aggregate around the small, solid particles and bind them together, thus causing the rapid sedimentation of the silts. An abundance of silt, therefore, meant that the major part of the colloidal silica would be removed from solution before it could be carried to the more distant parts of the interior sea which were relatively free from clastic material. The great abundance of plastic clays (plasticity in clays is largely due to colloids) and siliceous shales probably owe their origin to this tendency of colloids to be carried down with silts.

Very low lands, where chemical denudation exceeds mechanical, would mean relatively clear waters at the margins of the seas and this would permit the dispersal by shore currents of the abundant colloids added to the seas by the streams. Such silica would be deposited with the limestone. An abundance of silts carried into the sea water would mean the deposition of most of the colloidal silica near the shores and the deposition of relatively pure limestone beyond.

(*c*) *Form of the precipitated silica*—The result of the coagulation was the production of masses which were probably spherical. The microscope shows that the spherical form of these early molecular aggregates was retained in the larger masses. These parts are now largely chalcedony and are present in great numbers in the chert. There is absolutely no evidence that they are of organic origin. The spherical character of the first aggregates was thus passed on to the larger masses, primarily because of the effect of surface tension, which causes the gel to assume such a shape. The spherical aggregates increased in size as more material was added to them while they were being carried along by the currents. When the size of the gel-mass was sufficiently large to cause it to sink it found its way to the bottom.

If the waters were shallow, currents and waves might have shifted and rolled the masses of gel about, thus tending to form larger aggregates. This rolling aided in producing the banding of the chert, but only the relatively small masses were rolled about. Circular bands are found only in the smaller aggregates, those not exceeding 8 to 10 inches in diameter. If the currents were unable to move the masses, the latter would have grown through mass action, the larger aggregates attracting the smaller ones. As growth proceeded, the banding and mottling of the chert was developed, due to carbonaceous materials that are believed to have been included in the chert as it grew. The banding is not so common as the mottling because it was exceptional for the globular masses of colloidal silica to be rolled around by the sea water, thus acquiring the carbonaceous matter. These masses may have been broken up at times by movements of the sea water, especially after the gel had set, thus furnishing the angular fragments in other masses of chert. As no masses of limestone have ever been observed which contained these circular bands, it is concluded that they do not owe their origin to replacement, but are original structures of the chert.

These small gel masses would tend to become spherical and might retain this form up to a certain size. Above this size they would tend to become elliptical (see fig. 5) through their own weight, just as a drop of mercury does. The final shape would be due to the pressure of the overlying sediments which would tend to flatten the nodular masses. This is the typical shape of 99 per cent of the nodules seen in the Burlington limestone and there are millions of them in it. It is also the characteristic shape of the chert and flint nodules in other formations.

In this connection it is worth noting that iron, manganese and aluminum oxides often occur in rounded nodular forms which are evidently inheritances of a colloidal state.

A very common feature of the nodules is the great number of cracks developed in them. (See figs 8, 9, and 10.) These cracks are without definite orientation and extend down into the chert from a fraction of an inch to three inches or more and may be half an inch wide. They never pass through the chert. These cracks are filled with limestone that is continuous with the limestone surrounding the chert. This vein of limestone was forced into the chert while the limestone was still unconsolidated. Later, apparently while the stylolites were being formed, there was a reopening of some of the cracks and coarsely crystalline yellow or white calcite was deposited in them (see fig. 11).

These cracks developed during the consolidation of the silica gel. The colloidal silica gel contained large amounts of water which were gradually lost as the gel passed through the opaline state to the finely crystalline chalcedonic state, where it is essentially anhydrous. Much of the water was lost during the early stages of consolidation and this part left no evidence of its former presence in the structural features. During the last stages the results of the shrinkage caused the chert to crack. This was especially true in the large masses which were being flattened out by the weight of the overlying materials, and the soft calcareous muds from above forced into the cracks. When crystallization eventually occurred in the limestone the material in the veins crystallized along with the main mass.

The shrinkage of the gel through a loss of water developed small cracks on the interior of the nodule, into which some silica was carried and eventually crystallized as a drusy surface of quartz crystals. The slow loss of water from these internal cracks permitted the quartz to grow into large crystals. Rarely, various sulphides were deposited in these shrinkage cracks. Such cracks are usually found in the small, nearly round nodules.

When several nodules were formed close together they united to form a larger mass which shows a lobed circular outline from the flattening of the several spherical aggregates.

When an excessive amount of silica was added to the sea for a time a more or less continuous bed of chert was produced. This would occur when the rate of removal of silica from the land exceeded that of the calcareous materials, and during periods of peneplanation or base leveling.

(*d*) *Associated minerals.*—Colloids have strong absorption properties and since salts of the ordinary metals can freely pass into or through colloids the presence of sulphides in the resulting chert would be expected if the metallic ions were in the sea water. This is found to be true, as pyrite, sphalerite, chalcopyrite, and rarely galena occur in the chert nodules, usually in the cracks and in the interior of fossils. These minerals are generally well crystallized, which is a feature characteristic of minerals crystallizing under such conditions.

4. Relationship of Chert to the Enclosing Rock.

Everywhere in the Burlington limestone the chert occurs in nodules, elongated masses, and beds. The planes along which it occurs are at irregular intervals because of the variation in the rate at which the material was added to the water and the slowness of concentration. It may or may not appear along the bedding planes. When present in large amounts the numerous nodules and masses in the massive limestone beds are found along a common plane; that is not always a bedding plane. This absence of bedding planes is partly due to the rapid variation in the size of the materials deposited and largely to the absence of fine silts in the areas of limestone deposition. This absence of silty material is evidence favoring the view that low-lying lands were adjacent to the Mississippian sea.

The occurrence of the chert along a plane which is not a bedding plane should be noted, as those who think that chert is secondary hold that the bedding planes furnish places of egress for the solutions. If there are no bedding planes to guide the solutions, how can the distribution of the chert along a plane be explained? If there are solutions in the limestone in other places than along the bedding planes (which seems unlikely), it is not possible that they could develop the nodules and masses of chert along a plane without a physical guide. Furthermore, there is nothing of significance in the chemical composition of the limestone which could cause this type of distribution. Though it has been reported that all gradations of chert into limestone and dolomite can be found, the writer by careful examination has found that the contact of the chert with the limestone is usually sharp. However, this would not necessarily be the case if the silica were an original deposit, for there is no reason to believe that the deposition of silica should cease abruptly. Rather there should be more or less of a gradation, and the definiteness of the line of contact is, therefore, a remarkable feature. It is evidence of the control that the larger mass of silica has over that in the soft muds around it. The outer parts of the nodules are usually richest in fossils or calcite, a thing to be expected.

Silicified limestone, on the other hand, shows gradations which are easily detected.

The relationship of the chert to the limestone is best explained by the theory of their contemporaneous deposition.

5. *Fossils and the Silica.*

The relationship of the fossils to the chert is significant. Though not all of the chert is fossiliferous this is the usual mode of occurrence. The fossils are scattered throughout the chert, or they may be confined to the outer part, or to bands running through the nodules. This outer zone is from one to five inches wide. Some fossils occur in the lower parts of the chert nodules, but most of them are found in the upper parts. All the fossils found in the Burlington limestone may be obtained from the chert. Crinoid stems are the most numerous, just as they are in the limestone.

The numerous fossils in the chert are composed of calcite, only a small percentage of the total number being silicified. In the microscopic sections studied the outer part of the calcite of some of the fossils was slightly silicified, but this is not the rule, for the thousands of casts of fossils examined in the weathered chert show that the fine markings of the fossils are perfectly preserved in the silica. Often the spiralia of the brachiopods and the septa of the horn corals are perfectly preserved in the chert by being silicified or by being coated with silica. In many instances, when the fragment of the crinoid stem is not too long, the axial canal has been preserved by becoming filled with silica.

The fossils in the chert were included in it as it accumulated on the sea bottom. Organisms fell upon or into the soft colloidal silica and were buried. The hard parts of the organisms remained and the organic matter upon its removal gave rise to cavities in the silica. The remains of blastoids are almost always hollow, but both valves of a brachiopod must be present in order to form such a cavity on its interior. Some of the corals are hollow but most of them are partly filled with chert.

These internal cavities are lined with drusy quartz crystals, a feature which is readily explained, because the cavity remained open and was filled with water and some silica. The silica crystallized slowly from the solution and replaced the calcite of the spiralia of the brachiopod and the septa of the corals and then lined them with drusy crystals. Small crystals of sphalerite, pyrite and chalcopyrite are found on the interior of a few of these fossils. Salts of the metals when in solution readily penetrate colloids, as has been shown by Tolman and Clark,* and precipitation could have taken place on the interior by means of hydrogen sulphide, which was formed by the decay of the organic matter of the organism.

Several specimens have been found in which the chert entirely surrounds one of the Syringopora corals (see fig. 12). The tubes pass entirely through the nodules. Evidently the coral was surrounded by the colloidal silica and preserved. This mode of occurrence is interpreted to mean that the coral and the chert nodule were growing at the same time. It does not appear probable that the coral would be so perfectly preserved in an upright position if it had simply been buried like the numerous remains of the crinoids which apparently fell into the silica. Not a single occurrence has been found in which this coral was preserved elsewhere than in the chert.

Still another important feature is exhibited by the chert. This is the imprint of corals, crinoids, and brachiopods on the exterior of the nodules (see fig. 13). These imprints are very perfect and show how the fossil was forced down into the soft silica gel.

6. *Absence of Siliceous Organisms in the Burlington.*

If siliceous organisms furnished the silica for the chert, as is claimed by those who think chert was formed by concentration of silica from the surrounding rocks, evidence of this former existence should be found in either the chert or the limestone. A very careful search was made in the thin sections of the chert for traces of such organisms, but none were found. The

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* Tolman, C. F., Jr., and Clark, J. D., Econ. Geol., vol. ix, p. 559, 1914.

chances of finding such remains are considered to be best in the chert, because the formation of the nodules is supposed to take place around siliceous organic remains. Why such deposition would be the case it is difficult to see in view of the fact that the silica in the fossils is supposed to be readily soluble.

The limestone also was carefully examined for traces of siliceous organisms. A large quantity of the rock was carefully dissolved in weak acetic acid and the insoluble material examined with a microscope. No traces of siliceous fossils were found. There was a small amount of silica in the residue in the form of euhedral quartz crystals, the largest of which rarely exceeded $0{\cdot}1^{\mathrm{mm}}$ in diameter, most of them being much less. That all traces of any siliceous organisms which may have once been in the limestone have been removed is too improbable to believe.

Fig. 12

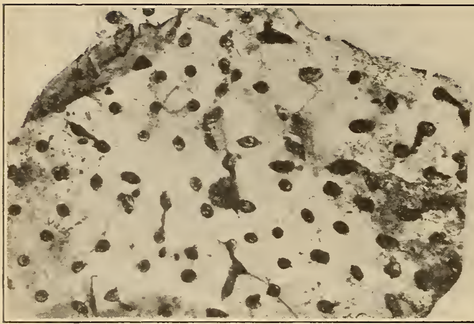

Fig. 13

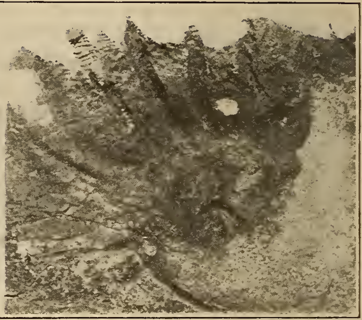

Fig. 12 (reduced one-half). Chert containing a Syringopora coral surrounded by chert. The tubes are nearly vertical in the chert. From Burlington limestone, Columbia, Mo.

Fig. 13 (slightly reduced). Impression of a crinoid on the exterior of a chert nodule. From Burlington limestone, Columbia, Mo.

It is concluded, therefore, that the silica in the chert was not derived from siliceous organisms in the adjacent limestone. The inclusion of the fossils in the chert is believed to have taken place when the nodule was forming on the sea bottom, the remains of the organism falling into the soft colloidal silica and being buried and preserved.

7. *Conclusions as to Origin under the Theory.*

It is believed that silica which formed the chert nodules in the Burlington limestone was deposited upon the sea bottom in the form of colloidal silica simultaneously with the deposition of the calcareous muds which formed the limestone. This silica is believed to have come from the land, probably during periods of peneplanation, and then to have been dispersed by the currents in the sea. Precipitation occurred by means of electrolytes in the sea water, and the silica gel assumed a globular form on the sea bottom, which form passed, in large part, into an elliptical shape through the weight of the gel itself and later on account of pressure from the beds above. The distribution of the chert in the formation and its relationship to the fossils are interpreted to favor this view. Absence of siliceous organisms in both chert and limestone is also evidence for the theory.

8. *Evidence Against the Replacement Theory.*

Since the view that chert owes its origin to the replacement of limestone by silica is so prevalent, the evidence which the writer has collected against that theory will be given. This evidence will be given under the following heads: (1) the position of the chert in the limestone; (2) no adequate source of the silica; (3) structure of the nodules; (4) the fossils in the chert, and (5) the weathering of chert.

(a) Position of the chert in the limestone.—Chert occurs in all parts of the beds of limestone. It may be along the bedding planes (not very common) or anywhere in a bed, but always it is along a plane, a fact which is recorded in many places in the literature concerning chert. This occurrence in any part of a bed or formation without reference to structural features which might induce deposition along a given plane is a fact that has not been suitably explained by the replacement theory. There is nothing in the chemical character of the rocks that will account for this method of distribution of the chert.

In this same connection there is the question of the permeability of the limestone. If replacement is to occur the solutions bearing silica must enter the rock in some way. Water does not circulate through limestone except along the divisional planes, and when the chert nodules are at a distance from such planes this distribution should be considered as evidence that the chert was not formed by replacement of the limestone. In most dense fine-grained limestone the porosity is less than one-half of one per cent, hence the permeability would be much less. Such spaces are primarily capillary, and it is not probable that the circulation of solutions in capillary spaces would ever replace a large mass of limestone with silica.

The belief that solutions are especially active as depositional agents along bedding and joint planes in limestone can be viewed in the opposite light, viz., that they are more active as solvents along these planes. It is well known that wherever there is an active circulation in limestones, there solvent action is greatest. So why should we think that such solutions will deposit silica? Cox, Dean, and Gottschalk* have recently shown that colloidal silica, which is the usual form in which silica is transported, is precipitated rapidly by calcium carbonate in the presence of carbon dioxide. As limestone dissolves when there is an abundance of CO_2 in the solution, there would be a rapid deposition of any silica present along the solution cavities. Such, however, is not the case. Throughout this area there is no evidence of any deposits of silica in fissures, joints or bedding planes, whatever their position may be. There is removal of limestone, but no silica is deposited in the opening so produced. The reactions in the limestone are dominantly those of solution and not deposition.

The position of the chert in the beds of limestone, its occurrence along planes in the absence of a localizing agent, and the impermeability of the limestone are evidence against the replacement theory, unless the replacement takes place on the sea bottom.

(b) No adequate source of the silica.—In order to have replacement occur in a rock, silica must be derived from the rock itself or be introduced into it from outside sources. In the case of the Burlington formation the limestone has been shown to contain but very little silica and that was in the form of quartz grains. Embedded in the limestone as these quartz grains are, they are less available than even silica in sandstone would be. Other limestone and dolomites which were studied prove that the silica could not have come from the beds themselves. In this case an outside source must be sought. What that source might be is not suggested by the advocates of the replacement theory, apparently because no source is evident. Even if a source were available the difficulties of taking the silica into solution and holding it there are great. Most ground waters are either carbonate or saline and thus are weak electrolytes and do not contain much colloidal silica. The exceptions to this are certain hot sodium chloride waters.† From the ground waters themselves there is little evidence favoring the view that they are actively transporting colloidal silica in more than very small quantities. In carbonate rocks the transportation difficulties are even greater, as in the presence of CO_2 in the water calcite rapidly causes the precipitation of silica, as shown by Cox, Dean, and Gottschalk. This might be taken as evidence favoring the formation of chert, but it must not be forgotten that the active circulation is along only the

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*Cox, G. H., Dean, R. S., and Gottschalk, V. H., Bulletin 2, vol. iii, pp. 9-12, 1916, Mining Exp. Sta., Mo. School of Mines, Rolla, Mo.

†Lindgren, W., Mineral Deposits, pp. 50-53.

larger divisional planes and if there is deposition it should occur there. This is not the case, for the chert is most often found in other places than along the divisional planes.

(c) Adverse evidence of the structure of the nodules.—The elliptical form of the nodules is assumed by many to mean that silica was deposited around a nucleus and, then, since the concretions were thought to occur always along bedding planes, that material was added to the sides of the nodules, thus giving them the elliptical shape. Since the nodules occur independent of such planes this argument has no weight.

If replacement has occurred, either the structural features of the replaced limestone should be preserved, or the limestone should be displaced by the growth of the concretion. Careful examination of thousands of specimens has failed to reveal a single one with the structural features of the limestone preserved. Neither has a single nodule showing displacement of the beds been found. It was thought that one such occurrence was found in the Jefferson City dolomite (Ordovician), but careful study led to the conclusion that the displacement was apparent only, being really due to the deposition of the overlying sediments around the mass of colloidal silica.

The occurrence of angular brecciated fragments of banded chert in the chert nodules is evidence against replacement, for no solution could deposit a small, sharply angular, banded area of chert within a larger mass. These fragments are not replaced limestone, for no such structural feature was ever found in the limestone. This feature is undoubtedly original.

The cracks in the chert were not developed in hard, solid chert, for if a deformative movement were to fracture such a rock, the crack would certainly extend through the nodule as the later fractures have done. However, the limestone-filled cracks which had developed in the chert did not extend through them and are not necessarily in the same position on the upper and lower sides.

Furthermore, the fact that the limestone in the cracks is continuous with that outside the chert nodule proves that the cracks developed before the limestone was consolidated. This being the case, the views that the chert is of recent (geologically speaking) origin are incorrect.

It is impossible to believe that any ground-water solution could replace a mass of limestone and leave a few long narrow areas as cracks, so this view can be dismissed. The cracks are undoubted proof of the early formation of the chert and of its deposition as an original mass of colloidal silica.

The cracks on the interior, which have drusy linings and occasional crystals of sphalerite, pyrite, or chalcopyrite, tell the same story as do those in the outer portions.

The mottling and banding in the nodules are readily explained by the original deposition theory but difficult to explain by the replacement theory unless they are (which they are not) structural features of the limestone, for replacement, molecule by molecule, does not shift materials about and cause them to become banded or mottled.

(*d*) *Fossils in the chert.*—The well-preserved internal structures of the calcareous fossils in the chert (brachiopods, entire blastoids and corals) show that they have been protected by some medium. These structures are lacking in the fossils in the limestone, in fact, the blastoids are rarely found in the limestone at all. The fossils in the chert do not show evidences of having been crushed, broken and deformed like those in the limestone do. According to the replacement theory this should have been the case, for not all the replacement occurred before the recrystallization of the limestone or the deformation movements of the region, in fact replacement should be going on now more actively than in past times. The great numbers of calcareous fossils in the chert (few of them having been silicified) point to some mode of protection. That protection was provided by the dense silica gel after it became firm.

Fossils comprise the most of the calcareous material in the chert. If replacement has occurred why were not the fossils replaced? The size of the particles could not have been a factor because many very small fossil remains are found in the chert. The axial canal of a crinoid stem which was filled with silica, though all other parts remained calcareous, was found, which shows that the fossils were simply surrounded by the silica and not replaced.

Thus the fossils in the chert are thought to be original constituents of the chert, the organic remains having fallen into the soft colloidal gel on the sea bottom and been completely covered by the addition of more material on the exterior. In this way they were protected and preserved.

(*e*) *Weathering of the chert.*—The chert shows a weathered zone on the exterior which is from a fraction of an inch to two inches or more in thickness. This zone consists of a white, porous material similar to the tripoli of Newton County, Missouri. It is coarser, however, and more porous than the tripoli, and although both have been interpreted as having the same origin the evidence is not yet conclusive.

This weathered zone has essentially the same chemical composition as the unaltered material (see analyses). The calcium carbonate is lower, as a rule, and it contains slightly more water. The microscope shows that it consists of grains of chalcedony and quartz which are smaller than those in the dense unaltered chert. The chalcedony appears to be growing at the expense of the quartz. Water may find access to the interior through joints and the same type of alteration takes place as on the exterior.

These changes show that the nodules, instead of increasing in size at the present time as they should be doing if they are due to circulating ground waters, are actually being attacked by the ground water where it can come in contact with them. However, the weathering of chert appears to take place very slowly, for chert on the slope and in the streams shows no evidences of alteration, while that in the conglomerate at the base of the Pennsylvanian and Ordovician is still fresh. The calcareous materials are slowly removed when the chert is exposed to the weather. This leaves the fossiliferous fragments of the chert very porous.

Shepard* has called attention to the fact that when a piece of chert is broken, the two pieces will not fit together exactly. This is due to the very brittle character of the chert. It has been involved in the movements that have occurred in the region and the stress to which it was subjected produced incipient cracks and strains. The chert when broken along these cracks springs back into its original unstrained shape. Temperature changes are very effective in the disaggregation of the chert. As a result the talus consists of small, sharp, angular fragments of chert and larger pieces of limestone. On the face of a bluff the chert weathers out faster, forming re-entrants.

There is no evidence to support the view of Ulrich,† Lee,‡ and others that the chert in the dolomites of S.E. Missouri is a product of weathering. Lee states that coarse chert float leads up to apparently non-siliceous dolomite, but that the weathered surface can be seen on close inspection to contain various shapeless forms of chert. These pieces are assumed to be in process of growth at present. He states further that "freshly cut surfaces of such beds in quarries and road cuts do not show chert." Yet Lee (page 13, of his report) gives a 215-foot section of the Gasconade formation with chert distributed throughout most of the formation, and on page 12 states that "the lower beds of the Gasconade penetrated by the drill holes are denser and contain more dense bluish chert than the upper part of the section." Evidently chert does not occur in the beds below the surface and certainly all this chert is not of the type which occurs in beds. In short, Lee furnishes sufficient

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* Shepard, E. M., Geology of Greene County, Mo., Geol. Surv., vol. xii, p. 111.

† Bain, A. F. and Ulrich, E. O., "Copper Deposits of Mo.," U. S. Geol. Surv., Bull. 267, p. 29.

‡ Lee, W., Mo. Bureau of Geol. and Mines, vol. xii, pp. 15–19, 39–40.

evidence to disprove his own and Ulrich's statements. The chert in the conglomerates at the base of the various formations in Missouri is sufficient proof that it is not due to weathering, especially in view of its fresh character in such conglomerates.

Naturally, chert could not accumulate on the face of a bluff, though such a very insoluble, resistant substance as chert could well be expected as a residual material on all slopes where the rate of erosion was not sufficiently fast to remove it. This is the condition over the entire Ozarks, and cannot be interpreted as evidence that the chert is growing at the surface at the present time.

It is always the resistant materials which are left behind in the mantle rock, and men have long recognized that the chert (usually called flint in Missouri by laymen and many geologists) is insoluble and accumulates abundantly at the surface. Certainly we cannot believe that the chert is growing in the residual clays. If the chert masses are increasing in size they should show signs of cementation at the surface, forming chert breccias, and in many parts of Missouri, at least, a solid sheet of chert over the entire surface, for there certainly is enough residual chert at the surface to supply all the silica necessary.

A careful study of the residual chert failed to show any fragments more or less dissolved or any to which material was being added.

Deep drill holes in all parts of the state, which have penetrated the formations below the Pennsylvanian, show much chert as a part of the sections. This is sufficient evidence that it is original and not formed at the surface by the process of weathering.

(*f*) *Conclusions as to replacement.*—That the chert in the Burlington limestone is not due to replacement is shown by the following lines of evidence:

1. The uniform distribution of the chert along planes in the limestone and the absence of structural control of these planes of chert.
2. The impermeability of the limestone.
3. Absence of a source of silica in the limestone or adjacent rocks.
4. No siliceous organisms in either chert or limestone.
5. Deposition of the silica does not occur in the main solution channels in limestone.
6. Elliptical or circular forms more readily explained by colloidal precipitation theory.
7. No structural features of the limestone preserved in the chert.
8. Occurrence of angular, brecciated fragments of chert in larger masses of chert.

9. The cracks in the chert and their filling of limestone are not due to replacement.

10. Banding and mottling of chert is not due to replacement, for such structures are not developed during replacement.

11. The fossils in the chert are too well preserved to be residuals from replaced limestone.

12. Weathering produces a porous (where fossiliferous), fragmental, more or less decomposed chert.

13. No evidence of growth at present time or since the period of deposition.

14. Presence of chert in conglomerates at the base of formations exactly like the chert in the underlying formation.

IV. APPLICATION OF THE COLLOIDAL PRECIPITATION THEORY TO OTHER CHERTY FORMATIONS.

It is of value and interest to determine to what extent the theory as developed from the occurrence of the chert in the Burlington formation is applicable to other occurrences of chert and flint.

The table on page 432 shows the extent to which chert occurs in the limestone and dolomites in North America. No period from the Cambrian to the Pennsylvanian is free from at least some cherty formations. Two important areas have long been noted for the abundance of chert they contain: the Mississippi Valley and the Appalachian trough. Other areas, as the Great Basin and Western Canada, also contain considerable chert. On the whole, the chert occurs mainly in the lower formations of the periods, although it may be found in the upper formations.

Wherever found the published descriptions show that its mode of occurrence is similar to that in the Burlington formation, nodules, lenticular bands, and beds being the chief forms. In all occurrences distribution is essentially along planes.

Fossils are common in chert, in fact in some formations essentially all the fauna of the formation has been derived from the chert, showing that fossils are best preserved in that material.

As to minor relationships, the published descriptions are very meager, and it is these minor facts which are of so much importance in determining the origin of the chert.

Studies of the Cambrian and Ordovician formations in southeastern Missouri showed many of the same features found in the Burlington formation. A detailed study of the chert in these formations, however, was not so fertile in results as was that of the much more recent Burlington formation.

Chert is often found in the lower limestone and dolomite members of the various formations of the periods. These formations were laid down in a sea which was advancing upon a more or less peneplained area and as a result were receiving the drainage from low-lying lands, a condition favorable to the removal of large amounts of silica, which would become a part of the formations being deposited. As the sea advanced and the land areas became reduced in size, smaller quantities of silica would be brought to the sea and less chert deposited. This relationship between the chert and the events of the larger periods of time appears to be significant and in accord with the theory here advanced.

Though the theory advanced to explain the origin of the chert in the Burlington formation has many points in its favor and would appear to have a wide application, it can not be taken as explaining all occurrences of chert. More detailed studies of each formation which contains chert are necessary to determine its more general application. The evidence as gathered from the literature appears to be favorable to the theory, however.

The notable features of the theory are its explanation of the minor features of the chert as it occurs in the Burlington limestone and its application to the larger occurrences of chert as a rock in the formations from the Cambrian to the Cretaceous. The theory, if its application to those points is correct, should be found applicable to other deposits of chert.

V. Summary and Conclusion.

The widespread occurrence of chert in the Burlington formation of Mississippian age has made a careful study of it possible. It is believed that this chert was formed from colloidal silica, derived in most part from streams which contributed it to the sea. This colloidal silica was widely dispersed through the sea water, and finally, after sufficient concentration, was deposited through the action of electrolytes. Upon coagulation the silica is believed to have aggregated into more or less globular masses which eventually assumed the more common elliptical form which they now possess. This elliptical form of the chert is attributed to the flattening of the colloidal mass under its own weight and later under the weight of the overlying sediments. The various structural features of the chert, its relationship to the enclosing limestone, its physical characteristics, and the abundance of calcareous fossils within the chert, are all readily explained by the theory.

The evidence that these same features cannot be explained by the replacement theory is then given.

The final conclusion is that the chert, being originally a chemical precipitate, was thrown down as colloidal silica upon the sea bottom through the action of salts in the sea water. The precipitation occurred contemporaneously with that of the limestone or dolomite, and the silica was derived from the land through ordinary processes of chemical weathering. The colloidal silica was then consolidated into the chert through pressure, loss of water, and crystallization.

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Art. XXXVI.—*Ionization and Polymerization in Cadmium Iodide Solutions*; by R. G. Van Name and W. G. Brown.

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

It is a well known fact that water solutions of cadmium iodide show an abnormally low electrical conductivity and freezing point lowering as compared with other salts of like type. This is generally ascribed to the presence in the solution of complex molecules and ions. In a previous article* we have described a method, based on the measurement of distribution coefficients of iodine between such a solution and a non-aqueous phase, by which it is possible, by extrapolation, to calculate the percentage of simple molecules and ions in a pure solution of cadmium iodide. The application of this method led to the conclusion that in 0·5-molar cadmium iodide at 25° about 6 per cent was present in the form of simple CdI_2 molecules, ionized and non-ionized, in 0·25-molar solution 10·6 per cent, in 0·125-molar solution 16·8 per cent, and in 0·01-molar solution 55 per cent.

These results may be compared with those of Walton,† who showed in 1904 that the rate of decomposition of hydrogen peroxide in a neutral solution containing an iodide is proportional to the concentration of the iodine ion, and used this kinetic method to determine the proportion of iodine ion in a series of rather dilute cadmium iodide solutions. With due allowance for ionization and for differences in concentration, our results, as will be shown later, are consistent with those of Walton, at least as to order of magnitude.

McBain‡ on the other hand, by a mathematical analysis of the data in the literature concerning conductivity, freezing points, and transport numbers of cadmium iodide solutions, has arrived at quite a different result. McBain concludes that in a 0·1 molar cadmium iodide solution, the only concentration quantitatively dealt with, most of the salt is in the form of simple non-ionized CdI_2 molecules, and that the complexes make up only about 8 per cent of the whole.

In the present investigation we have attempted to throw further light upon this question by a study of solutions of cadmium iodide containing dissolved iodine, by means of measurements of electromotive force and of freezing point lowering.

Electromotive Force Measurements.

The reversibility and reproducibility of iodine electrodes composed of platinum immersed in an iodide solution contain-

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* This Journal (4), xliv, 105, 1917.

† Zeitschr. phys. Chem., xlvii, 185, 1904.

‡ Zeitschr. f. Elektrochem., xi, 215, 1905.

ing free iodine, have been proved by the work of a number of investigators.* In its relation to the present problem the work of Laurie† is especially important. Laurie used the electromotive force of concentration cells composed of two such iodine electrodes as a means of calculating the iodine ion concentration in a potassium iodide solution saturated with iodine. The Nernst equation for the electromotive force of such a cell at 25° may be written

$$(1).\quad \pi = 0{\cdot}02955 \left\{ \left(\log \frac{(I_2)}{(I')^2} \right)_{\text{Sol. 1}} - \left(\log \frac{(I_2)}{(I')^2} \right)_{\text{Sol. 2}} \right\}.$$

The electromotive force is thus stated in terms of four concentrations. Under the conditions of Laurie's experiments three of these four concentrations were calculable from known data, and the fourth, the desired iodine-ion concentration, was calculated from the observed electromotive force. Concentrated ammonium nitrate solution was used to eliminate diffusion potentials.

The method pursued in our own experiments was similar to that of Laurie. The cells measured were of the type

$$\text{Pt} : \text{KI} + I_2 \text{ (saturated)} : NH_4NO_3 : CdI_2 + I_2 : \text{Pt}.$$

Each cadmium iodide electrode was measured against two different potassium iodide electrodes of different concentrations, designated hereafter as electrodes A, and B, respectively, the former containing 0·1 molar KI, the latter 0·01 molar KI, both saturated with iodine. These two electrodes were then measured against each other, thus furnishing a check upon the results. All necessary data concerning these iodine-potassium iodide solutions have been given by Bray and MacKay.‡

As intermediate solution to eliminate diffusion potentials, a concentrated solution of ammonium nitrate was employed, to which, following a suggestion due to Luther,§ enough sodium nitrate was added to make the mean cation velocity the same as that of the anion. This solution contained 8·3 mols NH_4NO_3 and 1 mol $NaNO_3$ per liter. For comparison a few measurements were made in which saturated potassium chloride solution was substituted for the mixed nitrates, but the results failed to show any difference large enough to be of importance in the present work. The nitrate solution was used in all the experiments recorded below.

Calculation of the diffusion potential by the Planck or the Henderson equation was practicable only when the ion concen-

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* See, for example, Maitland, Zeitschr. f. Elektrochem., xii, 263, 1906; also, Jones and Hartmann, Jour. Am. Chem. Soc., xxxvii, 757, 1915.

† Zeitschr. phys. Chem., lxvii, 627, 1909.

‡ Jour. Am. Chem. Soc., xxxii, 914, 1910.

§ See Bjerrum, Zeitschr. phys. Chem., liii, 438, 1905.

trations of both solutions were known, which was true in the case of the cell made up of the two potassium iodide electrodes, but not for a cell with a cadmium iodide electrode. For the potassium iodide concentration cell the value of the diffusion potential was calculated with the aid of the following data taken from the article of Bray and MacKay:

	Solution 1 0·1 molar	Solution 2 0·01 molar		Migration velocities
(K^+)	0·0865	0·00941	:	74·8
(I')	0·0430	0·00484	:	76·5
(I'_3)	0·0435	0·00457	:	41·5

Using the Planck formula the value of the potential so obtained was 0·0070 volt, while the Henderson formula gave from the same data the value 0·0069 volt. The measured value, as given by the difference between the electromotive force as observed with and without the use of the intermediate nitrate solution, was approximately 0·003 volt.

In the opinion of the writers this difference between the measured and calculated values of the diffusion potential is too large to be explained by experimental error, or by uncertainty in the data employed in the calculation, and is to be ascribed to some peculiarity in the behavior of liquid junctions which involve the tri-iodide equilibrium. Support for this view is given by the fact that the diffusion of iodine in an iodide solution is abnormal in at least one important respect, for the rate of diffusion of iodine in potassium iodide is known to increase with increasing concentration of the latter, while by the rule of Abegg and Bose* we should expect just the reverse. That the discrepancy is in all probability not due to the incomplete elimination of the diffusion potential by the nitrate solution is shown by the fact that the electromotive force of this concentration cell as measured with the nitrate solution as intermediate liquid (mean value of many determinations, 0·0560 volt), was in close agreement with the value calculated from Equation 1 (0·0561 volt).

Apparatus.—The type of half-cell used is shown in the figure. The tube carrying the electrode (of bright platinum foil) was fitted into the neck of the half-cell by a ground joint, so that the iodine solution came in contact with nothing but platinum and glass. Two such cells were clamped in a frame with their siphon tubes dipping into opposite arms of a U tube containing the intermediate solution, and the whole was immersed up to the necks of the half-cells in a thermostat kept at 25°. With stop-cocks closed the cell could be left set up for many days without danger of contamination of the solu-

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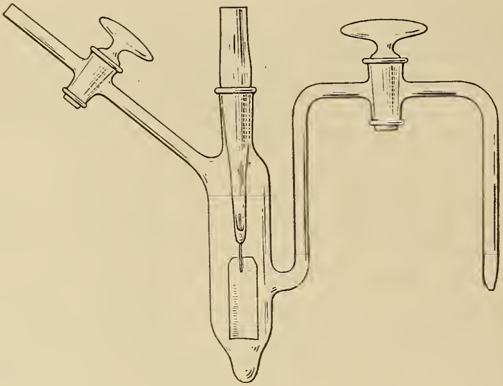
* Zeitschr. phys. Chem., xxx, 551, 1899.

tion, and could quickly be put into commission again by emptying the siphon arms and renewing the intermediate liquid. The stop-cocks in the siphon arms were generally left open during the actual measurement. In the earlier experiments, contact between dissimilar solutions was brought about in the U tube in a layer of sea-sand, as recommended by Bjerrum,* but the use of sand was later abandoned as troublesome and unnecessary for the present purpose.

The measurements were made by the Poggendorf compensation method with the aid of a galvanometer sensitive to 4×10^{-9} amperes. Owing, however, to the high resistance of the cells measured, the accuracy of a single bridge-reading did not much exceed one millivolt.



Preparation of the Reference Electrodes.—The complete saturation of the iodide solutions with iodine was accomplished by sealing the solution with powdered iodine in a large glass tube, which was attached to the stirring axle of the thermostat and rotated for a period of at least 24 hours. With solutions so prepared the two reference electrodes, when measured against one another, usually gave a constant potential difference within 12 hours, which retained its value practically unchanged for many days. Occasional shaking of the half-cells (which contained a little solid iodine) was found to favor constant results. The liquid in the siphon arms was emptied periodically, and the half-cell when necessary could be refilled with a portion of the original (iodine saturated) solution without altering the measured electromotive force. All measurements were at 25° C.

Experimental Procedure.—A cell composed of the two reference electrodes was first set up and its electromotive force

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* Zeitschr. f. Elektrochem., xvii, 58 and 389, 1911.

measured from time to time until the constant value 0·056 volt was reached. A half-cell was then filled with the iodine-cadmium iodide solution to be investigated, and measured in turn against each of the reference electrodes. Finally, as a check, the reference electrodes were again combined and measured. Obviously the difference between the electromotive forces of the two cells in which the iodine-cadmium iodide electrode was used should agree with the electromotive force of the cell made up of the two reference electrodes (0·056 volt). All measurements in which the difference above mentioned was within ± 0·001 volt of 0·056 volts were considered trustworthy.

The cadmium iodide solutions used were of four different concentrations: 0·5, 0·25, 0·125 and 0·01 molar, from each of which a number of electrodes containing varying amounts of dissolved iodine were prepared and measured against electrodes A and B. Since these concentrations of cadmium iodide were the same as employed in the determinations of distribution coefficients described in our previous article* the results of that work were used in calculating (I_2), the concentration of uncombined iodine, from the concentration of dissolved iodine as found by direct titration. For electrodes A and B (I_2) was obviously equal to 0·00132, the solubility of iodine in pure water, and the values of (I') for these two solutions were those given on p. 455 of this article. It was, therefore, possible to calculate (I') for each cadmium iodide solution from the observed electromotive force by means of Equation 1.

A summary of the results is given in Table I. Except where otherwise stated, concentrations in this and the following tables are expressed in millimols per liter. In the third column are the potential differences given by each iodine-cadmium iodide electrode against reference electrode A, while the potential difference for the same electrode against reference electrode B is found in the fourth column on the horizontal line next below. A negative sign prefixed to the recorded potential indicates that the reference electrode formed the negative pole. Usually the reverse was true. The iodine-ion concentrations calculated from these potential differences are recorded in the fifth and sixth columns, the former giving the two independent values for each solution, derived from the two potentials measured, and the latter the mean of the two. Finally, by graphical extrapolation of the values in column six to zero concentration of iodine, a value has been obtained for each cadmium iodide solution which should represent the concentration of iodine ion in the given cadmium iodide solution if it contained no dissolved iodine. These four extrapolated values are the important ones for our present purpose. Since

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* This Journal (4), xliv, 105, 1917.

TABLE I.

	Dissolved iodine	(I_2)	E. M. F. volt against A	against B	(I')	(I') mean
0·5 molar CdI_2	*55·5	1·32	0·0423		25·1	25·3
				—0·0134	25·5	
	39·29	0·955	0·0504		29·3	30·0
				—0·0046	30·7	
	26·06	0·605	0·0536		26·5	26·9
				—0·0029	27·3	
	21·63	0·505	0·0589		29·7	30·2
				0·0037	30·8	
	13·44	0·315	0·0648		29·5	29·7
				0·0090	29·8	
	7·57	0·175	0·0725		29·7	30·6
				0·0178	31·5	
	6·02	0·140	0·0751		29·4	30·2
				0·0203	30·9	
	0·0	0·0				30·4
0·25 molar CdI_2	*45·35	1·32	0·0470		30·2	29·7
				—0·0099	29·2	
	36·24	0·99	0·0490		28·3	28·8
				—0·0063	29·2	
	20·4	0·538	0·0592		31·0	30·8
				0·0027	30·5	
	9·69	0·255	0·0689		31·1	30·9
				0·0124	30·7	
	6·02	0·160	0·0745		30·4	31·1
				0·0193	31·8	
	3·387	0·090	0·0818		30·6	31·2
				0·0267	31·8	
	0·0	0·0				31·2
0·125 molar CdI_2	*35·7	1·32	0·0423		25·1	25·6
				—0·0137	26·0	
	18·63	0·648	0·0531		26·9	27·4
				—0·0021	27·8	
	7·26	0·250	0·0675		29·2	29·1
				0·0112	29·0	
	3·443	0·110	0·0770		28·1	28·3
				0·0213	28·5	
	1·641	0·051	0·0870		28·3	28·5
				0·0313	28·7	
	0·792	0·022	0·0962		26·5	27·0
				0·0410	27·5	
	0·0	0·0				27·5

* Solution saturated with iodine.

TABLE I.—Continued.

	Dissolved iodine	(I_2)	E. M. F. volt against A	against B	(I')	(I') mean
0·01 molar CdI_2	*8·16	1·32	0·0080		6·62	6·79
				−0·0468	6·95	
	2·540	0·2967	0·0342		8·69	9·16
				−0·0193	9·62	
	1·397	0·1569	0·0431		8·95	9·23
				−0·0114	9·52	
	0·646	0·0713	0·0535		8·94	8·94
	0·3104	0 0343	0·0654		9·93	10·42
				0·0116	10·90	
	0·1411	0·0168	0·0755		10·36	10·77
				0·0216	11·27	
	0·0	0·0				10·50

* Solution saturated with iodine.

all these iodine-ion concentrations are very low we can certainly afford to disregard here the slight error involved in the assumption that the results of electromotive force measurements represent concentrations rather than "activities" as defined by Lewis.*

Discussion.—In the previous investigation, as has already been stated, values were obtained for the proportion of simple molecules, ionized and non-ionized, in a pure solution of cadmium iodide at various concentrations. This quantity we shall designate, as in our former article, by the term "active fraction." The rest of the cadmium iodide must consist of associated cadmium iodide molecules, and of the ions, simple or complex, formed therefrom.

These values of the active fraction are calculated upon the assumption that the abnormally low power of cadmium iodide to unite with iodine is due entirely to the presence of complexes, a condition which may be only approximately fulfilled. The amount of iodine taken up by an iodide should be practically independent of its degree of ionization, provided that the tri-iodide is ionized to about the same extent, as is no doubt generally the case.† But although it is contrary to experience

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* For a discussion of the relation between activity and concentration for the iodine ion in potassium iodide solutions, see Bray and MacKay (Jour. Am. Chem. Soc., xxxii, 925, 1910).

† This is confirmed by the fact that for all metallic iodides so far investigated, with the exception of those of cadmium and mercury, the value of the equilibrium constant $K_1 = (\Sigma I)(I_2) / (\Sigma I_3)$ is the same. The list includes the iodides of di- and trivalent metals, Ba, Sr, Zn, Ni, and La, whose degrees of ionization are certainly somewhat different from those of the univalent iodides.

that two metallic salts of like type and as closely related as are cadmium iodide and cadmium tri-iodide should show any large difference in ionization, the possibility of slight differences is not excluded, which if present would cause small positive or negative errors in the value of the active fraction, calculated as above.

According to McBain* the observed transport numbers indicate that the complex ion present in predominating amount is CdI_3', formed by ionization of $(CdI_2)_3$ according to the reaction:

$$(CdI_2)_3 \rightleftarrows 2CdI_3' + Cd^{++}.$$

Whether or not this inference is correct it is probable that the above equilibrium is typical, and that the inactive fraction consists essentially of (*a*) associated molecules, (*b*) complex anions, and (*c*) simple Cd^{++} cations. It follows, therefore, that the degree of ionization of the simple CdI_2 molecules may be calculated, at least approximately, by dividing the concentration of the iodine ion, taken from Table I, by the equivalent concentration of the "active" cadmium iodide as derived from the data of the previous investigation.

Table II shows the results obtained in this way. The first three columns contain the concentrations of total cadmium iodide, of active cadmium iodide, and of the iodine ion, respectively. The fourth column gives the degree of ionization of the simple CdI_2 molecules as calculated from columns two and three, and the fifth shows, for comparison, the degrees of ionization of cadmium nitrate, a normally ionized salt of like type, at the same concentrations as those of $(CdI_2)_{active}$ in column two. The data for cadmium nitrate were obtained by interpolation from values given by Noyes and Falk.†

Table II.

(CdI_2)	$(CdI_2)_{active}$	(I')	$\gamma = \frac{(I')}{2(CdI_2)_{active}}$	γ for $Cd(NO_3)_2$ at 18°
500	30·	30·4	·51	·78
250	26·5	31·2	·59	·79
125	21·	27·5	·65	·80
10	5·5	10·5	·95	·87

According to these results the degree of ionization of the CdI_2 molecules is considerably lower, except in the most dilute solution, than that of the cadmium nitrate. A difference in this direction, though smaller in amount, would be expected on account of the presence in the cadmium iodide solution of

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* Zeitschr. f Elektrochem., xi, 215, 1905.

† Jour. Am. Chem. Soc., xxxiv, 475, 1912.

an excess of Cd^{++} ions resulting from the ionization of the associated molecules, and it would also be expected that the difference, if due to this cause, would decrease with increasing dilution, as is in fact the case. It is probable, however, that the actual difference between the degrees of ionization of these two salts is considerably smaller than these results would indicate, for the error in determining γ by the above method may easily be rather large.

The work of Walton,* whose kinetic method for determining iodine ion concentrations has already been referred to, is of interest here, since his results yield values of (I′) which can be compared with those in Table I. Unfortunately, Walton's experiments with cadmium iodide were confined to solutions more dilute than 0 05 molar. The comparison is shown in Table III, the second horizontal line giving the values of (I′) calculated from Walton's results† while the third contains our values for the same quantity. Figures enclosed in parentheses were obtained by graphical interpolation.

TABLE III.

(CdI_2)	4·9	10	19·4	31·8	42·1
(I′) Walton	6·5	(12)	19·3	26·5	31·2
(I′) V. N. & B.		10·5	(14)		(20)

The two sets of results agree in order of magnitude, though Walton's values are higher and increase more rapidly with the concentration. Since Walton's method has not yet been very thoroughly studied, particularly as to its sensitiveness toward secondary catalytic influences, the results of the electromotive force measurements deserve the greater weight.

Freezing Point Measurements.

Since the purpose of these measurements was to determine the effect of successive additions of iodine upon the freezing point of a given cadmium iodide solution, it was necessary to employ a method of the "undercooling" type, the very convenient and accurate method of Roloff,‡ as improved by Richards,§ being excluded by the fact that it would not permit the concentration of the cadmium iodide to be kept constant. After unsuccessful attempts to obtain sufficient accuracy with the aid of a modified Beckmann apparatus, using a cryohydric mixture for the cooling bath, and other special precau-

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* Zeitschr. phys. Chem., xlvii, 185, 1904.

† These values were obtained by dividing the observed velocity constants in each case by 1·45, the average value of the ratio, *Velocity constant* / (I′), as found by Walton's experiments with KI, NaI, and NH_4I.

‡ Zeitschr. phys. Chem., xviii, 572, 1895.

§ Jour. Am. Chem. Soc., xxv, 291, 1903.

tions, an apparatus was finally devised which satisfactorily met the needs of the case. The construction and manipulation of this apparatus have been fully described in a former paper,* so that only the principal points in the procedure need be given here.

The different cadmium iodide solutions used were kept in thoroughly steamed bottles of Jena glass. The freezing point of the water was first taken. The water was then replaced by the cadmium iodide solution, which had been prepared by dissolving the carefully dried and weighed salt in a portion of the same water, and diluting to an exact volume. At least three determinations of the freezing point were made, using varying degrees of undercooling, and no result was accepted unless the final temperature held constant within 0·001° (the maximum sensitiveness of the temperature reading) for at least five minutes. The volume of solution used in the freezing point apparatus was either 200 or 250^{cm^3}.

The pure cadmium iodide solution was next replaced by a portion of the same solution which had been shaken at room temperature with an excess of iodine in a Jena glass bottle for some hours. At 0° this solution was supersaturated with iodine. To insure equilibrium with both ice and solid iodine the liquid was allowed to partially freeze and was then kept at its freezing point with continual stirring for several hours. Equilibrium was assumed to have been reached when successive determinations of the freezing point agreed, and also successive titrations of the dissolved iodine. In this way the freezing points were obtained for solutions saturated with iodine, and for those containing no dissolved iodine. Data for the intermediate iodine concentrations were obtained by mixing varying amounts of the saturated solution with the original pure cadmium iodide solution, determining the freezing point as before, and, finally, estimating the iodine by titration.

In all these measurements care was taken to maintain the room temperature as constant as possible, and in a few cases where appreciable variation occurred the thermometer readings were corrected for change in the length of the projecting mercury thread with the aid of the usual formula, using the value 0·000156 for the apparent expansion coefficient for mercury in glass. This correction was applied only in working with the more dilute solutions where its importance was obviously greatest.

The results of these experiments are given in Table IV. The four concentrations of cadmium iodide studied are the same as in the measurements of electromotive force at 25°. Iodine concentrations are given in the second column, the starred values being those for solutions approximately saturated with iodine, having iodine present as a solid phase. In the

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* This Journal (4), xliii, 110, 1917.

third column are the observed freezing point depressions, which in nearly every case are the mean of two or three separate determinations. The fourth and fifth columns contain the observed values, for the pure cadmium iodide solution, of the van't Hoff coefficient *i*, and of the apparent degree of ionization γ, as calculated in the ordinary way from *i*.

TABLE IV.

(CdI_2)	Dissolved iodine	F. p. dep.	$i =$ van't Hoff coeff.	$\gamma = \frac{i-1}{2}$	Dep. due to iodine	Molec. dep. for iodine
500	0·0	1·067°	1·147	7·35%		
"	9·4	1·089			0·022°	2·34(?)
"	19·6	1·095			0·028	1·43
"	27 9	1·112			0·045	1·61
"	*40·4	1·125			0·058	1·44
250	0·0	0·533°	1·145	7·25%		
"	9·33	0·546			0·013°	1·40
"	19·4	0·558			0·025	1·29
"	24·9	0·567			0·034	1·37
"	*33·6	0·579			0·046	1·37
125	0·0	0·277°	1·193	9·65%		
"	5·93	0·285			0·008°	1·35
"	10·29	0·293			0·016	1·56
"	16·75	0·301			0·024	1·43
"	*27·5	0·317			0·040	1·46
10	0·0	0·0365°	1·962	48·1%		
"	2·344	0·0394			0·0029°	1·24
"	4·266	0·0424			0·0059	1·38
"	*7·53	0·0453			0·0088	1·17

Previous determinations of *i* for cadmium iodide by the freezing point method have been made by Arrhenius,* by H. C. Jones,† and by Chambers and Frazer.‡ Our values at the two lowest concentrations are in excellent agreement with those of Jones (whose results only cover concentrations up to 0·1 molar) and at the two higher concentrations they are close to the mean between the results of Arrhenius and those of Chambers and Frazer. No explanation is offered for the fact that *i* is slightly larger in 0·5 molar cadmium iodide than in the 0·25 molar solution, but the effect is real as it is even more evident in the results of the other investigators than in our own. Chambers and Frazer ascribe the phenomenon to hydration.

The last column of Table V shows the "molecular depression for iodine" as obtained by dividing the depression due to iodine (column six) by its total concentration as given in col-

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* Zeitschr. phys. Chem., ii, 491, 1888.

† Ibid., xi, 544, 1893.

‡ Am. Chem. Jour., xxiii, 512, 1900.

umn two. This quantity proves to be roughly constant irrespective of the concentration and to have a value between 1·3 and 1·4, or about three-fourths of 1·86, the normal molecular lowering for a non-electrolyte in pure water.

The relatively large amount of this increase proves that the cadmium tri-iodide formed is derived ultimately from some source which previously contributed a much smaller number of molecules and ions to the solution. Unless, therefore, we are willing to admit that the cadmium tri-iodide may have in the solution a degree of ionization many times greater than that of the simple cadmium iodide molecules,* these results must be regarded as clear proof of the existence of complexes in these solutions. On the other hand, if the effect is largely or wholly due to complexes, as is probably the case, the relative constancy of the values in the last column of Table IV is an indication that the complexes are present in considerable quantity even in the more dilute solutions. On account of the low solubility of iodine in water at 0° the depression due to the iodine which remains uncombined is so small† as not to affect the validity of this reasoning.

Owing to the presence of complexes it is of course impossible to get any accurate measure of the concentration of the iodine ion from the value of i, but in the present case the error so involved would not necessarily be very large. Of the various kinds of complex ions to be expected here the two simplest and most probable are CdI_3' and CdI_4'', formed as products of the equilibria

$$2CdI_2 \rightleftarrows (CdI_2)_2 \rightleftarrows Cd^{++} + CdI_4''$$

and

$$3CdI_2 \rightleftarrows (CdI_2)_3 \rightleftarrows Cd^{++} + 2CdI_3'.$$

In both of these cases the number of ions produced is the same as the number of CdI_2 molecules disappearing, so that the net result of the complex formation will be to diminish the freezing point depression by a small amount due to that part which remains in the form of non-ionized polymerized molecules, $(CdI_2)_2$ or $(CdI_2)_3$ as the case may be. Hence, if values for the concentrations of the iodine ion are calculated in the usual way from the freezing point lowerings the results will in general be low, but in sufficiently dilute solutions should not be very far from the truth.

In Table V the iodine ion concentrations, so calculated, are tabulated for comparison with those derived from the measurements of electromotive force. For the two lowest concentra-

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* A rough calculation shows that to account for the results in the absence of complexes the ratio of these two degrees of ionization would have to be over 2 in the 0·01 molar solution, about 8 in the next, and about 25 in the strongest.

† Its maximum value is 0·0012°, which is reached only when the solution is saturated with iodine.

tions the agreement is fairly good, but in the 0·25 molar solution the difference is not in the expected direction, and in the strongest solution the discrepancy is surprisingly large, far exceeding the probable experimental error. For this result there is no evident explanation, but it is significant that it coincides with a marked irregularity in the freezing point lowering. As was noted on page 463, the results of all cryoscopic measurements with cadmium iodide show that above about 0·3 molar the value of i apparently rises with the concentration, although the attendant decrease in ionization and increase in polymerization would both tend to lower it.

TABLE V.

(CdI_2)	(I') at 0° From freezing point	(I') at 25° From E. M. F.
500	74	30·4
250	36	31·2
125	24	27·5
10	9·6	10·5

Nature and Concentration of the Complexes.—Thus far the question of the nature of the complex ions and molecules has been left open. Of the various complex ions which may be present in the solutions, CdI_3', as McBain* has shown, is apparently the most probable one. The high transport number of the anion, which approaches 1·25 in the most concentrated solutions, cannot be explained by assuming the predominance of CdI_4'' without assigning to that ion an improbably high velocity. This objection, however, would not apply to such ions as Cd_2I_5' or Cd_3I_8'', though there would be less reason to expect their presence than that of the less complex ones just mentioned.

McBain has calculated the approximate composition of a 0·1 molar solution of cadmium iodide upon the assumption that CdI_3' is the only complex ion present in appreciable amount. This calculation, which is based entirely upon freezing point, transference, and conductivity data, gives the values $(CdI_3') = 0{\cdot}0084$ and $(I') = 0{\cdot}0126$. This would make $(Cd^{++}) = 0{\cdot}0105$, thus accounting for about 19 per cent of the total iodide. McBain concludes that the remaining four-fifths is present in the form of simple, non-ionized CdI_2 molecules, and that the proportion of complex molecules is negligible.

There are several serious objections to these figures: (*a*) If so large a part of the salt is in the form of simple CdI_2 molecules the power of the salt to combine with iodine should be but slightly lower than normal, while in reality the "active

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* Loc. cit.

fraction" at this concentration is only about 20 per cent.* (*b*) The molecular conductivity of the solution as calculated for 18° from the above composition is 22·5,† or less than half the value actually measured, which is 46·7. (*c*) The value of (I′) calculated by McBain is much lower than that given by the electromotive force method.

In a similar manner it is possible to calculate the approximate composition of cadmium iodide solutions from the experimental data furnished by our measurements of electromotive force, and by our previous study of the iodine-cadmium iodide equilibrium. These calculations will be confined to the 0·01 and 0·125 molar solutions, for which the data are presumably most accurate. It will be assumed that CdI_3' is the only complex ion present in significant amount, and that the degree of ionization of $(CdI_2)_3$ is of about the same order of magnitude as that of the average uni-bivalent electrolyte.

Allowing for the effect of the excess of Cd^{++} ions, which is much larger in the 0·01 molar than in the 0·125 molar solution, we may assume that the degree of ionization is 80 per cent in the former and 75 per cent in the latter. An error of a few per cent in the degree of ionization assumed will not greatly change the results. Using these degrees of ionization, the "active fractions" given on page 453 and the values of (I′) from Table I, we obtain the results recorded in Table VI. That these values differ greatly from those of McBain is evident. Interpolation of these results for 0·1 molar concentration gives, approximately, $(CdI_3') = 0·045$ and $(I') = 0·021$, figures which are respectively 5 and 1·7 times those of McBain.

TABLE VI.

	(CdI_3')	(Cd^{++})	(I')	(CdI_2)	$(CdI_2)_3$
0·01 molar.....	2·4	6·45	10·5	0·25	0·3
0·125 molar.....	52·	39·7	27·5	7·2	8·6

Since the values in Table VI depend upon neither freezing point nor conductivity measurements, their correctness may properly be tested by calculating the van't Hoff coefficient *i* and the molecular conductivity for each solution. For *i* we obtain 0·0199 / 0·01 = 1·90, and 0·135 / 0·125 = 1·08 respectively, while the measured values (see Table V) are 1·96 and 1·19.

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* This low power to unite with iodine cannot be explained by the low ionization of the CdI_2 molecules unless it is assumed that the degree of ionization of the cadmium tri-iodide is about nine times larger. This is obviously very improbable.

† For the method of calculation see p. 467. The ionic conductivities here used were those employed by McBain, namely, ½Cd = 51, CdI_3' = 41, and I′ = 66·4. If the values given on p. 467 be employed the result is 21·1 instead of 22·5.

To calculate the molecular conductivity we must obtain a value for the conductivity of CdI_3'. If we assume with McBain that the value 1·25, the limit which the observed (anion) transport number of a cadmium iodide solution tends to approach with increasing concentration, is that of the anion CdI_3', then the relative velocity of this ion must be $\frac{1·25}{3} = 0·42$, that is, $\frac{42}{58}$ that of Cd^{++}. For the equivalent conductivity of the Cd^{++} ion we may use the value 47 for 18°, which corresponds to 56 at 25°. This gives, for CdI_3', 34 at 18° and 40·5 at 25°. For iodine ion the values are 66·6 and 76·5 respectively. The molecular conductivity of the 0·01 molar solution at 25° should therefore be

$$\{(0·00645)(112) + (0·0024)(40·5) + (0·0105)(76·5)\} \div 0·01 = 162·2,$$

and for the 0·125 molar solution, calculated in the same way, 69·2.

These calculated conductivities are much too high, the measured values being 120 and 57 respectively, a result which seems to be due to some fault in the assumptions made rather than to experimental errors. It is not clear, however, how this discrepancy can be eliminated without introducing some other one. The evidence at hand is in some respects conflicting and is obviously insufficient for an exact solution of the problem. In short, though some of the values in Table VI are probably nearly correct, the figures as a whole can represent, at best, no more than a rough approximation to the truth.

The Iodine-Cadmium Iodide Equilibrium at 0°.—Each of the starred values in Table V represents the solubility of iodine in the given solution at its freezing point, which, as an approximation, may be assumed to be the same as the solubility at 0° in the same medium. By subtracting the solubility of iodine in pure water at 0° (0·000638 mols/liter*) we obtain (ΣI_3), the equivalent concentration of the tri-iodide formed, and can therefore calculate the approximate value of the equilibrium constant $K_1 = (\Sigma I)(I_2)/(\Sigma I_3)$.

The results so obtained are given in Table VII, which compares the values of K_1 for cadmium iodide at 0° and 25° with those for potassium iodide at the same temperatures and concentrations. All of these figures refer to solutions saturated with iodine. The values for cadmium iodide at 25° were taken from our previous article; those for potassium iodide at 0° were calculated in the way just described from data given by Jones and Hartmann;† those for potassium iodide at 25° were taken from the article of Bray and MacKay.

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* Jones and Hartmann, Jour. Am. Chem. Soc., xxxvii, 256, 1915.

† Loc. cit., p. 250.

TABLE VII.

Concentration. equiv./liter	Cadmium Iodide		Potassium Iodide	
	K_1 at 0° (approximate)	K_1 at 25°	K_1 at 0° Jones and Hartmann.	K_1 at 25° Bray and MacKay
1·0	0·0154	0·0234	....	0·00046
0·5	0·0090	0·0137	....	0·00088
0·25	0·0053	0·0082	....	......
0·10	.....	.....	0·000696	0·00131
0·02	0·0011	0·00247	0·000716	0·00137

These figures show that the value of K_1 for cadmium iodide at 0° is abnormal in the same way as at 25°, being larger throughout than for a normal iodide like potassium iodide, and increasing rapidly with the concentration. The effect upon K_1 of a change in temperature, however, is practically the same for the cadmium as for the potassium salt.

Summary.

1. Measurements have been made: (*a*) by the electromotive force method, of the iodine ion concentration in cadmium iodide solutions of 0·5, 0·25, 0·125, and 0·01 molar strength, containing various amounts of dissolved iodine; also (*b*) of the freezing point lowering of each of these cadmium iodide solutions, and of the further lowering produced by the addition of known amounts of iodine.

2. Values of (I') calculated in the ordinary way from the cryoscopic measurements should be slightly lower, if complexes are present, than those electrically measured. This was found to be the case in the 0·01 and 0·125 molar solutions, but not in the two stronger solutions.

3. The freezing point of a cadmium iodide solution was depressed by the addition of iodine in a nearly constant ratio, which in the stronger solutions was about 1·4° per mol, and only slightly smaller in the weakest solution. This indicates the presence of complexes in considerable quantity even in the 0·01 molar solution. Neither this result nor the abnormally low power of cadmium iodide to unite with iodine can be accounted for, in the absence of complexes, by the assumption that the degree of ionization of the cadmium iodide is very small, unless this low ionization is accompanied by high ionization of the cadmium tri-iodide, a state of affairs which is decidedly improbable.

4. A tentative calculation of the composition of the two more dilute cadmium iodide solutions, based upon the assumption that the ion CdI_3' and its parent molecule $(CdI_2)_3$ are the only complexes present, failed to give results in quantitative agreement with other experimental data.

Art XXXVII.—*Famatinite from Goldfield, Nevada;* by Earl V. Shannon.

During last year, through correspondence with Mr. Herbert N. Witt, geologist for Goldfield Consolidated Mining Co., the writer obtained a number of specimens of ore minerals from the Goldfield district, with the idea of investigating the mineral goldfieldite, reported by Ransome[1] from that region. With regard to the specimens, Mr. Witt writes as follows:

> "I am sending you under separate cover some specimens of the copper ore that occurs here. I believe that you will find that this consists principally of famatinite. However, we have found that almost any specimen of this ore will upon analysis give, not only copper, gold, and sulphur, but arsenic, antimony, bismuth, and tellurium. I do not believe that the mineral goldfieldite exists but is probably a mixture of famatinite, bismuthinite, and calaverite or sylvanite, with possibly some tetrahedrite. All of these have been recognized here and the one specimen that I have had in polished surface under the reflecting microscope indicates such a mixture. . . . You may be able to detect some of the whitish telluride in the famatinite specimens. This will then, I believe, give you all the constituents of the so-called 'goldfieldite'."

One of the specimens had, on one side, some very minute crystals, of a blackish-gray color and metallic luster, partly embedded in kaolin. These were carefully tested in the hope that they might be goldfieldite but although strong reactions were obtained for antimony, arsenic, copper, and sulphur, no bismuth or tellurium could be detected in the very small amount of material available. The crystals therefore seem to be of the same substance as the main mass of the specimen on which they occur, an arsenical famatinite. The crystals vary in greatest diameter from about 1 mm. down to about 0.1 mm., and are so attached to the matrix that they could not be detached without breaking. The larger crystals furthermore had curved faces which gave no dependable reflections. After repeated trials a small crystal was found giving moderately good reflections. In the literature at hand no axial ratios are given for famatinite. Dana[2] gives the forms observed by Rath, as *a*(100), *c*(001), *m*(110) and *l*(130), but gives no axial ratios, nor does he give any angles. Rath's original paper is not accessible to the writer, hence the angles found on the

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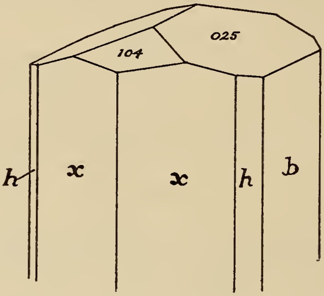
[1] Ransome, F. L., U. S. G. S., Prof. Paper, No. 66, 1909.

[2] System of Mineralogy, 6th ed., page 149.

Goldfield crystal are compared with the observed angles of enargite. The close agreement with enargite in the prism angles is shown below.

	Observed, famatinite	enargite (Dana)
$x:x'''$	60° 24′	60° 17′
$h:h'$	59° 12′	59° 43′

This will serve to show the orientation of the crystal and to indicate that the famatinite from the Goldfield district is isomorphous with enargite and the value for the *a* axis does not differ greatly from that of enargite. With this known orientation the domes observed were plotted on a stereographic projection and gave the indices (104) and (025). The reflections obtained from these faces were poor and the angles obtained were not considered sufficiently trustworthy to serve as a basis for calculating a value for the *c* axis. Both in the projection and in the accompanying drawing the axial ratios of enargite were used. The figure reproduces the form and appearance of the crystals. The locality is not given more nearly than one of the mines of the Goldfield Consolidated Co.



The base upon which the crystals, described above, are implanted is similar to the majority of specimens in the lot received. It consists of fine-grained, pinkish gray famatinite. When polished and examined under the reflecting microscope, the distinctly pink mineral is seen to contain graphic inclusions of a silver-white mineral which in its microchemical reactions agrees with bismuthinite. The ore reacts for bismuth but not for tellurium. The pink mineral contains both arsenic and antimony, the antimony preponderating. One of the samples consists of a fine clayey gouge containing finely triturated native tellurium. Nothing was observed in the specimens which seemed to correspond to the mineral goldfieldite.

ART. XXXVIII.—*On the Functions of the "Sacral Brain" in Dinosaurs*; by RICHARD SWANN LULL.

[Contributions from the Paleontological Laboratory, Peabody Museum, Yale University, New Haven, Conn., U. S. A.]

Branca, in a discussion of the fauna of Tendaguru, East Africa,[1] makes a number of thought-inspiring comments upon the huge sauropod dinosaurs which the formation contains. Among other points he is striving to account for the maintenance of their immense bulk upon a possibly meagre diet by assuming digestive powers of extraordinary efficiency. For this he offers the following explanation:

> "One may be inclined to look for the ability to take care of food solely in the stomach, intestines, or liver. However, in the dinosaurs we may take into consideration something else, *i. e.*, the 'sacral brain,' if we look upon the swelling of the spinal column in the sacrum as a 'brain.' According to Waldeyer, it is indeed thinkable that the sacral brain in dinosaurs had a certain independence, and cared for the functions of *nourishment, digestion,* and procreation [italics mine], also that through a particularly strong innervation it had become especially powerful, more powerful than the strongest digestive organs could be without such a sacral brain. In man there appear still to be traces of this, but here the sacral section of the spinal column is completely surpassed by the brain."

What Waldeyer based his argument upon I do not know, but the evidence which I have been able to secure seemingly does not justify such a speculation. This evidence is here presented.

Dinosaurian feeding habits.

Our assumption of feeding habits based upon the character of dinosaurian dentition justifies the following conclusions:

Theropoda.—These are the carnivorous dinosaurs in a strict sense, with teeth which were in the main prehensile and as such confined to the forward portion of the jaws. They must have been used for rending the prey, for in many instances, such as *Allosaurus* or *Megalo-*

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[1] W. Branca, Die Riesengrösse sauropoder Dinosaurier vom Tendaguru, ihr Aussterben und die Bedingungen ihrer Entstehung, Archiv für Biontologie, 3. Bd., 1. Heft, 1914, pp. 71-78.

saurus, they are sharp-pointed and compressed, with finely serrated cutting edges. In *Tyrannosaurus* they become so thick that the knife-like edge is gone, so that these huge beasts must have dismembered their prey by tearing rather than by cutting it. These latter theropods are analogous to the crocodiles in dental equipment; *Allosaurus,* on the other hand, possessed a more efficient dentition.

The digestive system of the crocodiles shows the highest degree of specialization of any living reptiles, as the stomach is very muscular, with lateral tendinous discs forming an organ very suggestive of the gizzard of the graminivorous birds. In front of this gizzard-like stomach is a capacious portion of the œsophagus, within which is held the excess of food over the rather small capacity of the stomach. The stomach digestion is highly efficient, due not alone to its muscular power, but to the strength of the gastric juice, so that even the bones of the prey are dissolved and not passed through the intestine, as with certain carnivorous birds like the owls. Crocodiles occasionally swallow stones to aid in the trituration of their food, just as do the graminivorous birds.

To what extent the gizzard was developed in the Theropoda is conjectural, but it would seem as though its need were nearly as great with them as with the crocodiles. One aberrant type of theropod, *Struthiomimus,* from the Belly River formation of Canada, has just been the subject of an authoritative paper by Professor Osborn.[2] This form is now known to have been absolutely toothless, and several theories have been advanced as to its feeding habits—that it was insectivorous, especially ant-eating, or that it fed on small crustaceans or molluscs of the seashore, or that it was ostrich-like in habits, browsing upon leaves and buds which its prehensile limbs drew within the reach of the horn-sheathed mouth. Such an assumption as the last, which bears the weight of Osborn's own opinion, would seem to imply the presence of a more or less efficient gizzard-like stomach functionally comparable to that of the struthious birds.

Sauropoda.—The sauropods are clearly of theropod derivation, but it has been pretty generally assumed that they had forsaken the carnivorous habits of their for-

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[2] H. F. Osborn, Skeletal adaptations of *Ornitholestes, Struthiomimus, Tyrannosaurus,* Bull. Amer. Mus. Nat. Hist., vol. xliii, 1917, pp. 733-771.

bears for a vegetative diet, and the tremendous growth of certain plants such as the water hyacinth in the Nile or the waters of New Zealand seems to offer an analogy to what might well have been true of certain aquatic vegetation of the Mesozoic upon which these creatures fed. The teeth were now solely prehensile, sufficiently so for their owners' purpose, but less efficient than those of the Theropoda. The food was in no sense masticated and the inference that a powerful muscular gizzard-like stomach was developed is irresistible, for which the presence of stomach stones, gastroliths, within the ribs of more than one specimen may be taken as added argument.

Predentates.—The predentate dinosaurs, on the other hand, had a differentiated mouth armament. The anterior or prehensile portion was toothless, except in *Hypsilophodon,* but was sheathed with a horny, turtle-like, cropping beak of varying form. The posterior portion of the jaws bore the actual dental battery, consisting of a series of successional teeth which also varied in efficiency and degree of development in accordance with their owners' food, as do those of the ungulate mammals. The Jurassic and early Comanchian forms, such as *Camptosaurus* and *Laosaurus,* were analogous to the browsing ungulates whose brachiodont teeth are fitted to succulent herbage, while the later trachodonts had a dental battery fully as efficient as that of a horse. These dinosaurs chopped their food into short lengths before swallowing, and it may be that the term mastication, which, however, implies a grinding or crushing rather than chopping, may be properly applied to them. Their need of a gizzard-like organ would seem to be less great than in the sauropods.

Stegosaurus, on the other hand, possessed a very imperfect dental battery, as the teeth were both small and relatively few in number—very inadequate apparently for their owner's needs. This genus, however, exhibits a number of characters which, in the Sauropoda, have been taken as indicating an aquatic or at least amphibious life. They are, first, the solid, massive character of the limb bones and the imperfection of their articular ends, those of the stegosaur showing a rugosity fully proportional to those of *Brontosaurus.* The high position of the ribs, bringing the lungs well toward the dorsal side of the body, and the strongly compressed tail with its high neural spines and well developed chevrons are also suggestive. Add to these a mouth armament no more effective than that of a sauropod, and the association of their remains in a common burial, and the inference of similarity of habitus and food is perhaps justified. Just what effect the tall upstanding armor plates would have upon the navigable powers of *Stegosaurus* is not so clear, but they may have incommoded him under such conditions no more than on land.

It may be fairly assumed, therefore, in view of the wide apparent range of feeding habits on the part of dinosaurs, and their relationship to the crocodiles on the one hand and to the birds on the other, that their digestive system was closely comparable both in the development of its parts and in its innervation to that of these living forms. With the birds, the degree of development of the gizzard varies directly with the consistency of the food. Graminivorous birds possess the strongest muscular layer and the thickest horny lining, while in the series from the insectivorous birds to the birds of prey this condition becomes gradually less marked and the division of labor between the glandular proventriculus and the mechanical gizzard less noticeable (Newton). The assumption of a similar gradation in the development of this organ in the dinosaurs seems also warranted.

Innervation of the alimentary canal.

In the reptiles such as the python, crocodile, or turtle, the *vagus* nerve (Xth cranial) is the principal transmitter of stimuli which *initiate* digestive activity, certain of its fibers being distributed to the muscles and mucous membrane of the fauces, the œsophagus, and the stomach, and it finally terminates at the beginning of the intestine at the pancreas.

Cranial casts of *Tyrannosaurus*[3] and of *Stegosaurus* and *Morosaurus,* representing, therefore, the three main dinosaurian groups, all show exits for the IXth to XIth cranial nerves, thus including the vagus, relatively larger if anything than in the crocodile. It is fair to assume, therefore, that this nerve was at least as well developed in the dinosaurs and that its distribution and function were comparable.

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[3] H. F. Osborn, Crania of *Tyrannosaurus and Allosaurus,* Mem. Amer. Mus. Nat. Hist., new series, vol. i, pt. 1, 1912, pp. 1-30.

Birds.—The vagus (X) of birds arises behind the glossopharyngeal (IX) and is connected therewith as well as with the sympathetic system. After receiving branches from the hypoglossal (XII) and taking up the spinal accessory (XI), the vagus runs down the side of the œsophagus to the ventral side of the proventriculus, where, joining its fellow from the other side, it spreads out to supply the stomach. Other branches, leaving the principal stem of each vagus, supply the liver, heart, and lungs, and, as the recurrent laryngeal branch, also supply the distal portions of the trachea and œsophagus. Some fibres of the vagus often extend beyond the stomach, and are connected with the sympathetic nerves of the trunk, supplying parts of the intestinal canal. (Newton.)

The approximate agreement in the innervation of both birds and crocodiles is further argument for dinosaurian innervation.

Certain of the spinal nerves (dorso-lumbar) communicate with the sympathetic system and thence with the alimentary canal, but their function, in so far as it has been observed, principally in man and certain mammals, is *inhibitory,* and hence the reverse of a stimulus to digestion. Such sacral nerves as do pass to the alimentary canal are distributed to the hinder portion only, beyond the glandular or digestive part. They are stimulating, not inhibitory nerves, but their function is merely the elimination of fæcal matter and is in no other sense digestive.

The stomach in the mammal at least is largely automatic in its movements, as is the heart, and while its activity may be initiated or inhibited by impulses from the vagus or sympathetic nerves, the stimuli which cause the rhythmic movement originate in the muscles themselves, for this movement will continue after the severance of all nerve connection with the cerebro-spinal or sympathetic centers. The reptilian heart is notorious for its automatic contraction after its excision from the body, and in all probability the heart and stomach of a dinosaur were fully as automatic.

All of this seems to show that we have no right in assuming for the dinosaur an innervation or functioning of the alimentary canal at variance with the standardized type of the living amniotic vertebrates.

The spinal canal of *Stegosaurus ungulatus* has been studied in detail by the author, who finds not only a sacral dilatation but a *brachial* one as well; that is, from vertebræ VIII to XIII, the maximum width, that of 38 mm., as compared with the average of 25 mm., is attained by vertebra XI, which is exactly opposite the shoulder articulations in the Yale mounted specimen. There is also a corresponding heightening of the canal, although this is a less constant feature, for further back (XV and XVII) there is evidence of a ligament or other delimiting structure below the bony roof of the neural arch itself. Brachial and sacral dilatations of the neural canal are most marked in the turtles among existing reptiles, owing to the immobility of the trunk and the consequent reduction of its musculature and associated nerves, the two enlargements being necessary where the nerves depart to the limbs. That this is the whole significance of these two enlargements in *Stegosaurus* and also in other dinosaurs I have no doubt, and the relative size of each dilatation bears an approximate ratio to that of the limbs innervated, plus in the hinder pair the huge caudo-femoral and other muscles which actuated the tail.

I still feel, despite the contention of the German writers, that the "sacral brain"—which should not be called by such a term—possessed no unusual function whatever, but only the normal one of transmission and reflex action in an unusual degree, and that to invoke any new and unknown function as a reason for its relatively immense size, especially one connected with digestive efficiency, is not justified by the evidence at hand.

Branca further says:[4] "We may also think of these animals as sluggish in habit, in consequence of which much less food was required than is the case in an active animal." On the other hand, in warm-blooded animals the largest species occur in cooler climates, because large animals have "a relatively smaller radiating surface than smaller ones, a factor of the greatest importance in the regulation of body warmth." To the first statement I can take no exception. The second, however, gives food for thought. In the first place, is it an invariable rule that the largest species of warm-blooded animals occur in cooler climates? The present-day distribution

[4] Loc. cit.

of the elephant, hippopotamus, and rhinoceros does not bear this out, and even in the Pleistocene the largest elephants, such as *Elephas imperator,* were southern forms compared with the smaller, cold-adapted *E. primigenius.* With marine creatures Branca's statement seems more nearly true, for the walrus and huge sea-elephants are both adapted to cold waters, and the same is true of the right whales, *Balæna mysticetus* and *B. australis.* The sperm whale, on the other hand, is tropical or subtropical, not occurring, except accidentally, in the polar regions (Flower and Lydekker), while the great rorquals (Balænoptera) are found in all seas except the Arctic and probably the Antarctic also. Of the deer, perhaps the largest living form is the Alaskan moose, while no bears in existence can compare in magnitude with the great Kadiak bear of the same region. But this argument loses weight if the dinosaurs were not warm-blooded, and though the supposition that they were has been advanced, it is not susceptible of proof. It is within the range of possibility that the temperature of the more agile dinosaurs rose appreciably during the time of their activity, as in many of the so-called cold-blooded (poikilothermous) creatures today, but whether or no any dinosaurs had a mechanism for even a partial maintenance of temperature is unknown. If their bodily heat varied with that of the surrounding air, the greater bulk and hence relatively smaller radiating surface would render them less susceptible to rapid temperature changes, and thus prolong their time of activity by tiding over a brief drop in temperature, but would hardly be available in an extended cooler period. That increase of size in dinosaurs was an adaptation for the conservation of energy, and in this way reduced the relative amount of nourishment necessary for their maintenance, seems hardly probable.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Colorimetric Determination of Manganese by Oxidation with Periodate.*—The rapid determination of small quantities of manganese by converting it into the form of permanganate and comparing the color with a solution of a known amount of the latter was suggested as long ago as 1845 by Crum, and later this principle has been very extensively employed in practical analysis, especially in the examination of iron ores and steels. Several oxidizing agents have been employed for this purpose, lead dioxide, an alkali persulphate in presence of silver nitrate, and sodium bismuthate, all of which are applied in nitric acid solution. H. H. Willard and L. H. Greathouse have now found a new reagent, periodic acid or its salts, for this purpose and they believe it to be free from all the faults of the previous methods. The periodate is reduced to iodate according to the following equation:

$$2Mn(NO_3)_2 + 5HIO_4 + 3H_2O = 2HMnO_4 + 5HIO_3 + 4HNO_3$$

Only a small excess of periodate is required, but the success of the reaction depends upon a sufficient concentration of the acid, for otherwise a precipitation occurs, either of manganese dioxide, or of manganic periodate.

The author recommends that the material to be analyzed be brought into a solution containing in 100 cc at least 10 to 15 cc of concentrated sulphuric acid, 20 cc of nitric acid or 5 to 10 cc of syrupy phosphoric acid, or mixtures of two or more of these acids. The solution should have been previously freed from reducing agents by boiling with nitric acid, with the addition of a persulphate if carbon compounds are present, as in the case of steel. Ammonium salts do not interfere, but it is best to remove any hydrochloric acid by evaporating with sulphuric acid, although small quantities may be removed by boiling after adding the periodate. The final reaction is obtained by adding 0.2 to 0.4 g of potassium periodate or of sodium periodate, or an equivalent amount of sodium metaperiodate, boiling for a minute, keeping hot for 5 to 10 minutes and finally cooling. The solution is then diluted to the proper volume and compared in a colorimeter with a standard of known manganese contents, similarly prepared. The solutions used for comparison should not contain more than 1 mg of manganese in 50 cc, for otherwise the color will be too strong.—*Jour. Am. Chem. Soc.*, xxxix, 2366.

H. L. W.

2. *The Preparation of Cyanamide from Calcium Cyanamide.*—E. A. Werner calls attention to the unsatisfactory yields of cyanamide, $CNNH_2$, by the methods heretofore used for the

preparation of this compound from commercial calcium cyanamide, CNNCa. This is due to the difficulty of evaporating water solutions of cyanamide, even at low temperatures at diminished pressures, on account of the decomposing influence of water upon the substance. He has, therefore, devised a new method for the operation, which gives very satisfactory yields. In the first place, the amount of pure acetic acid necessary to neutralize a gram of the commercial calcium cyanamide is determined, then to the proper amount of pure acetic acid diluted with nearly its own weight of water in a large mortar a charge of 100 g of calcium cyanamide is gradually added in portions of about 15 g with constant stirring while the mortar is kept standing in cold water to avoid much rise in temperature. A pasty mass is finally formed, which is well kneaded and allowed to stand in the air for 24 hours. At the end of this time the mass becomes friable and is coarsely powdered. It is important that a slight excess of acetic acid should have been used, so that the material is faintly acid throughout. The mixture is then extracted with ether in a Soxhlet apparatus, the ether is evaporated at a gentle heat by distillation and finally evaporated to dryness in a desiccator over sodium hydroxide. In this manner a yield of 95.6% of the theoretical cyanamide was obtained.—*Jour. Chem. Soc.*, cix, 1325. H. L. W.

3. *A New Method of Separating Tin and Tungsten.*—M. TRAVERS has described a method of analysis which he has applied to wolframites containing tin. The very finely divided substance is fused with anhydrous sodium sulphite in a porcelain crucible at a bright red heat. The decomposition is rapid and perfect, even with minerals containing as much as 50% of tin. The mass is extracted with boiling water, then diluted to 700 to 800 cc, and then slightly acidified with acid. The excess should not be more than 20 cc of normal acid. Brown stannous sulphide is thus precipitated. This carries down a little silica and sulphides of iron and manganese, but it is entirely free from tungsten. It is purified by solution in yellow ammonium sulphide, and the tin is determined as oxide in the usual way. The tungsten is determined in a separate sample, starting again with a fusion with anhydrous sodium sulphite. The complete details of the operation need not be given here, as the principal object of this notice is to call attention to the novel method used for decomposing the mineral.—*Comptes Rendus,* cxlvi, 1408.

H. L. W.

4. *Yellow Mercuric Oxide as a Standard in Alkalimetry.*—G. INCZE states that this oxide is a reliable substance for use in standardizing acid solutions, as it is readily obtained in a pure condition, is free from water of crystallization, and is not hygroscopic. Its use depends upon its reaction with potassium iodide:

$$HgO + 4KI + H_2O = K_2HgI_4 + 2KOH$$

At least 9 molecules of KI must be added for one of HgO, and in practice it is advisable to use a somewhat larger proportion, as for example, 10 cc of 60% KI solution for 0.4 g of HgO. As soon as the oxide has dissolved the mixture is titrated with the acid solution to be standardized with use of methyl orange, phenolphthalein, or methyl red as indicator. The yellow oxide can usually be bought pure, but it can be prepared by dissolving 100 g of mercuric chloride in 1 l. of warm water, cooling, and then adding with stirring 625 g of 6.4% NaOH solution. The precipitate is collected, washed until the washings are no longer alkaline to phenolphthalein, air-dried, and then stored in black glass bottles.—*Zeitschr. analyt. Chem.* lvi, 177 (through C.A.).
H. L. W.

5. *A New Oxychloride of Tin.*—HARRY F. KELLER has examined some brilliant tabular or acicular crystals found in cavities in a lenticular piece of metallic tin from an Indian burial mound on Hogtown Bayou, Florida. The crystals were easily crushed to a chalk-white powder, which on heating in the closed tube melted, turned dark, and gave off acrid fumes without a trace of water. The substance gave qualitative tests for tin in the stannous state and for a chloride. A quantitative analysis, made necessarily upon a small quantity, amounting to about 0.2 g, gave results corresponding fairly well with the formula $SnCl_2.SnO$. No reference to the existence of an anhydrous stannous oxychloride was found in chemical literature. No satisfactory explanation of the occurrence of the crystals in the cavities appears to be given, for the suggestion that some chloride solution had access through an opening at the surface does not account satisfactorily for the production of an anhydrous compound.—*Jour. Amer. Chem. Soc.*, xxxix, 2354.
H. L. W.

6. *Equilibrium Temperature of a Body Exposed to Radiation.*—This problem is discussed in a very lucid and interesting account recently published by CH. FABRY. The general equation of thermal equlibrium of a small body isolated in free space is derived in the following manner. The size of the body is assumed to be such that its temperature T is uniform throughout. S and s denote respectively the area of the surface of the body and the cross-section of the beam of intercepted radiation. For brevity, put $S/s = \eta$. The absorbing properties of the surface are defined by the absorbing power α which is a function of the wave-length $\lambda : \alpha = \phi(\lambda)$. The radiation received by the body is supposed to consist of waves that are sensibly plane. It is defined by the curve connecting the energy with the wave-length: $E = \psi(\lambda)$. That is, $E \cdot d\lambda$ means the power which each square centimeter receives from radiations comprised between λ and $\lambda + d\lambda$. It is also necessary to introduce the radiation formula for a black body, since this gives, for each temperature, the curve of energy of radiation for unit surface: $R = F(\lambda, T)$.

Then, the energy absorbed per second by the body is expressed by

$$s\int_0^\infty a E d\lambda$$

The energy radiated per second is given by

$$S\int_0^\infty a R d\lambda$$

For thermal equilibrium these two quantities must be equal, hence

$$\eta\int_0^\infty \phi(\lambda)F(\lambda,\ T)d\lambda = \int_0^\infty \phi(\lambda)\psi(\lambda)d\lambda$$

This equation contains but one unknown quantity—the equilibrium temperature T—and it always gives one, and only one, value for T. The numerical solution is always easy when the different functions that enter in the equation are given by tabulated data. The radiation equation F has a known analytical form.

The special cases outlined below depend upon a simplification of the general equation. The hypothesis is introduced that the incident radiation comes from a *black body* at a given temperature Θ and subtending a small solid angle Ω at the receiving body. The problem is accordingly reduced to that of the thermal equilibrium between two bodies isolated in space, of which one, the emitting body, has a black surface maintained at a given temperature, while the other, the receiving body, has arbitrary absorbing properties and acquires a temperature which is to be determined.

(1) *Black or Gray Body.*—Then $\phi(\lambda)$ is a constant that disappears from the equation. The integral of F is proportional to T^4 so that

$$T = \Theta M^{-\frac{1}{4}} \qquad (1)$$

where $M = \pi\eta/\Omega$. This result can also be derived at once from the law of Stefan.

(2) *Receiving Body having One Absorption Band.*—The wave-length of the center of the band is symbolized by λ_1. The width of the band must be small as compared with λ_1, otherwise it is arbitrary. The law of absorption within the band no longer enters into the analysis, and it is not at all necessary for the absorption to be complete for any wave-length. Using Planck's radiation formula for $F(\lambda, T)$ Fabry shows that

$$\frac{1}{T}=\frac{\lambda_1}{c}\left[\log M+\log\left(e^{\frac{c}{\lambda_1\Theta}}-1\right)\right] \tag{2}$$

When $c/\lambda_1\Theta$ is very large the last equation reduces to

$$\frac{1}{T}=\frac{1}{\Theta}+\frac{\lambda_1}{c}\log M \tag{3}$$

This amounts to using Wien's law instead of Planck's.

7. *Numerical Application: Solar Radiation.*—To obtain an approximate idea of the order of magnitude of the effects formulated the author considers the sun as being a black body at 6000° absolute. The receiving body is assumed spherical ($\eta=4$) and the apparent diameter of the sun is taken as 32′, so that $\log M = 12.1$ $c = 14{,}350$ micron × degree. Under these conditions equations (1), (2), and (3) lead to the following results:

λ_1	T	λ_1	T
0.4μ	1980°abs	5μ	250°
0.5	1700°	10	130°
1	1000°	black body	280°
2	550°		

It is thus seen that a spherical body having a single absorption band in the violet would attain a temperature approximately equal to the melting point of platinum, when exposed to radiation like that which is emitted by the sun and reaches the outer limit of the earth's atmosphere. This remarkable result is easily explained qualitatively by considering the fact that the body in question can only exchange energy under the form of violet radiation; for, this radiation commences to be emitted to an appreciable extent only at a very high temperature. Until then the sphere absorbs energy without emitting any, and thus its temperature rises. In conclusion it should be remarked that the author touches upon the question of the temperature of space and also gives a tentative explanation of the enhanced brilliancy of comets' tails when near the sun.—*Jr. de Phys.*, v, 207; May-June, 1916. H. S. U.

8. *Colored Flames of High Luminosity.*—A by-product of an investigation, by G. A. Hemsalech, on the spectrum of iron was the invention of an assemblage of apparatus which produces flames very intense in color and hence especially suitable for lecture demonstrations. The apparatus comprises four essential parts, which are, the sprayer, the collector, the mixing chamber, and the burner.

The sprayer is made of an ordinary glass tumbler the upper open end of which is fitted with a wooden cover sealed in place with suitable wax. The cover is pierced by four holes through which two electrodes and two tubes pass. The negative wire is sealed in a glass tube which allows only the lower end of the wire to project a few millimeters. This electrode is placed close to the inner wall of the tumbler and it runs down almost to the bottom of the vessel so as to have the exposed end of the wire immersed in the solution containing the metal, the spectrum of which is desired. The positive electrode has the same form and it coincides with the axis of the tumbler. The tip of the positive wire is adjusted so as to leave a spark-gap of a few millimeters length above the free surface of the liquid. To secure adequate insulation the capillary tube containing the positive wire is surrounded by a glass tube of much larger diameter which projects several centimeters both above and below the wooden lid. The wires are composed of iron or aluminium. The inlet tube for air under pressure runs down near the negative terminal to within a centimeter or two of the liquid surface. The outlet tube is flared at the receiving end which is just below the wooden lid and diametrically opposite to the inlet tube.

The collector is simply an inverted glass funnel closed by a wooden disk. Since six sprayers can be used with the same burner, there are six holes in the disk through each of which the outlet tube from a sprayer passes. The upper part of the funnel is joined by a short section of rubber tubing to a glass four-branch tube. The axial extension of the funnel tube passes through a stopper at the lower end of the coaxial mixing chamber. The two branches of the glass cross, that are at right angles to this axis, admit oxygen on one side and coal gas on the other.

The mixing chamber is made of a brass tube 2.2 cm in diameter and 15.2 cm high. The top of this tube which constitutes the burner consists of a brass disk 6 mm thick through which one or more holes are drilled. Each hole should have a diameter not exceeding 2 mm. One hole is generally sufficient, but four holes pierced close together at the vertices of a square produce a more brilliant resultant flame.

All the inlet tubes of the sprayers branch from one air-supply tube. Since all connections are made with sections of rubber tubing the sprayers can be started, regulated, or stopped by pinch-cocks. The positive electrodes are all permanently connected to one coating of a pint-size Leyden-jar. The negative terminals can be successively connected to the other coating of the condenser. An induction-coil giving a 15 cm spark is sufficient for working the sprayers. The flames should be from 30 to 45 cm high and not more than 1.3 cm in diameter. The cone should not exceed 2.5 cm in length.

"The flames obtained in this manner are exceedingly well suited for showing, in a large lecture theatre, the spectra of the more volatile elements, such as Ca, Sr, K, Cu, &c., to an audience

provided with small replica transmission gratings. The relatively great length and thinness of the flame obviates the necessity for a spectroscope slit.''—*Phil. Mag.*, xxxiv, 243, October, 1917.
H. S. U.

9. *X-Ray Band Spectra.*—An outline of two papers by DE BROGLIE on this subject was given in the June, 1917, number of this Journal. Essentially the same text has since appeared in another French journal (*vide infra*) with the addition of three excellent half-tone plates. The present notice is intended to call attention to the scientifically beautiful reproductions of the spectrograms of the absorption spectra produced when the X-rays from a tungsten target were allowed to fall upon metallic screens each of about 0.01 mm thickness. The first figure shows the lines of the K and L series of tungsten together with the dark bands due to the bromine and silver in the photographic emulsion. The remaining figures pertain to the absorption bands (light regions) of molybdenum, cadmium, antimony, barium, tellurium, iodine, mercury, gold, lead, uranium, and thorium. The wave-lengths of the edges of the bands of iodine and tellurium conform to the atomic numbers and chemical sequence of these elements and not to their supposedly anomalous atomic weights.—*Journal de Phys.*, v, 161, May-June, 1916.
H. S. U.

II. MINERALOGY AND GEOLOGY.

1. *New Mineral Names;* by W. E. FORD (communicated—continued from vol. xliii, pp. 493–494, June, 1917):—

Catoptrite. *Katoptrite.* Gustav Flink, Geol. För. Förh., xxxix, 431, 1917.—Monoclinic. $a : b : c = 0{\cdot}79223 : 1 : 0{\cdot}48985$; $\beta = 78^\circ\, 57'$. Observed forms: $a\,(100)$, $b\,(010)$, $c\,(001)$, $m\,(110)$, $l\,(210)$, $n\,(120)$, $d\,(012)$, $e\,(032)$, $o\,(21\bar{2})$, $p\,(23\bar{2})$, $q\,(27\bar{2})$, $r\,(212)$. Angles; $m : a = 37^\circ\, 52'$, $d : b = 67^\circ\, 29'$, $c : a = 78^\circ\, 57'$. Crystals commonly minute and tabular parallel to $b\,(010)$. Cleavage parallel to $c\,(001)$ very perfect. H. = 5·5. G. = 4·5. Color is black with metallic appearance. In thin splinters, red. Ax. pl. parallel to $b\,(010)$. Bx_{ac} makes 14–15° with trace of cleavage. Axial angle small. Inclined dispersion $\rho > v$. Strongly pleochroic, red-brown to red-yellow. Optically +. Comp.—$2SiO_2.Sb_2O_5.2(Al,Fe)_2O_3.14(Mn,Fe)O$. Anal. by Mauzelius, SiO_2 7·75, Sb_2O_5 20·76, Al_2O_3 9·50, Fe_2O_3 3·58, FeO 2·44, MnO 52·61, MgO 3·06, CaO 0·58, H_2O 0·11, Total 100·39. Found embedded in calcite with magnetite and other minerals in the Brattsfor mine at Nordmarken, Sweden. Name derived from κάτοπτεον, *a mirror*, in allusion to its brilliant cleavage surfaces.

Ectropite. *Ektropite.* Gustav Flink. Geol. För. Förh., xxxix, 426, 1917.—Probably monoclinic. In thin crystals, tabular parallel to (100) and somewhat elongated parallel to b axis. Dimensions 2 mm. by 1 mm. Other forms, rarely observed, are (110), (001), ($\bar{1}01$). Measured under microscope gave approximate angles; (100):(110) = 32° 50′, (001):(100) = 61° 5′ ($10\bar{1}$):(100) = 56° 50′. Axes $a : b : c = 0·74 : 1 : 0·84$; $\beta = 61° 5'$. Cleavage good probably parallel to (001). H. = 4. G. = 2·46. Luster vitreous to silky. Color light to dark brown. Opaque. In thin section shows yellow color. Non-pleochroic. $\alpha = 1·62$, $\gamma = 1·63$. Optical axial plane parallel to (010). Comp.—$Mn_2Si_8O_{28}.7H_2O$. Anal. by Sahlbom, H_2O 8·89, SiO_2 35·02, Al_2O_3 0·75, FeO 5·80, MnO 37·20, CaO 3·59, MgO 7·20, Na_2O 0·12, K_2O 1·13, other constituents 0·19, Total 99·89. Found on garnet crystals associated with barite and calcite in the Norrbotten iron mine at Långbanshyttan, Sweden. Name derived from ἐκτροπή, *evasive*, in reference to the difficulty in determining its characters.

Flokite. Karen Callisen, Medd. Dansk. Geol. För., v, No. 9, 1917.—Monoclinic. In thin slender prismatic crystals measuring 1–1½ cm. in length by ½ mm. in thickness. Observed forms: (110), (100), (010). Faces vertically striated, (100) : (110) = 41° 18′. Sections parallel to (010) show twinning on (100). Cleavage perfect parallel to (100) and (010). Conchoidal fracture across prism zone. H. = 5. G. = 2·102. Luster vitreous. Crystal transparent and colorless or with faint gold-green tint. At times dark colored from inclusions. Thin sections perpendicular to prism zone show a division into segments with different optical orientation. In the center of crystal the optical axial plane is perpendicular to (010). $b = \gamma$, $c : \alpha =$ about 5°. Axial angle large. Acute bisectrix probably nearly parallel to c axis and mineral is negative. In Na-light $\alpha = 1·4720$, $\gamma = 1·4736$. On warming to 117°–118° sign of double refraction changes. Comp.—A zeolite, $H_8(Ca, Na_2)Al_2Si_9O_{26}.2H_2O$. Anal. by Christensen; SiO_2 67·69, Al_2O_3 12·43, MgO 0·09, CaO 2·65, Na_2O 4·36, H_2O 13·35, Total 100·57. B. B. fuses easily with intumescence. Insol. in boiling HCl. Found on an old specimen in the Museum at Copenhagen labeled from "Eskefjord? Iceland." Named after the viking Floki Vilgerdarsen, who gave Iceland its name.

Margarosanite. This mineral, recently described from Franklin, N. J. by Ford and Bradley (this Journal, xlii, 159, 1916), has been found by Gustav Flink at Långbanshyttan, Sweden (Geol. För. Förh., xxxix, 458, 1917). The Swedish occurrence shows slender prismatic crystals, often in radiating groups. Usually the crystal faces are striated or curved. A few small and well developed crystals were observed upon which measurements were made. Triclinic. $a : b : c = 0·73998 : 1 : 1·2849$; $\alpha = 74° 37'$, $\beta = 50° 28'$, $\gamma = 78° 53'$. Observed forms, a (100), b (010), m (110), n ($1\bar{1}0$), c (001), d (011), e ($0\bar{3}4$)? Cleavage in three directions, b (010), very perfect, c (001) and ($\bar{5}04$) (not observed on crystals) good. Found associated with schefferite, apophyllite, calcite, nasonite and thaumasite.

Merrillite, a meteoritic calcium phosphate. Described by G. P. Merrill in Proc. Nat. Ac. Sc., i, 302, 1915; this Journal, xliii, 322, 1917. Considered by E. T. Wherry (Am. Min., ii, 119, 1917) as an independent species and given the above name. Similar to *francolite* but differs in important features. Biaxial, positive. Comp.—$x\mathrm{CaO}.y\mathrm{P_2O_5}$.

Spencerite. Previously described by T. L. Walker (Min. Mag., xviii, 76, 1916) and an abstract given in a previous list, has lately been found in crystals. Walker (Jour. Wash. Ac. Sc., vii, 456, 1917) gives the following new facts: Monoclinic. $a : b : c = 1·0125 : 1 : 1·0643$, $\beta = 63° 13'$. The crystals are small and tabular parallel to (100). Crystals are twinned on (100). Some twenty forms were observed of which the most important are, (100), (110), (120), (010), (001), $(\bar{1}02)$, $(\bar{1}01)$, $(\bar{2}21)$, $(\bar{2}41)$.

Crestmoreite. A. S. Eakle, Univ. Cal. Publ., x, 344, 1917. An alteration product of *wilkeite.* Compact. Color, snow-white. Luster vitreous to dull. Fuses quietly and easily. H. = 3. G. = 2·22. Easily soluble with separation of a small amount of flocculent silica. Shows parallel extinction, positive elongation, low birefringence, $\beta = 1·59$. Analysis shows it is a hydrous calcium silicate with small amounts of phosphate, sulphate and carbonate molecules. The latter radicals are considered to be small portions of those in the original *wilkeite.* The true composition of the mineral is taken to be approximately $4\mathrm{H_2CaSiO_4}.3\mathrm{H_2O}$. Found in the blue calcite at Crestmore, Riverside County, California.

Riversideite. A. S. Eakle, Univ. Cal. Publ., x, 347, 1917. Occurs in compact fibrous veinlets traversing massive vesuvianite. Silky luster. H. = 3. G. = 2·64. Fusible at 2 to a white glass. Easily soluble leaving flocculent silica. Parallel extinction. Fibers elongated parallel to c. $\alpha = 1·595$, $\gamma = 1·603$. A hydrous calcium silicate, $2\mathrm{CaSiO_5H_2O}$. Analysis shows also small amounts of phosphoric and sulphuric acids. Found at Crestmore, Riverside County, California.

2. *Descriptive Mineralogy;* by WILLIAM SHIRLEY BAILEY. Pp. xvii, 542; 268 figures. New York, 1917 (D. Appleton and Co.).—Professor Bailey has written this book, as he says in its preface, "with the purpose of affording a student a comprehensive view of modern mineralogy rather than a detailed knowledge of many minerals. The minerals selected for description are not necessarily those that are most common nor those that occur in greatest quantity. The list includes those that are of scientific interest or of economic importance, those that illustrate some principle employed in the classification of minerals." In addition to the body of the work which gives the descriptions of individual species there are short and excellent chapters on the composition and classification of minerals; the formation of minerals and their alterations; general principles of blowpipe analysis; characteristic reactions of the more important elements and acid radicals; also

appendices containing a simple determinative guide and various mineral tables.

In the description of individual minerals the author first gives the composition, crystallization, physical characters, chemical tests, etc. Practically no abbreviations or headings are used in this section. This makes the descriptions very readable but must detract from the convenience with which the book can be used by a student. The other paragraphs in a typical description are headed : Synthesis, origin, occurrence, localities, uses, production, etc. Much valuable and interesting information is given in these paragraphs that is not ordinarily found in such books. The typography is very good and the figures are unusually well chosen and reproduced. Professor Bailey is to be congratulated on producing, in an already well-filled field, a book that possesses such individual distinction and character. W. E. F.

3. *Wave Work as a Measure of Time: A Study of the Ontario Basin;* by A. P. COLEMAN. ERRATA.—The following corrections are to be made in this article as printed on pp. 351–359 of the November number:

Page 355, line 27, for *east* read *west*.
" 359, " 13, " *plueroceras* read *pleuroceras.*

III MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *National Academy of Sciences.*—The autumn meeting of the National Academy was held in Philadelphia on November 20, 21, in the Engineering Building of the University of Pennsylvania.

2. *American Association for the Advancement of Science.*—The winter meeting of the American Association, with those of the affiliated Societies, will be held at Pittsburgh during the week from December 28 to January 2.

3. *Negro Education. A study of the private and higher schools for colored people in the United States;* prepared in coöperation with the Phelps-Stokes Fund under the direction of THOMAS JESSE JONES, specialist in the education of racial groups, Bureau of Education. In two volumes. Vol. I. Pp. xiv, 423; Vol. II. Pp. 724 with 30 maps. Department of the Interior, Bureau of Education; Bulletins, Nos. 38, 39.—This report, distributed during the past summer, cannot fail to be appreciated by all intelligent people who are interested in the welfare of the colored people, one of the most vital problems with which the country is concerned. It is based upon the personal investigation of some 790 institutions. The scope of the work will be understood from the following summary of its contents:

Volume I contains the following: (1) General Survey; (2) Public School Facilities; (3) Secondary Education; (4) College and Professional Education; (5) Preparation of Teachers; (6) Industrial Education; (7) Rural Education; (8) Ownership and Control of Private and Higher Institutions; (9) Educational Funds and Associations; (10) Financial Accounts and Students Records; (11) Buildings and Grounds; (12) History of Negro Education; Appendix containing eight statistical tables.

Volume II is a presentation of Negro Schools arranged geographically, by States, counties, and cities. The chapter headings are as follows: (1) Methods and Scope of the Study; (2) Summary of Educational Facilities; (3) Alabama; (4) Arkansas; (5) Delaware; (6) District of Columbia; (7) Florida; (8) Georgia; (9) Kentucky; (10) Louisiana; (11) Maryland; (12) Mississippi; (13) Missouri; (14) North Carolina; (15) Oklahoma; (16) South Carolina; (17) Tennessee; (18) Texas; (19) Virginia; (20) West Virginia; (21) Northern States.

In addition an abstract will be issued for each Southern State. These abstracts will contain the following chapters selected from the above volumes: (1) Methods and Scope of the Study; (2) General Survey; (3) Summary of Educational Facilities; (4) State chapter.

4. *Science and Learning in France; with a Survey of Opportunities for American Students in French Universities. An Appreciation by American Scholars;* edited by John H. Wigmore. Pp. xxxviii, 455; illustrated. 1917. (The Society for American Fellowships in French Universities.)—This notable volume is dedicated to the scholars of France by their colleagues in America. Its chief object is to present to the American public at large a survey of what France has contributed to scientific knowledge and to show the position which she occupies on this account. It thus gives a record for the past century, at once comprehensive and concise, of French scholarship, with an account of the many eminent leaders who have contributed to it. There are also given statements as to the courses of instruction at the Universities, particularly the University of Paris and, further, the facilities available for study and research. The work is edited by Prof. J. H. Wigmore and the list of authors includes about one hundred names. Dr. Eliot contributes to the Introduction a paper on the "Mind of France" and Dr. Hale another on the "Intellectual Inspiration of Paris." There are a large number of special contributions by different authors from many American universities, and the interest of these is increased by the numerous portraits of French savants which are introduced. At the present time, when France and America are drawn more closely together than ever before, this expression of homage to the intellectual greatness of France and the value of her contributions to science is most opportune.

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* This Index contains the general heads, BOTANY, CHEMISTRY, GEOLOGY, MINERALS OBITUARY, ROCKS; under each the titles of Articles referring thereto are included.

CONTENTS.

SCIENTIFIC INTELLIGENCE.